LINKING TIME AND LENGTH SCALE IN COMPLEX SOLIDS WITH STATISTICAL MECHANICS

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To My Beloved Family and Friends

献给我的家人和朋友

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CHAPTER I

INTRODUCTION

1.1 A historical review of statistical mechanics and its application to condensed matter

The principal task of statistical mechanics is to start with the atomistic description of matter and derive macroscopic laws such as the laws of thermodynamics, fluid dynamics, elasticity, chemical kinetics, and so on.

The foundations of statistical mechanics are due to Gibbs [1], but its historical roots go back to the development of the kinetic theory of gases [3,5]. Maxwell first introduced the idea of statistical mechanics into the study of gases with the velocity distribution of molecules of a gas in equilibrium. Boltzmann went further to study the time dependence of the distribution function and its approach to equilibrium. His research culminated in the famous Boltzmann transport equation for the velocity distribution function. The Maxwell-Boltzmann kinetic theory, however, is successful in describing the macroscopic properties of only perfect or near-perfect gases. With the development of thermodynamics in the 19th century, a more general statistical method that goes beyond the kinetics of gases and is based on the laws of mechanics was needed.

The formal structure of equilibrium statistical mechanics was laid down by Gibbs in the 1870s [1,6]. According to Gibbs's theory, a state of the system corresponds to a point in phase space and the time average of an observable quantity is identical with its phase space average (ensemble average). Gibbs's ensemble theory is constructed on Liouville's equation which is purely a mechanical equation. The equilibrium theory of statistical mechanics has achieved a satisfactory general formulation at the hands of Gibbs and of later investigators. It provides a systematic interpretation from the atomic standpoint of the equilibrium behavior of thermodynamic systems. (Gibbs did not pursue detailed implementation of his formulism to describe complex solids)

There is an enormous range of phenomena, however, which are concerned with non-equilibrium or irreversible processes. For example, the thermoelectric phenomena, viscous flow, heat conduction, and atomic diffusion in fluids, have been known for more than a hundred years and their phenomenological descriptions have been established from experience. Similarly, plastic deformation of materials has been described by phenomenological models of stress-strain relations. With the progress of statistical mechanics, scientists tried to interpret these irreversible processes from microscopic dynamics [20,21]. In 1931, Onsager published an important paper in which he tried to explain such reciprocal relations as Thomson's thermoelectric relation from the assumption of microscopic reversibility [7, 8]. It is a milestone toward the understanding of irreversible processes. However, his discussion is still semi-phenomenological due to its heavy dependence on the experimentally established thermodynamic equations. Therefore, the problem of deriving equations of irreversible thermodynamics from statistical mechanics for general systems arises. A principal objective of non-equilibrium statistical thermodynamics is to start with the atomistic description and derive the macroscopic laws that govern such dynamic processes as diffusion, heat conduction, and viscous flow in fluids and plastic deformation in solids. Moreover, it is expected that such a theory is to achieve a generality comparable to that of equilibrium statistical mechanics.

The formulation of transport process in fluids based on statistical mechanics has achieved great success. The transport equations, such as the Navier-Stokes equation for viscous flow, Fourier's law of heat conductivity and Fick's law of diffusion can be derived from an atomistic description. However, non-equilibrium statistical thermodynamics is still in the process of development and is far from being completed. The state of the art for non-equilibrium statistical mechanics for fluids and solids is as follows:

(1) Fluids:

- The most highly developed method in the theory of irreversible processes is based on the *kinetic equation for the distribution function*, proposed by Boltzmann and substantiated and further developed by Bogolyubov [5], Enskog, Chapman [4], and others. This method enables us to derive the equations of non-equilibrium thermodynamics and to calculate the kinetic coefficients explicitly; in practice this method is very important, but it is applicable only to gases of sufficiently low density or with sufficiently weak interaction between the particles.
- A satisfactory theory exists for transport in dilute solutions, based upon the theory of Brownian motion, the foundations of which are due to Einstein. This theory, chiefly developed by Green [9,10], Kirkwood [2,11,12] and Mori [13], is also known as the correlation method. In this approach, an explicit form of the distribution function is not required. But the evolution of the distribution function is assumed to satisfy the Fokker-Planck equation [6], from which the transport equations are derived. The transport coefficients are expressed in terms of the *correlation functions* of equilibrium fluctuations of the appropriate dynamical quantities. The applicability of

this method is limited by the assumption of the Markovian random process for the state variables.

- In a series of papers published in the 1950s, Prigogine and coworkers developed a systematic theory for the interpretation of irreversible process [14]. They investigated in detail the dynamics of correlations in the irreversible process. They derived the well known '*master equation*' based on the perturbation assumption which is similar to that in Quantum Mechanics. Prigogine's theory offers a detailed fundamental interpretation of the origin of the macroscopic irreversibility. From the *master equation,* both the Boltzmann equation and the Fokker-Planck equation can be derived. The master equation, therefore, is a more general equation that describes the evolution of the distribution function. But in practical applications, it is the specific forms of the master equation such as the Boltzmann's equation or Fokker-Planck equation that are usually used. Moreover, because it is essentially a perturbation theory, it is only suitable for systems with weak interactions. Examples are the phonon gas in anharmonic solids, weakly coupled gases, and hydrodynamics of fluids.
- Due to the great success of equilibrium statistical mechanics based on the equilibrium ensemble of Gibbs, there has been a group of approaches that generalize the concept of equilibrium ensembles to the nonequilibrium systems. The key idea is to construct explicitly the nonequilibrium distribution function. Major contributions to the development of such approaches are by Kirkwood [2,11,12], MaClennan [16-19], Zubarev [15], etc.

(2) Solids:

Compared to the fruitful development of statistical mechanics in fluids, the formulation of statistical mechanics for solids has been limited to certain topics and areas [22-50].

- For electrons, there exists a well developed theory based on Fermi-Dirac statistical mechanics [1, 49, 50].
- A rigorous description also exists for phonons based on the Bose-Einstein statistical mechanics [6, 40-42, 49].
- The transport of phonons in a crystal can be formulated using the Boltzmann's equation [40-42]. Prigogine's master equation also applies [11].
- In the formulation of such phenomena as the diffusion of atoms, the Boltzmann distribution function for distinguishable particles is frequently used to estimate the probability of success of an atom to overcome the energy barrier [44]. This estimate, combined with the experimental transport equations such as Fick's equation for atomic diffusion, only gives a very simplified microscopic interpretation of diffusion in solids.
- There are methods based on the Boltzman transport equation applied to the study of defects. In these formulations, defects are treated like pseudo-particles [44, 89]. But this treatment brings a problem, i.e. the interaction between the defects is not clear. As a result, the method has to be combined with phenomenological equations [52,89] in order to include the interactions between defects.

- Statistical models of dislocation cells, shear bands or other organized dislocation structures have been advanced [26-30, 35-38], such as the Walgraef-Aifantis statistical model [51].
- Other examples include the formulation of the perfect crystal elasticity from atomic dynamics based on the assumption of homogeneous deformation [43].

We have seen that the current formulations for solids are mostly mixtures of phenomenological relations and statistical approaches. There exists no comprehensive theoretical framework for solids that is derived from theories of atoms, describes defect dynamics, and links to macroscopic deformation of solids. One major reason for this is the simultaneous existence of several distinguishable length scales coupling with each other in complex solids [53, 54]. At the smallest scale of Angstroms, atomic dynamics provides an underlying framework for the formation of a wide variety of defects in mesoscales. Higher-scale defect interactions (from nanometers to many microns) collectively operate to drive large-scale behavior. Long-range stress fields, on the other hand, can drive the motion of existing defects or cause the nucleation of new defects at the atomic-scale. As a result, the macroscopic behavior is a manifestation of the interaction and organization of this collection of atoms, defects and stress fields within a polycrystalline microstructure that may range in size from microns to millimeters. The transport processes in solids are therefore far more complicated than in fluids. Examples are Herring creep, the climb of dislocations, migration of grain boundaries, etc, which may also interfere with each other. This intrinsic multi-scale nature of solids imposes a great challenge on the theoretical formulations. Specifically, a proper treatment of defects and deformation from an atomistic point of view are major difficulties in a successful formulation from statistical mechanics. Some pioneering work in the general formulation of solids based on statistical mechanics can be found in papers by L.A.Pokrovsky [45,46], Sokrates Pantelides [47,48].

1.2 Current multiscale modeling of complex solids

The current multi-scale modeling in solids is mainly pursued by computational means [53,54], either by passing information from calculations at one scale to another (also known as serial or sequential linking) [55-78] or by constructing a composite simulation with different features treated at different length scales (also termed concurrent linking) [79-87]. The two approaches are respectively demonstrated by Figure 1.1 and Figure 1.2.

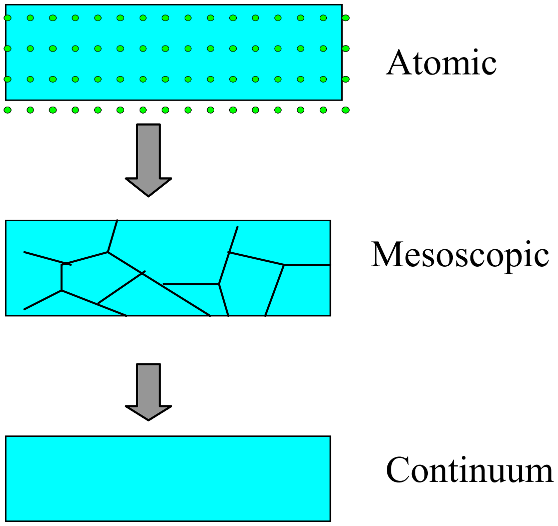


Figure 1.1 Serial linking

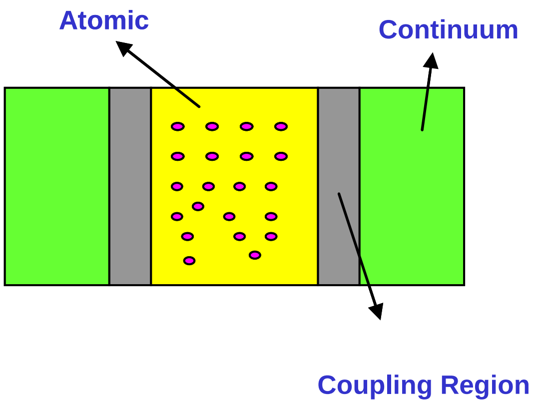


Figure 1.2 Concurrent linking

In the serial linking methods [53-78], simulation is applied to the entire system at one scale. The result of this calculation is used as input to the next up the length/time scale hierarchy. Note that there is only one scale for the entire system in each calculation. A good example of this was the formulation of the perfect crystal elasticity [43]. An empirical potential was used to simulate atomic dynamics, from which the elastic constant is calculated. The result of this calculation is then inserted into the macroscopic Hook’s law to evaluate the stress-strain relationship. We can see that this approach relies on the preliminary knowledge of dynamical laws at each length scale. In other words, the phenomenological theories have to be first established from experiment before the inputs of information derived from calculations at lower scales. The method is, therefore, a mixture of the atomistic simulation and the phenomenological theories. Moreover, the direction that the information is passed is a one-way direction, i.e. only from lower scale to the upper scale in the hierarchy. As a result, the influence of dynamics at higher scales on the lower scales, such as the stress induced defect motion, is excluded. This method, therefore, is only suitable to simulate solids in which the coupling between scales is weak.

The concurrent linking [71-78], as a comparison, is a more suitable approach in simulating complex solids where defects and stress field interact with each other. Crack propagation is a good example in which it is necessary to know what is happening simultaneously in each region since one is strongly coupled to another. In this approach, the system is divided into regions with different characteristic scales. Simulations for regions of different scales are performed at the same time. Necessary information is dynamically transmitted to and from simulations of other regions. For example, the system with a dislocation may be divided into two regions. In one region where the dislocation is located, atomistic mechanics is applied while on the other region far from the dislocation, continuum mechanics is applied, the implementation of which is via finite elements. One pioneering concurrent approach was the work by Abraham [53,81]. The idea of their work was to concurrently link tight-binding, molecular dynamics, and finite elements together in a unified approach. Other pioneering work on coupling atomistic to finite elements has been performed by Tadmor, Ortiz and Philips [78,79-81]. The concurrent linking approach, however, still requires a preliminary knowledge of the constituents of the system such as the distribution of defects and the phenomenological theories for each scale. It is essentially a one-scale calculation for each region. Different regions connect with each other through boundary conditions.

The application of computational methods is limited by the power of computers. Even with today's most powerful parallel computers, the simulations of a heterogeneous material remain beyond reach. The state-of-the-art, massively-parallel supercomputer simulations can handle about 10^9 atoms, amounting to a volume of less than 1 cubic micron. It is therefore not feasible to attain the scale at which most collective defect process happen such as fracture, solely from atomistic simulation.

1.3 Overview

This thesis is an effort to formulate the equilibrium and non-equilibrium statistical mechanics for a complex solid. Here we begin only with an atomistic description of a solid, and apply the principles of statistical mechanics to derive the dynamics of defects and ultimately describe the macroscopic behavior such as plastic deformation with different scales naturally coupled together. In particular, we put emphasis on the formulation to describe defects and deformation. We wish that the formulation will be in the future combined with the computational method to give a general elegant description of the dynamics of solids as well as predict new phenomena.

The thesis is therefore organized as follows:

Chapter II

We present the general procedures of applying non-equilibrium statistical mechanics to formulate the *transport process in fluids*. Some basic concepts in equilibrium statistical mechanics are reviewed. We especially review two methods. Each of them represents one of the two main lines of formulating hydrodynamic equations. The review of statistical mechanics of fluids in this chapter will be a background for the formulation of statistical mechanics of complex solids in following chapters.

Chapter III

The current formulation capitalizes on the essential difference between a crystal and a fluid. In Chapter II, we use a perfect crystal to introduce the most fundamental ideas underlying the formulation of the statistical mechanics of a solid. The methods introduced in this chapter form our basis for the following formulations of a crystal with defects.

Chapter IV

In this chapter, we interpret point defects based on the description of a perfect crystal in Chapter III. The general theoretical framework is constructed for a crystal with only vacancies, a crystal with only interstitials, and a crystal with both vacancies and interstitials. Some complexities are also discussed.

Chapter V

In Chapter IV, we formulate the nonequilibrium statistical mechanics of a complex crystal. Here we demonstrate that the dynamics on different intrinsic time scales can be naturally coupled together with the statistical mechanics developed in previous chapters. Applications include Herring creep and transport of point defects.

Chapter VI

In Chapter VI, we give a preview of future work on including dislocations into the theory.

CHAPTER II

FLUIDS

In this chapter, we shall demonstrate the procedures to formulate the statistical mechanical theory of transport processes in fluids; e.g., diffusion, heat transfer, fluid flow, etc [5-10]. We select two nonequilibrium statistical methods for the formulation. Both methods are developed within the framework of Gibbs' ensemble theory. The first method, called the nonequilibrium ensemble theory, generalizes Gibbs' equilibrium ensembles to nonequilibrium systems with the help of time averaging [15]. We will describe in detail the formulation of transport equations of fluids with the nonequilibrium ensemble theory in Chapter 2.2. The second method concerns the time evolution of the distribution function which describes how a system approaches equilibrium [16-19]. The essence of the second method will be briefly presented in Chapter 2.3.

We shall always assume that electrons are always at their ground state that corresponds to the instantaneous positions of the nuclei. Thus, we will not be doing statistical mechanics of electrons, but only of the nuclei. So the electrons have been integrated out as in the Born-Oppenheimer approximation [49]. We shall restrict ourselves to the classical description of atomic dynamics, and we shall formulate the transport theory within the frame of classical statistical mechanics. The quantum-mechanical generalization will not be discussed.

2.1 Equilibrium statistical mechanics of fluids

For simplicity and demonstration, we consider a fluid consisting of one kind of particle. A particle in the system is described by its coordinates r_i measured from a single origin. The canonical momentum corresponding to r_i is p_i. Particles interact with each other through a potential denoted by $V(r_1,...r_N)$. The Hamiltonian H (abbreviation for $H(r_1,..r_N;p_1,..p_N)$) of the fluid has the form:

$$H=\sum_i \frac{p_i^2}{2m}+V(r_1,...r_N) \tag{2-1}$$

The interaction energy $V(r_1,...r_N)$ is a function of all the atomic coordinates. It can be expressed in terms of density function theory [70, 80] or expressed as an expansion,

$$V(r_1,...r_N)=V_0+\frac{1}{2}\sum_i\sum_{j\neq i}V\left(r_{ij}\right)+\frac{1}{6}\sum_i\sum_{j\neq i}\sum_{k\neq i,j}V\left(r_{ij},r_{ik},r_{jk}\right)+... \tag{2-2}$$

where r_{ij} denotes the separation between two particles $r_{ij}=\left|r_i-r_j\right|$; V_0 is the reference energy usually chosen to be zero; the second term is a sum over all pair interactions $V\left(r_{ij}\right)$ and the third term denotes the sum of three particle interactions $V\left(r_{ij},r_{ik},r_{jk}\right)$, and so on.

The motion of the system with Hamiltonian expressed in (2-1) is classically described by the canonical equations, namely

$$\dot{r}_i=\frac{\partial H}{\partial p_i},$$

$$\dot{p}_i=-\frac{\partial H}{\partial r_i}. \tag{2-3}$$

The state of a system is then determined by the momenta and coordinates of all particles. The phase space of the system is $6N$ in dimension. A state of the system is represented by a point of $\{r_i, p_i\}$ in the phase space. It is then possible to introduce a distribution function $f(\{r_i, p_i\})$ according to Liouville's theorem, which states that the density of states in phase space is constant with time. With $f(\{r_i, p_i\})$, the average of any microscopic quantity $A(\{r_i, p_i\})$ is expressed as

$$\bar{A} = \int f(\{r_i, p_i\} A(\{r_i, p_i\}) d\Gamma, \tag{2-4}$$

where the integration is over the phase space and $d\Gamma$ is the abbreviation for $dp_1..dp_N dr_1..dr_N$.

If all the phase points representing the system are strictly confined to a surface of $E(\{r_i, p_i\}) = E$ in phase space, the ensemble of phase points is called microcanonical ensemble. If a small fluctuation in energy is allowed, the ensemble is called canonical ensemble. According to Gibbs, the entropy is then defined as,

$$S = -k \int f \ell n f d\Gamma . \tag{2-5}$$

The canonical distribution function $f(\{r_i, p_i\})$ is then determined by the maximization of entropy under the constraint that the total energy is on the average constant with time,

$$\delta S(f) + \lambda \bar{E}(f) = 0, \tag{2-6}$$

where λ is a Lagrangian parameter. This parameter is identified with $\beta = -1/kT$, where T is the absolute temperature and k is Boltzmann's constant. The canonical distribution function is found to be,

$$f(\{r_i, p_i\}) = Q^{-1} e^{-\beta E(\{r_i, p_i\})}, \tag{2-7}$$

where Q is the normalization constant defined by $Q = \int e^{-\beta E(\{r_i, p_i\})} d\Gamma$. The Q is known as the partition function. The average energy is then calculated by

$$\bar{E} = -\frac{\partial}{\partial \beta} \ell n Q . \tag{2-8}$$

From (2-7), one can derive the thermal dynamics of equilibrium:

$$kT \ell n Q = \bar{E} - TS \tag{2-9}$$

The canonical distribution corresponds to a system in equilibrium with a large reservoir characterized by a constant temperature T. If the number of particles contained in the system changes with time, we need to add a constraint of constant average particle number in equation (2-6). The distribution function with this constraint is called Grand canonical distribution,

$$f(\{r_i, p_i\}) = Q^{-1} e^{-\beta(E - \mu N)} , \tag{2-10}$$

where μ is called the chemical potential of the particle. The system represented by grand canonical ensembles is in contact with a large reservoir characterized by a constant μ.

2.2 Statistical mechanics of fluids based on non-equilibrium ensembles

Equilibrium statistical mechanics is formulated based on invariants of motion, such as the constant energy and particle number. This is true only if the reservoirs in contact can be considered infinite. Otherwise, the system cannot maintain a constant state. Moreover, the Gibbs entropy, defined in (2-5), is reversible with time and cannot increase in time. So it is only suitable to describe a system in thermal equilibrium.

A system in nonequilibrium state is characterized by an increase in entropy. A system deviates from equilibrium either by contact with reservoirs, or by the change in internal thermal parameters such as a temperature gradient that generates heat in the system. The Gibbs's ensemble theory needs adaptation in both cases.

There are generally two directions to formulate irreversible processes with statistical mechanics:

The first one concentrates on the part of distribution function that is invariant with time, i.e. the time average of distribution function. An example is the method of the non-equilibrium ensemble proposed by D. Zubarev [15]. The process of formulating the transport of fluids by constructing non-equilibrium ensembles is described in detail in Chapter 2.2.

The second one, on the other hand, is focused on finding the evolution equation of the distribution function. An example is the method proposed by MacLennan [16-19], which derives the evolution equation of the distribution function of a system by introducing external reservoir. The method is briefly described in Chapter 2.3.

Note that both methods are based on Gibbs's ensemble theory.

2.2.1 Microscopic conservation laws in fine-grained space

Let $\hat{x}$ be the continuous coordinate in the space in which the particles composing fluids move. We shall call this coordinate space as the fine-grained coordinate space. In this coordinate space, we introduce the density of particles expressed in terms of atomic coordinates and momenta as,

$$n(\hat{x}) = \sum_i \delta(\hat{x} - r_i)\,. \tag{2-11}$$

In a similar way, the microscopic form of momentum and energy density are expressed by

$$g(\hat{x}) = \sum_i p_i \delta(\hat{x} - r_i), \tag{2-12}$$

and

$$h(\hat{x}) = \sum_i \left[\frac{p_i^2}{2m} \right] \delta(\hat{x} - r_i) + \frac{1}{2} \sum_i \left\{ \sum_{j \neq i} V\left(r_{ij}\right) \right\} \delta(\hat{x} - r_i) + \frac{1}{6} \sum_i \left\{ \sum_{j \neq i} \sum_{k \neq i, j} V\left(r_{ij}, r_{ik}, r_{jk}\right) \right\} \delta(\hat{x} - r_i) + \ldots \tag{2-13}$$

For purpose of demonstration, we will truncate the cluster expansion of energy at the pair interactions, so the energy density is approximated as

$$h(\hat{x}) = \sum_i \left[\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} V\left(r_{ij}\right) \right] \delta(\hat{x} - r_i). \tag{2-14}$$

This expression for energy density is used throughout the whole formulation for purpose of demonstration.

Differentiating the densities in (2-11), (2-12) and (2-14) with time, we obtain the following equations based on the conservation of total particle number, momentum and energy:

$$\frac{\partial n(\hat{x})}{\partial t} = -\nabla \cdot j(\hat{x}), \tag{2-15}$$

$$\frac{\partial g(\hat{x})}{\partial t} = -\nabla \cdot \tau(\hat{x}), \tag{2-16}$$

$$\frac{\partial h(\hat{x})}{\partial t} = -\nabla \cdot j_h(\hat{x}), \tag{2-17}$$

in which

$$j(\hat{x}) = \sum_i \frac{p_i}{m} \delta(\hat{x} - r_i) , \tag{2-18}$$

$$\tau(\hat{x}) = \sum_i \left[\frac{p_i p_i}{m} + \frac{1}{2} \sum_{j \neq i} r_{ij} F_{ij} \right] \delta(\hat{x} - r_i) , \tag{2-19}$$

$$j_h(\hat{x}) = \sum_i \left[\frac{p_i p_i}{2m} + \frac{1}{2} \sum_{j \neq i} V\left(r_{ij}\right) I + \frac{1}{2} \sum_{j \neq i} r_{ij} F_{ij} \right] \cdot \frac{p_i}{m} \delta(\hat{x} - r_i) . \tag{2-20}$$

where I denotes the unit tensor and F_{ij} represents the interacting force exerted by the jth atom on the ith atom,

$$F_{ij} = -\frac{\partial V\left(r_{ij}\right)}{\partial r_i} = \frac{\partial V\left(r_{ij}\right)}{\partial r_j} . \tag{2-21}$$

Note that $\delta(\hat{x} - r_i)$ here refers to the particle whose position is r_i in the fine grained space. The $j(\hat{x})$, $\tau(\hat{x})$, and $j_h(\hat{x})$ are respectively the microscopic atomic flux, stress tensor, and energy flux. According to (2-19), the stress tensor is composed of two terms: the first term arises from momentum transport while the second term arises from interactions of particles. Equation (2-20) also shows that the energy transport is composed of two terms: one is associated with kinetic energy transport, and the other is associated with energy transport by intermolecular forces. In fluids, the interactions between particles are of short distance and particles therefore typically move long distances. Thus, the kinetic energy dominates in a particle’s energy. As a result, the momentum transport should dominate in both the stress flux and the energy flux.

2.2.2 Galilean transformations

We suppose that all particles in a fluid are moving with the same constant velocity υ. Let a canonical transformation be made to the reference frame $\hat{x}'$ moving with υ.This transformation is defined by

$$p_i = p'_i + m\upsilon, \tag{2-22}$$

where the primed variable p'_i refers to the relative momentum in the moving frame. We substitute equations (2-22) in equations (2-15)-(2-17) and we get: (we drop $(\hat{x})$ in the following equations for clarity and use the prime variables to denote quantities in the moving frame)

$$n = n', \tag{2-23}$$

$$g = g' + \rho'\upsilon, \tag{2-24}$$

$$h = h' + \upsilon \cdot g' + \frac{1}{2}\rho\upsilon^2, \tag{2-25}$$

$$j = j' + n'\upsilon, \tag{2-26}$$

$$\tau = \tau' + 2\upsilon g' + \rho\upsilon\upsilon, \tag{2-27}$$

$$j_h = j_h' + (h' + \upsilon \cdot g' + \frac{1}{2}\rho\upsilon^2)\upsilon + \frac{1}{2}\upsilon^2 g' + \tau' \cdot \upsilon, \tag{2-28}$$

where ρ is the microscopic mass density defined by $\rho(\hat{x}) = mn(\hat{x})$.

We suppose that when $\upsilon = \upsilon_0$, the fluid is in equilibrium in the moving frame. According to the canonical distribution function (2-7), we find the average momentum for every particle in the moving frame to be,

$$\langle g_i' \rangle = \int f g_i' d\Gamma = 0 \tag{2-29}$$

where the bracket $\langle\ \rangle$ refers to the statistical average. The $\langle g'\rangle$ equals zero because the canonical distribution is an even function of momenta. The average momentum density is therefore zero, which means that there is no flux in equilibrium. The system is homogeneous in equilibrium, and $\langle\rho'\rangle$ is the same everywhere. The momentum density in the laboratory frame x is calculated by

$$g=\langle\rho'\rangle\upsilon_0, \tag{2-30}$$

which shows that υ_0 is just the velocity of the center of mass of the fluid. Because the mass density is uniform in space, according to (2-30), the momentum density is also uniform in space.

2.2.3 Coarse graining in space

A fluid is in equilibrium state is homogeneous, and if it flows, the momentum density is the same everywhere. When there is nonuniform distribution in the system, such as nonuniform velocity, the system is then in nonequilibrium state. In this section, we present the formulation of hydrodynamic transport of fluids.

Because the system is not uniform now, we divide the coordinate space $\hat{x}$ occupied by the fluid into cells, so that in each cell, the fluid can be seen as homogeneous. We denote the coordinate of the center of mass of a cell as x. The velocity of the center of mass is denoted by $\upsilon(x)$. The distance between two cells is Δx. It is assumed that Δx is macroscopically small, so that it is a continuous space and we can replace Δx by dx. But Δx is microscopically large in the fine grained space $\hat{x}$, so dx contains many particles. This coordinate space x, defined by positions of cells, is called the coarse-grained coordinate space. The macroscopic dynamics is assumed to be described in the coarse-grained space. The procedure of coarse graining in space is demonstrated in Figure2.1.

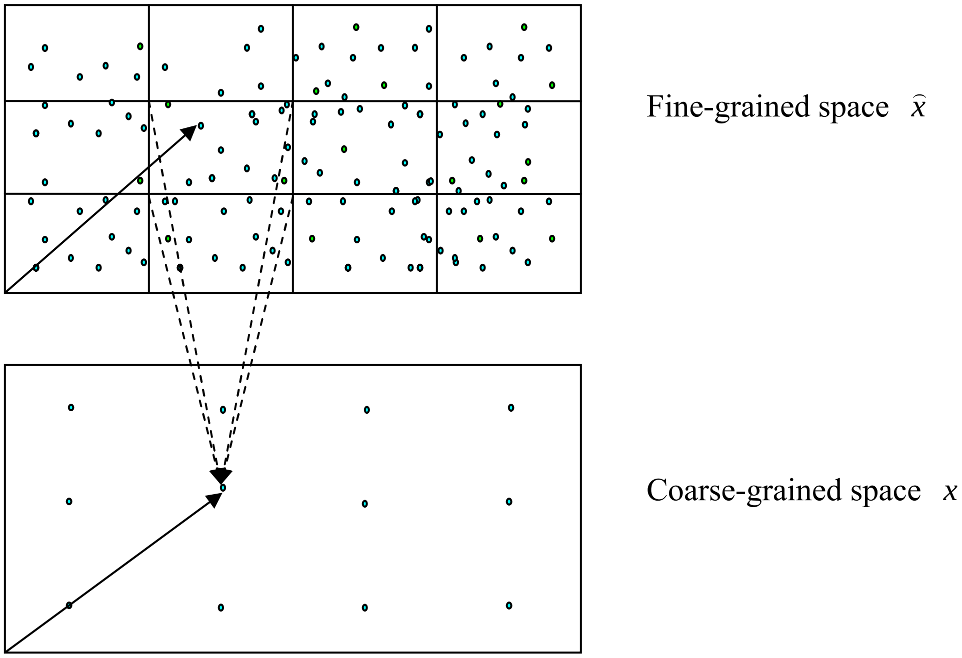


Figure 2.1 Coarse graining in an inhomogeneous fluid

It is further assumed that a nonequilibrium fluid approaches equilibrium through two states: equilibrium is first established for each cell, and then the whole system gradually approaches a uniform state. This assumption implies that the time needed to establish equilibrium in each cell must be much less than the time needed for the whole system to attain equilibrium. The transport of fluids derived based on this assumption yields the hydrodynamic equations.

Up to now all the equations given in (2-15)-(2-17) are microscopic in the sense that all the field variables are functions of the atomic coordinates and momenta. Thus, the next step is to construct the distribution function f and take the ensemble-average of variables (2-11)-(2-20). The average densities are calculated by

$$P_m(x) = \int P_m(\widehat{x})\, f\, d\Gamma\,, \tag{2-31}$$

where P_m is a general notation for microscopic form of densities, P_m is the average density in the coarse-grained space and the integration is over the phase space in the cell. For example, when $P_0(\widehat{x}) = h(\widehat{x})$, we obtain

$$h(x) = \int h(\widehat{x})\, f\, d\Gamma\,. \tag{2-32}$$

The corresponding fluxes in the coarse-grained space are calculated as,

$$j_m(x) = \int j_m(\widehat{x})\, f\, d\Gamma\,, \tag{2-33}$$

where j_m is a general notation for microscopic form of fluxes and j_m is the average flux in the coarse-grained space. As an example, the energy flux is calculated as

$$j_h(x) = \int j_h(\widehat{x})\, f\, d\Gamma\,. \tag{2-34}$$

The task ahead is then to construct the distribution function f. First we construct for a fluid the local-equilibrium distribution function denoted by f_l.

2.2.4 Local equilibrium state of fluids

Now let the nonequilibrium state be specified by a nonuniform distribution of energy and particle number, described respectively by the energy density $h(\widehat{x})$ and particle number density $n(\widehat{x})$. The corresponding Fourier components are,

$$h_k = \int e^{-ik\cdot\widehat{x}} h(\widehat{x})\, d\widehat{x}\,, \tag{2-35}$$

$$n_k = \int e^{-ik\cdot\hat{x}} n(\hat{x}) d\hat{x} \,. \tag{2-36}$$

We assume that the correlations between neighboring cells are very small, so that during the process in which particles in a cell approach equilibrium, the external correlations from other cells can be ignored. As a result, each Fourier component of the energy density and particle number density are conserved quantities. We suppose that there is a non-equilibrium distribution function f , abbreviation for $f(\{r_i, p_i\})$ and we can still define the entropy by

$$S = -\langle \ell n f \rangle, \tag{2-37}$$

where the bracket $\langle \ \rangle$ indicates the statistical average over f in the phase space. Let f_l denote the distribution function that maximizes the entropy subjected to the following constraints:

$$\begin{aligned} &\langle h_k \rangle = const\,, \\ &\langle n_k \rangle = const\,, \end{aligned} \tag{2-38}$$

and the normalization condition:

$$\int f d\Gamma = 1 \tag{2-39}$$

where $d\Gamma$ denotes the volume element in the phase space $dr_1 dp_1 ... dr_N dp_N$. The f_l is therefore determined by the equation,

$$\delta\left(\int f \ell n f d\Gamma - \sum_k \beta_{-k} \int f h_k d\Gamma + \sum_k \alpha_{-k} \int f n_k d\Gamma \right)\Bigg|_{f_l} = 0\,, \tag{2-40}$$

where β_{-k} and α_{-k} are the Lagrangian multipliers introduced corresponding to the constraints (2-38).

The resulting form for f_l is therefore,

$$f_l = Q_l^{-1} \exp\left[-\left(\sum_k \beta_{-k} h_k - \alpha_{-k} n_k \right) \right], \tag{2-41}$$

where

$$Q_l = \int \exp\left[-\left(\sum_k \beta_{-k} h_k - \alpha_{-k} n_k \right) \right] d\Gamma$$

is the normalization constant. Going over from the Fourier components h_k and n_k to the $h(\hat{x})$ and $n(\hat{x})$, we write the distribution function in the form,

$$f_l = Q_l^{-1} \exp\left[-\int \left\{ \beta(\hat{x}) h(\hat{x}) - \alpha(\hat{x}) n(\hat{x}) \right\} \right] d\hat{x} \tag{2-42}$$

where

$$Q_l = \int \exp\left[-\int \left\{ \beta(\hat{x}) h(\hat{x}) - \alpha(\hat{x}) n(\hat{x}) \right\} d\hat{x} \right] d\Gamma \tag{2-43}$$

We can therefore obtain

$$\left\langle h(\hat{x}) \right\rangle_l = \frac{\partial \ell n Q_l}{\partial \beta(x)}$$

$$\left\langle n(\hat{x}) \right\rangle_l = \frac{\partial \ell n Q_l}{\partial \alpha(x)} \tag{2-44}$$

Note that the parameters $\beta(x)$ and $\alpha(x)$ are still not specified. Now we require that the average local density over f_l equals the value when we average the local density with the corresponding equilibrium distribution function in the cell, i.e.

$$\left\langle h(\hat{x}) \right\rangle_l = \left\langle h(\hat{x})_l \right\rangle$$

$$\langle n(\hat{x}) \rangle_l = \langle n(\hat{x})_l \rangle \tag{2-45}$$

The $\beta(x)$ is then called the local temperature, and $\mu(x) = -\dfrac{\alpha(x)}{\beta(x)}$ is called the local chemical potential. The general expression of local-equilibrium distribution function is

$$f_l = Q_l^{-1} \exp\left\{ -\sum_m \int \lambda_m(\hat{x}) P_m(\hat{x}) d\hat{x} \right\}, \tag{2-46}$$

where $P_m(\hat{x})$ is a general notation for the locally conserved quantity and $\lambda_m(\hat{x})$ is the conjugate parameter. An example is when $P_0(\hat{x}) = h(\hat{x})$, $\lambda_0(\hat{x}) = \beta(\hat{x})$.

We observe that f_l is even with respect to time reversal. In contrast, except for $\tau'(x)$, all fluxes are odd. Thus, if we take the average of fluxes over f_l, we get

$$\langle j' \rangle_l = 0, \tag{2-47}$$

$$\langle j_h' \rangle_l = 0. \tag{2-48}$$

The local-equilibrium average of the off-diagonal elements of the tensor $\tau'^{\alpha\beta}$ also goes to zero

$$\left\langle \tau'^{\alpha\beta} \right\rangle_l = 0 \quad \text{for } \alpha \neq \beta, \tag{2-49}$$

where $\langle \ \rangle_l$ indicates the ensemble average over f_l. This is because according to (2-19), $\tau'^{\alpha\beta}$ is composed by two elements: the first arises from momentum transport which is an odd function of momenta except for diagonal elements; and the second term arises from interaction of particles whose ensemble average contains a product of $\left(r^\alpha{}_i - r_j{}^\alpha\right)\left(r^\beta{}_i - r_j{}^\beta\right)$ with the two-particle distribution function that depends only on $\left|r_i - r_j\right|$ in the local approximation and is therefore zero for all off-diagonal elements. The vanishing of the off-diagonal elements in the stress tensor τ' suggests that the shear stress is absent in the local-equilibrium fluid. The diagonal elements of τ' are generally nonzero, and we use them to define the fluid pressure:

$$p = \frac{1}{3}\sum_{\alpha}\left\langle \tau^{\alpha\alpha} \right\rangle_l . \tag{2-50}$$

Because the molecular flux, energy flux and shear stress all vanish on the average, dissipative processes are absent in a local-equilibrium fluid, i.e., no diffusion, thermal conduction, or viscosity. This is not surprising, because in the local equilibrium state each cell is intrinsically in equilibrium. We especially noticed the absence of shear stress in the local equilibrium. This is because when particles in each cell are in equilibrium, they are also distributed homogeneously. As a result, when we exchange the positions of two particles, there would be no change to the state of the cell. This symmetry in space suggests that the average momentum in any direction in the cell must be zero. So there exists no shear stress in the local equilibrium state.

The local equilibrium state is finite in time. The states of particles inside depend on the state of associated cell. So the internal equilibrium will be perturbed when the cells change states under the weak correlations between each other.

2.2.5 Euler's equations

Assuming that there is now a velocity field $\upsilon(x)$, we make a canonical transformation to the reference frame moving with $\upsilon(x)$.This transformation is defined by

$$p_i = p'_i + m\upsilon , \tag{2-51}$$

where the primed variable p'_i refers to the relative momentum in the moving frame. We replace the velocity υ in (2-23)-(2-28) by $\upsilon(x)$ and obtain (we drop $(\hat{x})$ in the following equations for clarity and use the prime variables to denote quantities in the moving frame)

$$n = n', \tag{2-52}$$

$$g = g' + \rho'\upsilon, \tag{2-53}$$

$$h = h' + \upsilon \cdot g' + \frac{1}{2}\rho\upsilon^2, \tag{2-54}$$

$$j = j' + n'\upsilon, \tag{2-55}$$

$$\tau = \tau' + 2\upsilon g' + \rho\upsilon\upsilon, \tag{2-56}$$

$$j_h = j_h' + (h' + \upsilon \cdot g' + \frac{1}{2}\rho\upsilon^2)\upsilon + \frac{1}{2}\upsilon^2 g' + \tau' \cdot \upsilon, \tag{2-57}$$

where ρ is the mass density defined by

$$\rho(\hat{x}) = mn(\hat{x}).$$

If we assume that the fluid is in local equilibrium in the moving frame, which suggests,

$$\langle g'(\hat{x}) \rangle = 0, \tag{2-58}$$

we immediately find from (2-58) that $\upsilon(x)$ must satisfy,

$$\upsilon(x) = \frac{\langle g(\hat{x}) \rangle}{\langle \rho(\hat{x}) \rangle}, \tag{2-59}$$

where the bracket $\langle \ \rangle$ refers to the statistical average. Equation (2-59) specializes the prime frame to be the local center-of-mass frame, which in continuum mechanics is known as the material frame. The transformation from the laboratory frame to the rest frame is a Galilean transformation. The local equilibrium in the moving frame is maintained by the Galilean transformation.

There are no fluxes according to (2-47)-(2-49) except the pressure specified in (2-50). The densities and fluxes in the laboratory frame are found to be, from (2-52)-(2-56) (we drop the bracket $\langle\ \rangle$ for visual clarity),

$$n = n' , \tag{2-60}$$

$$g = \rho \upsilon , \tag{2-61}$$

$$h = h' + \frac{1}{2}\rho\upsilon^2 , \tag{2-62}$$

$$j = n\upsilon , \tag{2-63}$$

$$\tau = pI + \rho\upsilon\upsilon , \tag{2-64}$$

$$j_h = \left\{ h + \frac{1}{2}\rho\upsilon^2 \right\}\upsilon , \tag{2-65}$$

Consequently we obtain the hydrodynamic equations of fluids after taking the average of microscopic conservation laws, with the help of the set of equations (2-60)-(2-65),

$$\frac{dn'}{dt} = -n'\nabla\cdot\upsilon \tag{2-66}$$

$$\frac{dh'}{dt} = -(h' + p)\nabla\cdot\upsilon \tag{2-67}$$

$$\frac{d\upsilon}{dt} = -\nabla p \tag{2-68}$$

These equations are known as the Euler’s equations in continuum mechanics. Fluids that satisfy Euler’s equations are called ideal fluids.

To summarize, the local-equilibrium state of fluids is an equilibrium state finite in time. It corresponds to an equilibrium state in each cell. The existence of local equilibrium state is based on the assumption that the time needed to establish equilibrium in each cell is much shorter than the change in the local densities. We can therefore neglect the correlations between the motion of cells and the states of internal particles. However, if the two time scales are comparable, then the two processes interfere with each other. Usually in the fluid when the correlation between cells is strong and cannot be neglected, we would have such interference. This stronger non-equilibrium process is the topic of next section.

2.2.6 The distribution function for non-equilibrium fluids

In a non-equilibrium fluid, the λ_m varies with both time and space. One possibility to construct a non-equilibrium distribution function would be to replace $\lambda_m(\hat{x})P_m(\hat{x})$ in (2-46) by the time-invariant part of $\lambda_m(\hat{x},t)P_m(\hat{x},t)$. Let $\overline{\lambda_m(\hat{x},t)P_m(\hat{x},t)}$ denote the invariant part of $\lambda_m(\hat{x},t)P_m(\hat{x},t)$. According to Zubarev's theory , the $\overline{\lambda_m(\hat{x},t)P_m(\hat{x},t)}$ is defined by

$$\overline{\lambda_m(\hat{x},t)P_m(\hat{x},t)} = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'} \lambda_m(\hat{x},t+t')P_m(\hat{x},t')dt', \qquad (\varepsilon \to 0) \qquad \text{(2-69)}$$

The resulting non-equilibrium distribution function takes the following form,

$$f = Q^{-1} \exp\left\{ -\sum_m \int \left[\lambda_m(\hat{x},t)P_m(\hat{x}) - \int_{-\infty}^{0} e^{\varepsilon t_1} J^m(\hat{x},t') \cdot X_m(\hat{x},t+t')dt' \right] d\hat{x} \right\} \qquad \text{(2-70)}$$

where J^m is called the thermodynamic flux and X_m is called the thermodynamic force. They are defined by,

$$J_0 = j_h' - \frac{h'+p}{\rho} g', \qquad X_0 = \nabla\beta, \qquad \text{(2-71)}$$

$$J_1 = \tau' - \left(\frac{\partial p}{\partial h'}\right)_n h' I - \left(\frac{\partial p}{\partial n}\right)_u nI\,, \qquad X_1 = -\beta \nabla \upsilon\,, \tag{2-72}$$

$$J_2 = j' - \frac{1}{m} g'\,, \qquad X_2 = -\nabla \beta \mu\,. \tag{2-73}$$

The Q in (2-73) is determined by the normalization of f. For visual clarity, the distribution function f is generally written as,

$$f = Q^{-1} e^{-A-B} \tag{2-74}$$

where

$$A = \sum_m \int \lambda_m(\hat{x},t) P_m(\hat{x}) d\hat{x}$$

$$B = -\sum_m \int\int_{-\infty}^{0} e^{\varepsilon t'} J^m(\hat{x},t') \cdot X_m(\hat{x},t+t') d\hat{x} dt' \tag{2-75}$$

Assuming that J^m and X_m are sufficiently small, the linear approximation to f takes the form

$$f = f_l \left[1 - (B - \langle B \rangle_l)\right]. \tag{2-76}$$

It follows that f reduces to f_L when B is set equal to zero.

2.2.7 Viscosity, thermal conduction and diffusion

The transport relations of fluids are obtained by a calculation of the mean fluxes, averaged over the nonequilibrium distribution function f approximated by (2-76),

$$\left\langle j^m(\hat{x}) \right\rangle = \left\langle j^m(\hat{x}) \right\rangle_l - \sum_n \int L_{mn}(x,x') \cdot X_n(x',t) dx'\,, \tag{2-77}$$

where $L_{mn}(x,x')$ is called transport coefficient defined by,

$$L_{mn}(x,x') = \int_{-\infty}^{0} e^{\varepsilon t'} \left\langle j_m(\hat{x}) \left(J_n(\hat{x}',t') - \left\langle J_n(\hat{x}',t') \right\rangle_l \right) \right\rangle_l dt'\,. \tag{2-78}$$

The form (2-77) exhibits a nonlocal dependence of the flux at points on conditions throughout the surrounding medium and at earlier times. Assuming further that $X_n(x',t)$ varies sufficiently slowly that it can be treated as constant, we obtain from (2-78),

$$\langle j_m(\hat{x})\rangle = \langle j_m(\hat{x})\rangle_l + \sum_n L_{mn}(x)\cdot X_n(x,t) \tag{2-79}$$

where $L_{mn}(x)$ is expressed by,

$$L_{mn}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t}\left(j^m(\hat{x}), J^n(\hat{x}',t')\right)dt'd\hat{x}', \tag{2-80}$$

in which $\left(j^m(\hat{x}), J^n(\hat{x}',t')\right)$ is a simplified notation for $\left\langle j_m(\hat{x})\left(J_n(\hat{x}',t') - \langle J_n(\hat{x}',t')\rangle_l\right)\right\rangle_l$ in (2-78). The transport relation (2-79) is Onsager's law expressed in local form. It shows the linear relationship between the flux and the thermodynamic force at the same position.

The specifications of $L_{mn}(x)$ is restricted by Curie's theorem [87], which indicates that fluxes and thermodynamic forces of different tensor dimensions cannot be connected with each other. As a result, only the following transport coefficients exist,

$$L_{00}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t'}(j_h(\hat{x}), J^0(\hat{x}',t'))d\hat{x}'dt' \tag{2-81}$$

$$L_{11}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t}(\tau(\hat{x}), J^1(\hat{x}',t'))d\hat{x}'dt' \tag{2-82}$$

$$L_{02}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t'}(j_h(\hat{x}), J^2(\hat{x}',t'))d\hat{x}'dt' \tag{2-83}$$

$$L_{20}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t'}(j(\hat{x}), J^0(\hat{x}',t'))d\hat{x}'dt' \tag{2-84}$$

$$L_{22}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t'}(j(\hat{x}), J^2(\hat{x}',t'))d\hat{x}'dt'. \tag{2-85}$$

For homogeneous and isotropic fluids, the coefficients L_{00}, L_{02} and L_{22} are reduced to scalars,

$$L_{00}^{\alpha\beta} = L_0 \delta^{\alpha\beta} \tag{2-86}$$

$$L_{02}^{\alpha\beta} = L_{20}^{\alpha\beta} = L_{20} \delta_{\alpha\beta} \tag{2-87}$$

$$L_{22}^{\alpha\beta} = L_2 \delta^{\alpha\beta} \quad . \tag{2-88}$$

The coefficient L_{11} for the stress tensor also takes a simplified form,

$$L_{11}^{2\alpha\beta\alpha_1\beta_1} = L_{11}^{(2)} \frac{1}{2} \left\{ \delta_{\alpha\alpha_1} \delta_{\beta\beta_1} + \delta_{\alpha\beta_1} \delta_{\beta\alpha_1} - \frac{2}{3} \delta_{\alpha\beta} \delta_{\alpha_1\beta_1} \right\}, \tag{2-89}$$

where $L_{11}^{(2)} = \int \int_{-\infty}^{0} e^{\varepsilon t} (\tau^0(\hat{x}), \tau^0(\hat{x}', t)) d\hat{x}' dt$. For convenience, we introduce the following coefficients for a homogeneous and isotropic fluid:

$$\lambda_1 = -\frac{L_0}{T^2}, \tag{2-90}$$

$$\lambda_2 = -\frac{L_{20}}{T^2}, \tag{2-91}$$

$$\xi = -\frac{L_{11}^1}{T}, \tag{2-92}$$

$$\eta = -\frac{L_{11}^{(2)}}{2T}. \tag{2-93}$$

Let $\hat{j}^m$ denote the diffusive flux in a non-equilibrium fluid defined by

$$\hat{j}^m = \left\langle j^m \right\rangle - \left\langle j^m \right\rangle_l. \tag{2-94}$$

As an example, we list the diffusive fluxes in a fluid characterized by the field of temperature, chemical potential and velocity:

$$\hat{j}_h = \lambda_1 \nabla T + L_2 \nabla \frac{\mu}{T} \tag{2-95}$$

$$\hat{j} = \lambda_2 \nabla T + L_2 \nabla \frac{\mu}{T} \tag{2-96}$$

$$\hat{\tau} = \eta \left\{ \frac{\partial \upsilon_\alpha}{\partial x_\beta} + \frac{\partial \upsilon_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \upsilon \right\} + \xi \nabla \cdot \upsilon \delta_{\alpha\beta} . \tag{2-97}$$

If μ is hold constant in equation (2-95), one obtains the Fourier's law of heat conduction,

$$j_h = \lambda_1 \nabla T , \tag{2-98}$$

where λ_1 is called the thermal conductivity coefficient and is explicitly expressed in (2-90). If T is hold constant in the diffusion equation (2-96), one recovers the Fick's law of diffusion,

$$j = \lambda_2 \nabla T \tag{2-99}$$

where λ_2 is named the diffusion constant explicitly calculated through (2-91). The η and ξ in equation (2-97) are identified as shear and bulk viscosity coefficients.

The set of equations (2-95)-(2-97) are the constitutive equations for dissipative fluxes. Combining them with the conservation equations, we obtain a set of equations that describe the dissipative process in a non-equilibrium fluid,

$$\frac{\partial \rho \upsilon_\alpha}{\partial t} + \nabla_\beta \left(\rho \upsilon_\alpha \upsilon_\beta + p \delta_{\alpha\beta} \right) = \nabla_\beta \eta (\frac{\partial \upsilon_\alpha}{\partial x_\beta} + \frac{\partial \upsilon_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \upsilon) + \nabla_\alpha \xi \left(\nabla \cdot \upsilon \right) \tag{2-100}$$

$$\frac{\partial}{\partial t} (h' + \frac{1}{2} \rho \upsilon^2) + \nabla \cdot (h' + p + \frac{1}{2} \rho \upsilon^2) \upsilon = \nabla (\lambda \nabla T) + 2 \nabla \cdot (\eta (\nabla \upsilon) \cdot \upsilon) + \nabla \cdot (\xi \upsilon \cdot (\nabla \cdot \upsilon)) \tag{2-101}$$

$$\frac{\partial n}{\partial t} + \nabla \cdot n \upsilon = - \nabla \cdot \left(\lambda_2 \nabla T \right) - \nabla \cdot \left(L_2 \nabla \frac{\mu}{T} \right) \tag{2-102}$$

Equation (2-100) is known as the Navier-Stokes equation [15].

The accuracy of formulating irreversible process with this method depends on the transportation equations used to calculate the time average of the distribution function. For example, Euler's equations are used in the time average of the local equilibrium distribution function. The equation resulting from this time average is the Navier-Stokes equation. So if one wishes to obtain more accurate equations for the momentum density, the Navier-Stokes equation should be inserted into the distribution function again to smooth out more fluctuations in time. The non-equilibrium distribution function is therefore a series of expansion in time.

The above method is based on the preliminary assumption of local equilibrium, the distribution function of which is constructed from the maximization of local entropy. It is from this local equilibrium state that one derives more non-equilibrium processes. In other words, the initial state of system needs to be known in order to obtain the state in the next stage. In the following we present another method, which directly derives the evolution equation without requirement of preliminary knowledge about the history.

2.3 Evolution equation of the distribution function

2.3.1 Liouville equation for a system interacting with surroundings

Consider a classical system surrounded by and interacting with external reservoirs and mechanical devices [16-19]. The system and surroundings collectively will be referred to as the universe. The Hamiltonian of the universe is H_u, which is assumed to be decomposed into

$$H_u = H + H_s + V , \tag{2-103}$$

where H denotes the Hamiltonian of the system dependent on variables referring only to the system, H_s denotes the Hamiltonian of the surroundings and dependends on variables referring only to the surroundings, and V is the interaction between the system and surroundings, which is assumed to be independent of the momentum variables. According to Liouville's theorem, the distribution function of the universe f_u satisfies the Liouville equation,

$$\frac{\partial f_u}{\partial t} + \left\{ f_u, H_u \right\} = 0, \tag{2-104}$$

where the bracket $\{ \}$ denotes the Poisson bracket. Let f represent the distribution function of the system defined by

$$f = \int f_u d\Gamma_s, \tag{2-105}$$

where the integration is taken over the phase space of the surroundings Γ_s. Similarly, we define the distribution function for the surroundings,

$$g = \int f_u d\Gamma, \tag{2-106}$$

where the integration is taken over the phase of the system Γ. The distribution function for the universe is related to f and g through the relation,

$$f_u = fg(1+\chi), \tag{2-107}$$

where χ indicates the correlation between f and g. The χ vanishes if the system is completely uncorrelated with the surroundings.

Integration of equation (2-104) over the phase space of the surroundings Γ_s yields,

$$\frac{\partial f}{\partial t} + \left\{ f, H \right\} + \int d\Gamma_s \left\{ f_u, H_s \right\} + \int d\Gamma_s \left\{ f_u, V \right\} = 0. \tag{2-108}$$

The integrand in the fourth term above is the divergence in the phase space of the surroundings; the integral then vanishes if f_u is assumed to vanish sufficiently rapidly in the remote regions of phase space. The final equation for the evolution of the distribution function of the system is

$$\frac{\partial f}{\partial t}+\left\{ f,H\right\} +\sum_i \partial\left(fF_i\right)/\partial p_i =0\,, \tag{2-109}$$

where

$$F_i = -\int g(1+\chi)\partial V/\partial r_i d\Gamma_s\,. \tag{2-110}$$

The r_i and p_i here are the coordinates and momenta of the system. Equation (2-109) is the Liouville equation for the system interacting with surroundings.

2.3.2 Specification of the external force from reservoirs and mechanical devices

The F_i defined by (2-110) is the external force representing the effect of the surroundings on the system. It is generally time dependent. However if the surroundings are large compared to the system, the time dependence of F_i will be sufficiently slow that over long periods of time they may be treated as constant. It is further assumed that under such conditions the system will attain an approximately steady state in which its distribution function is substantially constant.

For the purpose of demonstration, the system is assumed to interact with a single reservoir characterized by a temperature $T_r = 1/k\beta_r$. Assume that due to the interaction with the reservoir, the system can ultimately reach an equilibrium state described by the Liouville equation,

$$\frac{\partial f_r}{\partial t} + \left\{ f_r, H \right\} = 0, \tag{2-111}$$

so the condition for the system to establish equilibrium with the reservoir is,

$$\sum_i \partial\left(fF_i^r \right) / \partial p_i = 0. \tag{2-112}$$

Assume that f_r is a canonical distribution, i.e.

$$f_r = \exp\left(-\ell nQ - \beta_r H \right), \tag{2-113}$$

with Q being the normalization constant. It follows that the balance equation (2-112) is explicitly written as,

$$\partial F_i^r / \partial p_i = \beta_r F_i^r \partial H / \partial p_i, \tag{2-114}$$

which also gives another specification of the external force F_i^r exerted by the reservoir characterized by β_r. Assume that the system is initially characterized by $\beta \neq \beta_r$. It follows from equation (2-114) that the system is subjected to a driving force given by

$$F_\Delta = \left(\beta - \beta_r \right) F_i^r \partial H / \partial p_i \tag{2-115}$$

where $F_i^r \partial H / \partial p_i$ is the rate at which energy is transferred from the reservoir to the system. Denoting this quantity by j_r^h,

$$j_r^h = F_i^r \partial H / \partial p_i, \tag{2-116}$$

we express the driving force in terms of j_r^h,

$$F_\Delta = \left(\beta - \beta_r \right) j_r^h. \tag{2-117}$$

According to Maclennan's theory [16-19], the general expression for the effective force on an open system which can exchange energy and particles with more than one reservoirs or mechanical devices takes the form,

$$F_\Delta = \sum_i \left(\beta - \beta_r^{\,i}\right)\left(j_r^{\,h}\right)^i - \sum_i \left(\beta\mu - \beta_r^{\,i}\mu_r^{\,i}\right) j_r^{\,i} - \beta W \,. \tag{2-118}$$

Here $j_r^{\,i}$ is the rate at which particles are added to the system from the i^{th} reservoir; μ and $\mu_r^{\,i}$ are the chemical potentials for the system and i^{th} reservoir; and W is the rate at which mechanic work is done by the system.

The discussions so far are confined to systems interacting with discrete reservoirs. Now assume that the reservoirs are continuously distributed around the boundary of the system. For simplicity, assume that the system interacts with thermal reservoirs characterized only by their temperatures. It follows from equation (2-118) that the external forces satisfy

$$F_\Delta = -\int dA \beta(x,t)\, j_r^{\,h}(x)\,, \tag{2-119}$$

where the integration is taken over the boundary surface of the system. $T(x,t) = 1/k\beta(x,t)$ is the temperature at time t of the reservoir located at x and $j_r^{\,h}(x)$ is the energy flux density. Note that the dependence of $j_r^{\,h}(x)$ on r_i and p_i is not indicated explicitly for visual clarity. Let $h(x)$ denotes the energy density related to the total energy H by

$$H = \int h(x) dx \,.$$

After using the conservation of the energy density

$$\frac{\partial h(x)}{\partial t} = -\nabla \cdot j_h(x)\,, \tag{2-120}$$

one finds

$$F_\Delta = -\frac{d}{dt}\int \beta(x,t)h(x)dV + \int dV\left[\nabla\beta(x,t)\cdot j_r^{\,h}(x) + \frac{\partial\beta(x,t)}{\partial t}h(x)\right]. \tag{2-121}$$

2.3.3 Local equilibrium distribution and non-equilibrium distribution

With the force specified in (2-121), one wishes to find the solution of $f(t)$ satisfying equation (2-109). Assuming that initially $(t=-\infty)$ the system is in an equilibrium state characterized by a canonical distribution function,

$$f_0 = \exp\left(-\ell n Q_0 - \beta_0 H\right) \tag{2-122}$$

where $T_0 = 1/k\beta_0$ is the initial temperature, and Q_0 is the initial partition function determined by the normalization of f_0.

The solution to the Liouville equation (2-109) with initial condition (2-122) is given by McLennan [16-19] as

$$f(t) = \exp\begin{Bmatrix} -\ell n Q_0 - \int \beta(x,t) h(x) dV \\ +\int_{-\infty}^{t} \int dV \left[\nabla\beta(x,t')\cdot j_r^{\,h}(x,t,t') + \dfrac{\partial\beta(x,t')}{\partial t'} h(x,t',t) \right] \end{Bmatrix}. \tag{2-123}$$

The next step is to separate off from $f(t)$ a factor $f_l(t)$ that characterizes the state of local equilibrium. Let $Q(t)$ be determined in such as way that

$$f_l(t) = \exp\left\{-\ell n Q(t) - \int \beta(x,t) h(x) dV\right\} \tag{2-124}$$

is normalized. As a result, $f_l(t)$ yields a canonical distribution function for each volume element when correlations between volume elements can be neglected. The $Q(t)$ is related to Q_0 by

$$\ell n Q(t) = \ell n Q_0 + \int_{-\infty}^{t} dt' \int dV \frac{\partial\beta(x,t')}{\partial t'} h_e(x,t'), \tag{2-125}$$

where $h_e(x,t') = \left\langle h(x,t) \right\rangle_l$. Hence $f(t)$ is related with $f_l(t)$ by

$$f(t) = f_l(t) \exp\left[D(t)\right], \tag{2-126}$$

where

$$D(t)=\int_{-\infty}^{t}\int dV\left\{\nabla\beta(x,t')\cdot j_r^{\,h}(x,t,t')+\frac{\partial\beta(x,t')}{\partial t'}\left[h(x,t',t)-h_e(x,t')\right]\right\}. \qquad (2\text{-}17)$$

If we compare the two methods described in Chapter 2.2 and Chapter 2.3, we find:

The key idea of the method described in Chapter 2.2 is the “time average” in addition to the ensemble average, i.e. the distribution function is further averaged over a duration of a time. To take the time average, one must know in advance the detailed relationships between densities and fluxes. The construction of the distribution function is therefore dependent on the accuracy of the dynamical equations. For example, the local equilibrium distribution function is constructed based on the conservation of the local integrals of motion. The hydrodynamic equations obtained with the local equilibrium distribution function then further serve as the dynamical equations needed to construct the non-equilibrium distribution function.

The method in Chapter 2.3, on the other hand, describes how a non-equilibrium system approaches equilibrium. One obtains a general form of the time-dependent distribution function by solving the evolution equation. This general distribution function is then expanded in powers of time. The whole process then amounts to extracting the parts of this general distribution function that meet the conditions of the system. For example, the local-equilibrium distribution function is derived if the expansion is truncated at the zeroth order of time.

Both methods, although from different angles, gave a good description of irreversible transport of fluids not far from equilibrium.

We will take advantage of both methods when we formulate the properties of solids in later chapters. Solids, however, are fundamentally different from fluids in many aspects. These differences require new forms of distribution function that are characteristic of solids.

CHAPTER III

SOLIDS VERSUS FLUIDS

Beginning from this chapter, we construct the statistical mechanics of solids that capitalizes on the essential difference between a solid and a fluid. We first investigate the fundamentals that distinguish a crystal from a fluid.

3.1 Essence of solids: the existence of lattice

In a fluid, atoms execute long range motions and are described by coordinates $r_i (i=1,..N)$ measured from single origin. A fluid containing N atoms is therefore associated with $3N$ absolute degrees of freedom.

In a solid, however, atoms are associated with a lattice or network structure, the existence of which is the essence of a solid. A lattice is a mathematical abstraction of periodic points in a crystal and is of key importance in the deformation of a solid as well as the formation of defects. We therefore wish to develop a formulation based on statistical mechanics that explicitly captures the presence of a lattice and ultimately enables us to describe both the slow deformation of solid and the extremely fast atomic vibrations.

When we discussed fluids in Section 1, we assumed that it is made of “atoms”. In fact both fluids and solids are made of nuclei and electrons. For a complete statistical mechanical description of a solid, we start with nuclei and electrons. The latter are described by quantum mechanics. We invoke the Born-Oppenheimer (BO) approximation that allows us to separate the electrons and nucleus degrees of freedom because electrons are much faster than nuclei [49]. We will describe the BO approximation in some detail because we will adopt it as a generic model to develop a hierarchy of BO-like approximations to separate fast and slow degrees of freedom that operate in solids.

For simplicity and clarity, we introduce the philosophy underlining the formulation for a monatomic perfect crystal (one atom is associated with each lattice site). The formulation will be developed further for monatomic crystals containing defects.

3.2 The Born-Oppenheimer approximation for electron-nuclei system

The time-dependent Schrödinger equation to be solved for the system of electrons and nuclei is,

$$\hat{H}(r,R)\Psi(r,R,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,R,t)\,, \tag{3-1}$$

where r and R are brief notation for the electronic $\{r_i\}$ and nuclear $\{R_I\}$ degrees of freedom. The $\Psi(r,R,t)$ is the wave function of the electron-nuclei system. The total Hamiltonian H is expressed as,

$$\hat{H}(R,r) = \sum_I \frac{\hbar^2}{2M}\nabla_I^2 + \sum_i \frac{\hbar^2}{2m}\nabla_i^2 + V(R_I,..R_J) + V(r_i,..,r_j) + V(r_i,..,r;R_I,..R_J)\,. \tag{3-2}$$

The Born-Oppenheimer (BO) approximation arises from the observation that electrons, being extremely light particles, move very much faster than the comparatively heavy nuclei [49]. The electrons are therefore able to arrange themselves into an equilibrium state with respect to the instantaneous position of the nuclei. Based on the Born-Oppenheimer approximation, the dynamics of the system are able to be separated into one of electrons and one of nuclei. Because electrons and nuclei have degrees of freedom operated at different time scales, we write the total energy (3-2) as

$$H(r,R) = H(R) + H_R(r), \tag{3-3}$$

and

$$\hat{H}(R) = \sum_I \frac{\hbar^2}{2M}\nabla_I^2 + V(R_I,..R_J), \tag{3-4}$$

$$\hat{H}_R(r) = \sum_i \frac{\hbar^2}{2m}\nabla_i^2 + V(r_i,..,r_j) + V(r_i,..,r;R_I,..R_J). \tag{3-5}$$

The $H_R(r)$ here denotes the energy of electrons in an instantaneously fixed nuclei configuration $\{R_I\}$. In the expression for the electronic potential energy, the nuclei configuration is treated as parametric.

The Born-Oppenheimer approximation thus enables us to write $\Psi(r,R)$ as a product form

$$\Psi(r,R) = \phi(R)\psi_R(r) \tag{3-6}$$

in which $\psi_R(r)$ is the wave function of electrons in a fixed nuclear coordinate space denoted by R. Electrons are assumed to establish equilibrium in the fixed nuclei configuration. The $\psi_R(r)$ therefore satisfies the eigen-value equation

$$\hat{H}_R(r)\psi_R(r) = E_{el}(R)\psi_R(r), \tag{3-7}$$

from which we obtain the expectation value of the electronic energy while keeping the nuclear positions fixed at their instantaneous values $R(t)$,

$$E_{el}(R) = \left\langle \psi_R(r) \middle| \hat{H}_R(r) \middle| \psi_R(r) \right\rangle. \tag{3-8}$$

The nuclei, therefore, move according to classical mechanics in an effective potential $V_{eff}(R)$ that includes the electronic energy

$$M\ddot{R}_I(t) = -\nabla_{R_I} V_{eff}(R), \tag{3-9}$$

where

$$V_{eff}(R) = V(R_I,..R_J) + E_{el}(R). \tag{3-10}$$

We assume that electrons are always at their ground state that corresponds to the instantaneous positions of the nuclei. Thus, we will not be doing statistical mechanics of electrons, but only of the nuclei.

A nucleus in a perfect crystal, however, is associated with a lattice point. So the next step is to construct the statistical mechanics of a perfect crystal that captures the existence of lattice.

3.3 Statistical mechanics of a perfect crystal

3.3.1 Lattice displacements as auxiliary degrees of freedom

In a crystal, the position of each atom can in principle be described by its coordinates r_i measured from a single origin. The corresponding momenta are,

$$p_i = m\dot{r}_i. \tag{3-11}$$

In terms of r_i and p_i, the Hamiltonian of a crystal $H(r)$ (the abbreviation for $H(\{r_i, p_i\})$) is:

$$H(r) = \sum_i \frac{(p_i)^2}{2m} + V(r_i,..r_j). \tag{3-12}$$

Here $V(r_i,..r_j)$ is the total energy of the electron-nuclei system for the configuration $\{r_i\}$ and acts as a potential energy in a classical Hamiltonian. The coordinates r_i and p_i obey the canonical equations,

$$\dot{r}_i = \frac{\partial H(r)}{\partial p_i}, \tag{3-13}$$

$$\dot{p}_i = -\frac{\partial H(r)}{\partial r_i}. \tag{3-14}$$

According to the Liouville theorem, the distribution function $f(r)$ (the abbreviation for $f(\{r_i, p_i\})$ satisfies the Liouville equation,

$$\frac{\partial f(r)}{\partial t} + \{ f(r), H(r) \} = 0, \tag{3-15}$$

where

$$\{ f(r), H(r) \} = \sum_i \frac{\partial f}{\partial r_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial r_i} \quad . \tag{3-16}$$

is the Poisson bracket. However, the existence of lattice, which distinguishes a crystal from fluids, is not captured in equations (3-12) and (3-15). As a result, these equations are not good enough if we wish to study the deformation of a crystal.

The reason that the lattice doesn't appear in (3-15) is because the coordinates of each atom r_i are measured from a single origin just as in a liquid. However, in a crystal we have the nominal lattice (e.g., fcc, bcc, etc.) with the i^{th} lattice site being at R_i^0. We now write the position of each atom in a deformed crystal as

$$r_i = R_i^0 + u_i, \tag{3-17}$$

where u_i is the atomic displacement measured from the corresponding nominal lattice site R_i^0. With expression (3-17), we are able to include the lattice into the description of a crystal. The momenta conjugate to u_i are,

$$p_{u_i} = m\dot{u}_i. \tag{3-18}$$

The Hamiltonian in terms of u_i is now,

$$H(u)=\sum_i \frac{\left(p_{u_i}\right)^2}{2m}+V(u_i,..u_j)\,. \tag{3-19}$$

For $H(u)$, the Liouville equation (3-15) becomes,

$$\frac{\partial f(u)}{\partial t}+\left\{ f(u),H(u)\right\}=0\,. \tag{3-20}$$

Although the existence of lattice has been taken into consideration, the $f(u)$ is still not good enough for the purpose of describing deformation, because the difference between the deformation and the motion of phonons is not captured.

We now tackle this problem by envisioning a possible lattice deformation. We denote the deformed lattice sites by $R_i, i=1...N$, and define the corresponding displacements s_i by writing,

$$R_i=R_i^0+s_i\,. \tag{3-21}$$

We then assume that an atom has a relative displacement of q_i with respect to its corresponding lattice site, so that the position of an atom r_i is,

$$r_i=R_i+q_i\,. \tag{3-22}$$

The q_i describes the vibration of atoms around lattice site and is the fast variable; while s_i in equation (3-21) describes the displacement of a lattice site from the nominal position and is the slow variable. With equations (3-21) and (3-22), we associate with each atom six variables q_i and s_i, despite the fact that an atom has only three degrees of freedom. However, the q_i and s_i are not independent variables, because from equations (3-17), (3-21) and (3-22) we have the following constraints:

$$u_i = s_i + q_i \,, \tag{3-23}$$

$$\dot{u}_i = \dot{s}_i + \dot{q}_i \,. \tag{3-24}$$

Note that the same index i is used in (3-23) and (3-24), since each atom is associated with a lattice site in a perfect crystal.

We have discussed that one cannot obtain the deform equation if an atom is described by its coordinates r_i or by its displacement u_i measured from the nominal position. Thus our philosophy underling the formulation of solid is:

In order to capture deformation we have to associate with each atom ***six*** *variables,* q_i *and* s_i. *However, because each atom can have only three absolute free coordinates, if means that we must impose* ***three constraints*** *on the six variables in the extended coordinate space. The same analysis also applies to the conjugate momenta. We will then try to formulate the statistical mechanics of a perfect crystal in the extended phase space of atoms subjected to constraints.*

Table 3.1 compares the degrees of freedom and the resulting form of distribution function in fluids and crystals.

Table 3.1 Degrees of freedom: fluids versus crystals

	Fluids	Crystals
Degrees of freedom	3 absolute degrees of freedom per atom r_i	6 degrees of freedom per atom with 3 constraints q_i, s_i
Distribution function	$f(r,p)$	$f(s,p_s;q,p_q)$ but with constraints

Up to now, we have described the fundamental difference between a crystal and a fluid in terms of the degrees of freedom. The task ahead is then to find the constraints to be imposed on the $6N$ variables $\{q_i\}_N$ and $\{s_i\}_N$ assigned to a perfect crystal.

3.3.2 Constraints: the Born-Oppenheimer-like approximation for lattice deformation and phonons

The Hamiltonian expressed in terms of q_i and s_i is,

$$H(s,q)=\sum_i \frac{1}{2} m\dot{s}_i^2+\sum_i m\dot{s}_i\,\dot{q}_i+\sum_i \frac{1}{2} m\dot{q}_i^2+V\,. \tag{3-25}$$

If q_i and s_i were unconstrained degrees of freedom, we could construct a distribution function $f(s,q)$ (abbreviation for $f(\{s_i,q_i\})$) that satisfies the Liouville equation,

$$\frac{\partial f(s,q)}{\partial t}+\left\{f(s,q),H(s,q)\right\}=0\,. \tag{3-26}$$

This equation, however, is not directly applicable to the crystal because we do not have $6N$ atomic degrees of freedoms. To find constraints, we invoke the fact that q_i and

s_i are degrees of freedom operating on different time scales. Thus the motion of the lattice is effectively frozen while atomic vibrations about the lattice points are establishing an equilibrium state (the vibrations can be quantized and the associated quanta are elementary excitations called phonons). In other words, we are dealing with three degrees of freedom per atom in the instantaneous lattice configuration. Based on this physical picture, we invoke an analog of the BO approximation in the description of electron-nuclei system and impose the constraints on the form of Hamiltonian $H(s,q)$ in (3-25) so that it is written as,

$$H(s,q) = H(s) + H_s(q)\,, \tag{3-27}$$

where

$$H(s) = \sum_i \frac{1}{2} m\dot{s}_i^2 + V(s_i,..s_j)\,, \tag{3-28}$$

and

$$H_s(q) = \sum_i m\dot{s}_i\,\dot{q}_i + \sum_i \frac{1}{2} m\dot{q}_i^2 + V_s(q_i,..q_j)\,. \tag{3-29}$$

The key point here is that we will view the dependence of $H_s(q)$ on s as parametric, which will act as a form of constraint that reduces the number of degrees of freedom from $6N$ to $3N$. The term $H_s(q)$ represents the atomic energy in an instantaneous fixed lattice configuration. Based on the constrained form of $H(s,q)$ in (3-27), we construct the distribution function $f(s,q)$ which must obey the separation ansatz:

$$f_c(s,q) = f(s)\,f_s(q)\,, \tag{3-30}$$

where the dependence of $f_s(q)$ on s is again treated as parametric. The $f_s(q)$ is the distribution function of phonons with which we derive such average quantities as the phonon pressure in the instantaneous lattice configuration. When phonons are averaged out with $f_s(q)$, the motion of the atoms becomes equivalent to the motion of lattice points. We are therefore dealing again with three degrees of freedom per atom. Thus the total degrees of freedom per atom are always three during the process, although six variables are involved. As a result, by treating s as parametric as in equation (3-27), equations (3-23) and (3-24) are automatically satisfied.

The Liouville equation (3-26) together with the equations of constraints (3-27) and (3-30) form the fundamental equations to describe the deformation of a perfect crystal. The motion of phonons is captured through $f_s(q)$. Meanwhile, by solving $f(s)$ from equation (3-26) with constraints, one is able to obtain the dynamics of lattice deformation.

The separation ansatz (3-30) for slow and fast variables is analogous to the Born-Oppenheimer (BO) approximation in the description of electronic structure of crystal. We should keep in mind, however, that in the system of nuclei and electrons there are truly $6N$ absolute degrees of freedom (i.e. no constraints) while in a crystal there are $6N$ variables with $3N$ constraints, i.e. $3N$ absolute degrees of freedom. We shall therefore call the separation ansatz in a crystal "the BO-like approximation". The BO-like approximation acts as the constraint on the $6N$ variables so that the total absolute degrees of freedom are still $3N$.

3.3.3 Solving Liouville equation with constraints

To obtain the dynamics of lattice deformation, we now solve the Liouville equation (3-26) augmented by constraints (3-27) and (3-30). We invoke the derivation of dynamics of electron-nuclei system with BO approximation and follow similar procedures to derive the equations for phonons and lattice deformation. Because $\{q_i\}$ are fast variables, the time step for phonons to establish equilibrium is much shorter than the time step to change lattice configuration. As a result, for each 'fixed' lattice configuration, we write down a Liouville equation for $f_s(q)$,

$$\frac{\partial f_s(q)}{\partial t}+\{f_s(q),H_s(q)\}=0. \tag{3-31}$$

Inserting the separation ansatz (3-30) into Liouville equation (3-26), integrating over the phase space of phonons Γ_q with the help of (3-31), one obtains

$$\frac{\partial f(s)}{\partial t}+\left\{f(s),H(s)+\frac{1}{\beta}\ell n Q_{ph}(s)\right\}=0, \tag{3-32}$$

where $Q_{ph}(s)$ is the partition function for phonons expressed by

$$Q_{ph}(s)=\int \exp[-\beta H_s(q)]d\Gamma_q. \tag{3-33}$$

Here the parameter β is introduced during the averaging process of phonons, and is expressed as $\beta=1/kT$, where k is Boltzmann's constant and T is the Kelvin temperature. Equation (3-32) demonstrates that the effective Hamiltonian of lattice points is now

$$H'(s)=H(s)+\frac{1}{\beta}\ell n Q_{ph}(s). \tag{3-34}$$

The $\ell n Q_{ph}(s)$ will later be interpreted as the Helmholtz energy of phonons. Just like $E_{el}(R)$ adding to the potential field in which nuclei move according to equation (3-39), phonons affect the lattice deformation by contributing to the potential in which the lattice moves. In the Liouville equation (3-32), the Poisson bracket is now expressed as,

$$\left\{ f(s), H(s) + \frac{1}{\beta} \ell n Q_{ph}(s) \right\} = \sum_i \frac{\partial f}{\partial s_i} \frac{\partial H'}{\partial p_{s_i}} - \frac{\partial f}{\partial p_{s_i}} \frac{\partial H'}{\partial s_i}, \tag{3-35}$$

Now we have a system of lattice points each of which is described by s_i and corresponding momentum $p_{s_i} = m\dot{s}_i$. The Hamiltonian of the system is $H'(s)$ expressed in (3-34). We therefore treat lattice points as if they are real particles, and their dynamical motion will be determined by the canonical equations:

$$\dot{s}_i = \partial_{p_{s_i}} H'(s), \tag{3-36}$$

$$\dot{p}_{s_i} = -\partial_{s_i} H'(s). \tag{3-37}$$

Table 3.2 lists the analogy between the electrons-nuclei system and lattice-phonon system. Specifically, we compare solving the time-dependent Schrödinger equation for electron-nuclei system with BO approximation and solving the Liouville equation for a perfect crystal with BO-like approximation.

Table 3.2 The analogy between the electrons-nuclei system and lattice-phonon system: the time-dependent Schrödinger equation of electron-nuclei system with BO approximation and the Liouville equation of a perfect crystal constrained by BO-like approximation.

Electrons-Nuclei (r,R)	*Atomic motion- Lattice(s,q)*
fast: electrons r; slow: nuclei R r and R are independent	fast: phonon q slow: lattice s q and s are constrained
Schrödinger equation for the system, $\hat{H}(r,R)\Psi(r,R,t) = i\hbar\frac{\partial}{\partial t}\Psi(r,R,t)$ with APPROXIMATION: $H(r,R) = H(R) + H_R(r)$ $\Psi(r,R) = \phi(R)\psi_R(r)$	Liouville Equation for the system, $\frac{\partial f_c(s,q)}{\partial t} + \left\{ f_c(s,q), H(s,q) \right\} = 0$ with CONSTRAINTS: $H(s,q) = H(s) + H_s(q)$ $f_c(s,q) = f(s) f_s(q)$
Electrons in equilibrium $\hat{H}_R(r)\psi_R(r) = E_{el}(R)\psi_R(r)$ $E_{el}(R) = \left\langle \psi_R(r) \middle| \hat{H}_R(r) \middle| \psi_R(r) \right\rangle$	Atomic motion in equilibrium $f_s(q) = Q_{ph}^{-1}(s)\exp\left[-\beta H_s(q)\right]$ $Q_{ph}(s) = \int \exp(-\beta H_s(q)) d\Gamma_q$
Dynamic equation of nuclei, $M\ddot{R}_I(t) = -\nabla_{R_I}\left(V(R) + E_{el}(R)\right)$ effective potential: $V_{eff}(R) = V(R) + E_{el}(R)$	Equation for distribution function, $\frac{\partial f(s)}{\partial t} + \left\{ f(s), H(s) + \frac{1}{\beta}\ell n Q_{ph}(s) \right\} = 0$ Effective Hamiltonian: $H'(s) = H(s) + \frac{1}{\beta}\ell n Q_{ph}(s)$

The derivation of dynamic equations of lattice points can be simplified when a perfect crystal is already in absolute equilibrium. To begin with, we again invoke the Born-Oppenheimer approximation for electrons-nuclei system. If the whole electrons-nuclei system is already in absolute equilibrium, the time dependent Schrödinger equation (3-1) is reduced to the eigen-value equation,

$$\hat{H}(r,R)\Psi(r,R) = E\Psi(r,R), \tag{3-38}$$

where the expectation value of the total energy is,

$$E = \left\langle \Psi(r,R) \middle| \hat{H}(r,R) \middle| \Psi(r,R) \right\rangle. \tag{3-39}$$

Solution of the eigenvalue equation for electrons (3-7) is substituted into (3-38) to obtain equations for nuclei,

$$\psi_R(r)\left(\hat{H}(R)+E_{el}(R)\right)\phi(R)-\sum_I \frac{\hbar^2}{2M}\left(\phi\nabla_I^2\psi_R(r)+2\nabla_I\psi_R(r)\nabla_I\phi(R)\right)=E\phi(R). \qquad (3\text{-}40)$$

If the last term on the left of equation (3-40) is neglected, the electrons and nuclei motion are effectively decoupled. For the movement of nuclei, the equation of the form

$$\left(\hat{H}(R)+E_{el}(R)\right)\phi(R)=E\phi(R) \qquad (3\text{-}41)$$

would follow.

By analogy, if a perfect crystal is already in absolute equilibrium, solving Liouville equation (3-26) is reduced to the maximization of total entropy S subject to the constraint of the conservation of the mean energy H, i.e,

$$\delta S+\lambda\delta H=0 \qquad (3\text{-}42)$$

in which λ is the Lagrangian multiplier. The λ here shall be later identified as $\beta=1/kT$. The S and H in (3-42) are expressed as,

$$H=\int H(s,q)\,f_c(s,q)d\Gamma_u, \qquad (3\text{-}43)$$

$$S=-k\int f_c(s,q)\ell n f_c(s,q)d\Gamma. \qquad (3\text{-}44)$$

In equation (3-43) an (3-44), the expression of $f_c(s,q)$ is restricted by (3-30). Phonons have a canonical distribution function for each ‘frozen’ lattice configuration,

$$f_s(q)=Q^{-1}{}_{ph}(s)\exp\left[-\beta H_s(q)\right]. \qquad (3\text{-}45)$$

Substituting (3-27), (3-30), (3-45) into (3-42) yields following expression for $f(s)$,

$$f(s)=Q_l^{-1}\exp\left[-\beta(H(s)+\frac{1}{\beta}\ell n Q_{ph}(s))\right], \qquad (3\text{-}46)$$

where Q_l is the partition function for lattice points defined by,

$$Q_l = \int \exp\left[-\beta(H(s) + \frac{1}{\beta}\ell n Q_{ph}(s))\right] d\Gamma_s . \tag{3-47}$$

In the state of absolute equilibrium, the average force on each lattice point must vanish according to equation (3-37). It follows that the equilibrium form of $f(s)$ is restricted by,

$$\partial_s \ell_n Q_l(s) = 0 . \tag{3-48}$$

Table 3.3 lists the analogy between the BO approximation for electron-nuclei system when the electrons are assumed to be in ground state and the BO-like approximation for lattice-phonons system when phonons are assumed to be in equilibrium state.

Table 3.3 The analogy between the minimization of energy of electron-nuclei system (time-independent) and maximization of entropy in lattice-phonons system:

Electrons-Nuclei	*Atomic motion- Lattice*
fast: electrons r_e ; slow: nuclei R_n	fast: phonon q_i slow: lattice s_i
$H(r,R) = H(R) + H_R(r)$	$H(s,q) = H(s) + H_s(q)$
$\Psi(r_e, R_n) = \phi(R_n)\psi_{R_n}(r_e)$	$f_c(s,q) = f(s) f_s(q)$
Eigenvalue Equation for the system, $\hat{H}(r_e,R_n)\Psi(r_e,R_n) = E\Psi(r_e,R_n)$ $E = \left\langle \Psi(r,R) \middle| \hat{H}(r,R) \middle| \Psi(r,R) \right\rangle$	Entropy maximization for the crystal, $\delta S - \beta\delta H = 0$ $H = \int \tilde{H}(s,q) f(s,q) d\Gamma$
Electrons in equilibrium $\hat{H}_{R_n}(r_e)\psi_{R_n}(r_e) = E_{el}\psi_{R_n}(r_e)$ $E_{el} = \left\langle \psi_{R_n}(r_e) \middle| \hat{H}_{R_n}(r_e) \middle| \psi_{R_n}(r_e) \right\rangle$	Atomic motion in equilibrium $f_s(q) = Q^{-1}{}_{ph}(s)\exp[-\beta H_s(q)]$ $Q_{ph}(s) = \int \exp[-\beta H_s(q)] d\Gamma_q$

Equation for nuclei $\left(\hat{H}(R_n)+E_{el}(R_n)\right)\phi(R_n)=E\phi(R_n)$	Distribution function for lattice points $f(s)=Q_l^{-1}\exp\left[-\beta(H(s)+\frac{1}{\beta}\ell nQ_{ph}(s))\right]$
effective potential: $V_{eff}(R_n)=V(R_n)+E_{el}(R_n)$	Effective energy: $H'(s)=H(s)+\frac{1}{\beta}\ell nQ_{ph}(s)$

3.3.4 Deformation of a perfect crystal

3.3.4.1 The transport equation for the distribution function of lattice

Up to now we have obtained the microscopic equations (3-36) and (3-37) which describe microscopic lattice deformation. The distribution function is constructed by solving the Liouville equation (3-32). The next step is then to apply the principles of statistical mechanics to microscopic variables and equations so that we can ultimately obtain the macroscopic properties of a perfect crystal.

To derive the macroscopic dynamics of a solid, we again adopt the idea of coarse graining introduced in chapter 1. Let $\hat{x}$ be the continuous coordinate in the space in which the reference lattice is defined (similar to fluid, we use $\hat{x}$ to represent fine-grained space, and x to denote the coarse-grained space). We assume that there exists a displacement field described by a continuous function $\overline{s}(\hat{x})$, so that the displacement of a lattice point at $\hat{x}=R_i$ can be written as

$$s_i=s_i'+\overline{s}(R_i) \quad , \tag{3-49}$$

where s_i' is the relative displacement of the lattice point with respect to the displacement field $\overline{s}(\hat{x})$. The $\overline{s}(R_i)$ can be written in terms of δ functions as,

$$\overline{s}(R_i)=\int\overline{s}(\hat{x})\delta(\hat{x}-R_i)d\hat{x}\,. \tag{3-50}$$

It is therefore instructive to introduce the displacement density expressed in terms of δ functions:

$$s(\hat{x}) = \sum_i s_i \delta(\hat{x} - R_i)\,, \tag{3-51}$$

$$s'(\hat{x}) = \sum_i s_i{}' \delta(\hat{x} - R_i)\,, \tag{3-52}$$

where $s(\hat{x})$ represents the exact displacement density and $s'(\hat{x})$ denotes the relative displacement density. It follows from equations (3-49)-(3-51) that

$$s(\hat{x}) = s'(\hat{x}) + n(\hat{x})\bar{s}(\hat{x}) \quad , \tag{3-53}$$

in which $n(\hat{x})$ is the density of lattice points expressed in terms of δ functions by,

$$n(\hat{x}) = \sum_i \delta(\hat{x} - R_i)\,. \tag{3-54}$$

The displacement field $\bar{s}(\hat{x})$ will later be interpreted as the systematic deformation of lattice.

Note that we have introduced a function $\bar{s}(\hat{x})$ into the description of the displacement of each lattice point. So instead of using s_i to describe the displacement of a lattice point, we associate with it three variables $s_i{}'$ plus a function $\bar{s}(\hat{x})$ which shall be evaluated at the lattice site. The $s_i{}'$ and $\bar{s}(R_i)$ are not independent variables, because they must satisfy equation (3-49). So we again adopt the method of extending the phase space while imposing constraints, which was introduced earlier to describe the lattice-phonon system.

Let $H'(s_i{}', \bar{s})$ denote the Hamiltonian $H'(s_i)$ expressed in terms of $s_i{}'$ and $\bar{s}(x)$. If there were no constraints, we obtain the distribution function $f(s_i{}', \bar{s})$ which obeys the Liouville equation,

$$\frac{\partial f(s_i',\bar{s})}{\partial t}+\left\{ f(s_i',\bar{s}),H'(s_i',\bar{s})\right\}=0\,. \tag{3-55}$$

Equation (3-55) must be supplemented by equations of constraint. We assume that $\bar{s}(x)$ is a smooth function which varies slowly. Meanwhile s_i' has the physical meaning of fluctuation with respect to the $\bar{s}(x)$. So we apply the separation of the fast-slow variable again, and impose the following two equations of constraints:

$$H'(s_i',\bar{s})=H'(\bar{s})+H_{\bar{s}}'(s_i')\,, \tag{3-56}$$

$$f_c(s_i',\bar{s})=f(\bar{s})f_{\bar{s}}(s_i')\,. \tag{3-57}$$

Note that although $\bar{s}(x)$ is introduced as a function, it is evaluated at each lattice site. The specification of $H'(\bar{s})$ and $H_{\bar{s}}(s_i')$ depends on the expression for $H'(s)$. For a perfect crystal, $H'(s)$ is specified by equation (3-34). It follows that the expression of $H'(s)$ in terms of $\{s_i'\}$ and $\bar{s}$ (abbreviation for $\bar{s}(x)$) is

$$H'(s_i',\bar{s})=H(\bar{s})+\frac{1}{\beta}\ell nQ_{ph}(\bar{s})+H_{\bar{s}}(s_i')+\frac{1}{\beta}\ell n\left(Q_{ph}\right)_{\bar{s}}(s_i')\,, \tag{3-58}$$

so that the expressions of $H'(\bar{s})$ and $H'_{\bar{s}}(s_i')$ in equation (3-56) are

$$H'(\bar{s})=H(\bar{s})+\frac{1}{\beta}\ell nQ_{ph}(\bar{s})\,,$$

$$H^{e}{}_{\bar{s}}(s_i')=H_{\bar{s}}(s_i')+\frac{1}{\beta}\ell n\left(Q_{ph}\right)_{\bar{s}}(s_i')\,. \tag{3-59}$$

Assume that the system $\{s_i'\}$ can establish equilibrium state in the instantaneously fixed displacement field $\bar{s}(x)$. The Liouville equation for $f_{\bar{s}}(s_i')$ is,

$$\frac{\partial f_{\bar{s}}(s_i')}{\partial t}+\left\{ f_{\bar{s}}(s_i'),H_{\bar{s}}(s_i')\right\}=0\,. \tag{3-60}$$

From equations (3-55)-(3-60) we obtain the following *equation for lattice deformation*:

$$\frac{\partial f(\bar{s})}{\partial t} + \frac{\partial f(\bar{s})}{\partial \bar{s}} \dot{\bar{s}} + \frac{\partial f(\bar{s})}{\partial P} \dot{P} = -\frac{\partial}{\partial P}\left[f(\bar{s}) \frac{\partial \ell n Q'(\bar{s})}{\partial \bar{s}} \right], \tag{3-61}$$

where $P = m\dot{\bar{s}}$. Here $Q'(\bar{s})$ is the partition function of $\{s_i'\}$ system expressed by

$$Q'(\bar{s}) = \int \exp\left[-\beta H_{\bar{s}}(s_i')\right] d\Gamma_{s'}, \tag{3-62}$$

and $\ell n Q'(\bar{s})$ will later be interpreted as the Helmholtz function of the system $\{s_i'\}$ in a fixed systematic deformation denoted by $\bar{s}(x)$.

The equation (3-61) is reminiscent of the Boltzmann transport equation for the distribution function $f(r,p,t)$, which is defined so that

$$f(r,p,t) d^3 r d^3 p \tag{3-63}$$

is the probability of finding a molecule which, at time t, has a position lying within a volume element $d^3 r$ about r and momentum lying within a momentum-space element $d^3 p$ about p. The Boltzmann transport equation is expressed as,

$$\left(\frac{\partial}{\partial t} + \frac{p}{m} \cdot \nabla_r + F \cdot \nabla_p \right) f(r,p,t) = \left(\frac{\partial f}{\partial t} \right)_{coll}, \tag{3-64}$$

where F denotes the external force exerted on the molecule. The equation shows that the change of $f(r,p,t)$ is determined by two mechanisms: one is the transport of molecules in and out of a given volume element in the phase space as is described by the streaming term $\left(\frac{p}{m} \cdot \nabla_r + F \cdot \nabla_p \right)$; the other is the molecular collisions represented by the collision term $\left(\frac{\partial f}{\partial t} \right)_{coll}$. The 'streaming' term sets a rather slower time scale than the collision terms. So the absolute equilibrium condition is determined by the collision term. If the system is in absolute equilibrium, it must satisfy the 'detailed balance', i.e. both the streaming term and the $\left(\frac{\partial f}{\partial t}\right)_{coll}$ must vanish by themselves, namely,

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = 0\,, \tag{3-65}$$

$$\left(\frac{p}{m}\cdot\nabla_r + F\cdot\nabla_p\right) f(r,p,t) = 0\,. \tag{3-66}$$

If the streaming term and the collision term are nonzero but cancel each other, the system is in a steady state described by,

$$\left(\frac{p}{m}\cdot\nabla_r + F\cdot\nabla_p\right) f(r,p,t) = \left(\frac{\partial f}{\partial t}\right)_{coll}\,. \tag{3-67}$$

In a similar way, equation (3-61) shows that the change of the distribution function is determined by two factors: one is the systematic lattice deformation as is demonstrated by the streaming term $\frac{\partial f_c(\overline{s})}{\partial \overline{s}} v + \frac{\partial f_c(\overline{s})}{\partial P}\dot{P}$; the other is the coupling of the displacement field to the $\{s_i'\}$ system which generates an internal driving force calculated by $\frac{\partial \ell n Q'(\overline{s})}{\partial \overline{s}}$. The streaming term sets a slower time than the dynamics of the system $\{s_i'\}$. So the equilibrium condition of the whole system is determined by the absolute equilibrium condition of system $\{s_i'\}$. As a result, in the absolute equilibrium state is determined by the 'detailed balancing', in which both the streaming term and the driving force from $\{s_i'\}$ must vanish by themselves,

$$\frac{\partial \ell n Q'(\overline{s})}{\partial \overline{s}} = 0\,, \tag{3-68}$$

$$\frac{\partial f_c(\overline{s})}{\partial \overline{s}} v + \frac{\partial f_c(\overline{s})}{\partial P}\dot{P} = 0\,. \tag{3-69}$$

Let $\bar{s}^0(x)$ denote the equilibrium lattice configuration. According to equation (3-68) the Hemholtz free energy of the system $\{s_i'\}$ is a minimum at $\bar{s}^0(x)$. If the steaming term and the coupling term are nonzero but cancel each other, the system is said to be in a steady state described by,

$$\frac{\partial f(\bar{s})}{\partial \bar{s}}\dot{\bar{s}} + \frac{\partial f(\bar{s})}{\partial P}\dot{P} = -\frac{\partial}{\partial P}\left[f(\bar{s})\frac{\partial \ell n Q'(\bar{s})}{\partial \bar{s}} \right]. \tag{3-70}$$

The Boltzmann equation only describes the change of state of a moving particle in near perfect gas. The equation (3-70), on the other hand, describes the change of state of a deforming lattice in a crystal. Moreover, we can use the ensemble theory to calculate the average of driving force exerted by the 'microscopic' system $\{s_i'\}$ on $\bar{s}$ in (3-70). So this transport equation can be applied to systems where interactions between particles cannot be ignored. We call the equation (3-61) the transport equation for the distribution function of lattice points. It is the basic equation that we derive for the dynamics of deformation.

3.3.4.2 Elastic deformation of a perfect crystal under external force

1. Equilibrium in the presence of external force

We have mentioned that the absolute equilibrium state of the lattice corresponds to the lattice deformation $\bar{s}^0(x)$ that minimizes the partition function in (3-68). The lattice, therefore, undergoes a finite deformation from the nominal configuration $\bar{s}(x) = 0$ to $\bar{s}(x) = \bar{s}^0(x)$. The driving force to the deformation is $\frac{\partial \ell n Q'(\bar{s})}{\partial \bar{s}} \neq 0$. Let us now define a force density by,

$$\chi(\overline{s}) = -\frac{\partial \ell n Q'(\overline{s})}{\partial \overline{s}}. \tag{3-71}$$

Insertion of (3-71) into (3-70), and we obtain:

$$\frac{\partial f_c(\overline{s})}{\partial t} + \frac{\partial f_c(\overline{s})}{\partial \overline{s}} v + \frac{\partial f_c(\overline{s})}{\partial P} \dot{P} = \partial_P \left(f_c(\overline{s}) \chi(\overline{s}) \right), \tag{3-72}$$

$$-\frac{\partial \ell n Q'(\overline{s})}{\partial \overline{s}} = \chi(\overline{s}). \tag{3-73}$$

Equation (3-73) suggests that the lattice could attain equilibrium state for configurations $\overline{s} \neq \overline{s}^0$, if an external force

$$F_{ext}(\overline{s}) = -\chi(\overline{s}) = \frac{1}{\beta} \partial_{\overline{s}} \ell n Q'(\overline{s}) \tag{3-74}$$

is applied. With (3-74), we construct a new partition function defined by,

$$\ell n Q''(\overline{s}) = \ell n Q'(\overline{s}) + \beta F_{ext}(\overline{s}) \overline{s}, \tag{3-75}$$

or, more generally,

$$\ell n Q''(\overline{s}) = \ell n Q'(\overline{s}) + \int_0^{\overline{s}} \beta F_{ext}(\overline{s}) d\overline{s}. \tag{3-76}$$

The equilibrium condition when the external force is present is, therefore,

$$\partial_{\overline{s}} \ell n Q''(\overline{s}) = 0. \tag{3-77}$$

Consequently, the lattice could maintain an equilibrium state during a continuous deformation as long as the applied external force satisfies equation (3-74). The deformation that satisfies (3-77) is called elastic deformation.

In terms of the densities of quantities, equation (3-75) becomes,

$$\int \Omega dx = \int \beta \left(\Omega' + (\nabla \cdot \sigma) \overline{s} \right) dx, \tag{3-78}$$

where the following densities are defined so that:

$$\ell n Q''(\bar{s}) = \int \Omega(x)dx, \tag{3-79}$$

$$\ell n Q'(\bar{s}) = \int \Omega'(x)dx, \tag{3-80}$$

$$F_{exe}(\bar{s}) = \int \nabla \cdot \sigma(\bar{s})dx. \tag{3-81}$$

For the partition function $Q'(\bar{s})$ expressed in equation (3-62), we will show in the next chapter that $\ell n Q'(\bar{s})$ is explicitly expressed as

$$\ell n Q'(\bar{s}) = \left\langle H_{\bar{s}}(s_i') \right\rangle - TS(\bar{s}), \tag{3-82}$$

where $\left\langle H_{\bar{s}}(s_i') \right\rangle$ denotes the lattice energy averaged over $f_{\bar{s}}(s_i')$ and $S(\bar{s})$ is the entropy of the system when holding the displacement field $\bar{s}(x)$ fixed. We now introduce the energy density $h_{\bar{s}}'(x)$ and entropy density $S_{\bar{s}}(x)$ by

$$\left\langle H_{\bar{s}}(s_i') \right\rangle = \int h_{\bar{s}}'(x)dx, \tag{3-83}$$

$$S(\bar{s}) = \int S_{\bar{s}}(x)dx. \tag{3-84}$$

Inserting (3-83) and (3-84) into (3-78) and integrating by parts, we obtain the first law of thermodynamics for a deformed perfect crystal,

$$\Omega(x) = \beta\left(h_{\bar{s}}' - TS_{\bar{s}}(x) + \sigma\nabla\bar{s}\right). \tag{3-85}$$

The $\nabla\bar{s}$ is the strain tensor $e(x)$ in continuum mechanics,

$$e(x) = \nabla\bar{s}(x). \tag{3-86}$$

Equation (3-70) is rewritten in terms of $e(x)$,

$$\Omega(x) = \beta\left(h' - TS_{\bar{s}}(x) + \sigma e\right). \tag{3-87}$$

2. The elastic constant of a perfect crystal at finite temperature

Note that the stress tensor σ which entering the equation (3-87) is the external stress tensor which is a function of $\bar{s}(x)$. According to its definition (3-67), the external force can be explicitly expressed as,

$$F_{ext}(\bar{s}) = \int f_{\bar{s}}(s_i')\partial_{\bar{s}}H_{\bar{s}}(s_i')d\Gamma_{s'} . \tag{3-88}$$

For a perfect crystal, $H_{\bar{s}}(s_i')$ has the form expressed in (3-59), so one finds

$$F_{ext}(\bar{s}) = \int f_{\bar{s}}(s_i')\partial_{\bar{s}}H_{\bar{s}}(s_i')d\Gamma_{s'} + \int \frac{1}{\beta} f_{\bar{s}}(s_i')\partial_{\bar{s}}\ell n\left(Q_{ph}\right)_{\bar{s}}(s_i')d\Gamma_{s'} . \tag{3-89}$$

Equation (3-89) demonstrates that there are two factors contributing to the value of external force. One is the force needed to change the internal energy of a lattice,

$$F(\bar{s}) = \int f_{\bar{s}}(s_i')\partial_{\bar{s}}H_{\bar{s}}(s_i')d\Gamma_{s'} . \tag{3-90}$$

The other is the force needed to balance the change in phonon energy,

$$F_{ph}(\bar{s}) = \int \frac{1}{\beta} f_{\bar{s}}(s_i')\partial_{\bar{s}}\ell n\left(Q_{ph}\right)_{\bar{s}}(s_i')d\Gamma_{s'} . \tag{3-91}$$

It means that the magnitude of external force needed for the same amount of elastic deformation varies with the phonon pressure. We therefore wish to calculate the relationship between external stress and corresponding elastic strain, for certain state of phonons.

It follows from (3-89) that the external stress is expressed as

$$\sigma(x) = \bar{\tau}(x) - \bar{\tau}^0(x) \tag{3-92}$$

where the stress tensors $\bar{\tau}(\hat{x})$ and $\bar{\tau}^0(\hat{x})$ are defined by

$$F(\bar{s}) = \int \nabla \cdot \bar{\tau}(x)dx , \tag{3-93}$$

$$F_{ph}(\bar{s}) = \int \nabla \cdot \bar{\tau}^0(x)dx \ . \tag{3-94}$$

Note that the first stress tensor is directly related to the atomic stress tensor, while the second one is associated with the driving force from phonons. If we assume that the phonon gas is homogeneous, the $\overline{\tau}^0$ is reduced to a scalar which defines the phonon pressure

$$p^0 = \frac{1}{3}\sum_{\alpha} \overline{\tau}^0_{\alpha\alpha} . \tag{3-95}$$

Equation (3-92) is then rewritten as

$$\sigma_{\alpha\beta} = \overline{\tau}_{\alpha\beta} - p^0 \delta_{\alpha\beta} . \tag{3-96}$$

The external stress is a function of the lattice deformation as is shown by its definition (3-71). Let $C_{\alpha\beta\mu\nu}$ denote the elastic constant defined by

$$\sigma_{\alpha\beta} = C_{\alpha\beta\mu\nu} e^{\mu\nu} \tag{3-97}$$

where $C_{\alpha\beta\mu\nu}$ can be calculated by

$$C_{\alpha\beta\mu\nu} = \partial_{e^{\alpha\beta}} \partial_{e^{\mu\nu}} \ell n Q'(\overline{s}) = \partial_{e^{\mu\nu}} \left(\overline{\tau}_{\alpha\beta} - p^0 \delta_{\alpha\beta} \right) . \tag{3-98}$$

The elastic constant $C_{\alpha\beta\mu\nu}$ here is called isothermal elastic modulus. If we introduce a coefficient $\overline{C}_{\alpha\beta\mu\nu}$ defined by

$$\overline{C}_{\alpha\beta\mu\nu} = \partial_{e^{\mu\nu}} \overline{\tau}_{\alpha\beta} , \tag{3-99}$$

the elastic modulus $C_{\alpha\beta\mu\nu}$ is then related with $\overline{C}_{\alpha\beta\mu\nu}$ through the relation

$$C_{\alpha\beta\mu\nu} = \overline{C}_{\alpha\beta\mu\nu} \left(1 - \frac{p^0 \delta_{\alpha\beta}}{\overline{C}_{\alpha\beta\mu\nu} e_{\mu\nu}} \right) . \tag{3-100}$$

The $\overline{C}_{\alpha\beta\mu\nu}$ defined by (3-99) is interpreted as the elastic modulus of the nominal perfect crystal where no phonons are excited. We therefore see from equation (3-100) that at finite temperature, the elastic modulus of a perfect crystal is modified due to the excitation of phonons.

3.3.4.3 Thermal expansion of perfect crystal

In the previous sections, all derivations are based on the assumed physical picture that phonons drive the lattice to deform when the external force is absent. Now let us undertake a more detailed analysis.

According to equation (3-37), each lattice point is subjected to a force exerted by phonons expressed by

$$F_{s_i} = \frac{1}{\beta}\partial_{s_i}(\ell n Q^{ph}(s)) = \frac{1}{\beta}\left\langle \partial_{s_i} H_s(q) \right\rangle_q , \tag{3-101}$$

where the explicit expression for $\ell n Q^{ph}$ is,

$$\ell n Q^{ph}(s) = \beta(\bar{H}^{ph}(s) - TS_{ph}(s)) . \tag{3-102}$$

The microscopic form of phonon energy in a fixed lattice is

$$H_s(q) = V_s(q) + \sum_i \frac{1}{2} m \dot{q}_i^{\,2} , \tag{3-103}$$

where $V_s(q)$ is the potential energy in a fixed lattice configuration. The $V_s(q)$ can be expanded in powers of q about the lattice site,

$$V_s(q) = \frac{1}{2}\sum_{i,j} V_{ij}(s) q_i q_j + \frac{1}{6}\sum_{i,j,k} V_{ijk}(s) q_i q_j q_k + ... \tag{3-104}$$

where the dependence of $V_s(q)$ on the lattice configuration $\{s_l\}$ is demonstrated by the expansion coefficients $V_{ij}(s)$ and $V_{ijk}(s)$ etc. The harmonic approximation to $V_s(q)$ in (3-104) takes the form,

$$V_s(q) = \frac{1}{2}\sum_{i,j} V_{ij}(s) q_i q_j \ . \tag{3-105}$$

In order to examine how phonons are coupled to the lattice, we further expand $V_{ij}(s)$ around the nominal lattice configuration to the first order of s_l, assuming that s_l is small,

$$V_{ij}(s) = V_{ij}(0) + \sum_l \left.\frac{\partial V_{ij}(s)}{\partial s_l}\right|_{s=0} s_l , \tag{3-106}$$

where $V_{ij}(s) = \frac{\partial^2 V_s(q)}{\partial q_i \partial q_j}$. Substitute equation (3-106) into (3-105), and we obtain

$$V_s(q) = \sum_{i,j} V_{ij}(0) q_i q_j + \sum_{i,j,l} \left.\frac{\partial V_{ij}(s)}{\partial s_l}\right|_{s=0} s_l q_i q_j \, . \tag{3-107}$$

According to (3-101), the force on a lattice point is therefore,

$$F_{s_l} = \left\langle \partial_{s_l} V_s(q) \right\rangle_q , \tag{3-108}$$

where $\langle \ \rangle_q$ indicates the statistical average over the distribution function of phonons $f_s(q)$. The first term in equation (3-107) is the potential energy of phonons in the nominal lattice. It generates zero force on the lattice point and does not contribute to the lattice deformation. The driving force thus comes from the second term in (3-107),

$$F_{s_k} = \left\langle \sum_{i,j,l} \left.\frac{\partial V_{ij}(s)}{\partial s_l}\right|_{s=0} \delta_{lk} q_i q_j \right\rangle_q , \tag{3-109}$$

We denote

$$\gamma_{ijl}(s) = \left.\frac{\partial V_{ij}(s)}{\partial s_l}\right|_{s=0} . \tag{3-110}$$

If s_l is sufficiently small, we can approximate $\gamma_{ijl}(s)$ as the third order expansion coefficient in the expression of $V_s(q)$ by (3-104), so that

$$\gamma_{ijl}(s) = \left.\frac{\partial V_{ij}(s)}{\partial s_l}\right|_{s=0} \approx \frac{\partial V_{ij}}{\partial q_l} = V_{ijl} \,. \tag{3-111}$$

Expression (3-108) can therefore be approximated as,

$$F_{s_k} = \left\langle \sum_{i,j,l} V_{ijl} \delta_{lk} q_i q_j \right\rangle_q \,. \tag{3-112}$$

It follows that if $\gamma_{ijl}(s) = V_{ijl} = 0$, phonons are completely decoupled from the lattice and generate no driving force for the lattice to deform according to equation(3-112). We thus conclude that the condition for a lattice to deform under phonon pressure is

$$\gamma_{ijl}(s) \neq 0 \,. \tag{3-113}$$

In other words, the phenomenon of thermal expansion is an anharmonic effect. Through the above discussion, we also see that the decomposition of the deformation into that of lattice and phonons implicitly includes the anharmonic forces, even if harmonic approximations are made separately for the lattice and phonons.

Thermal expansion of a perfect crystal is the deformation induced by the change in external temperature. Now we would like to use the equation of lattice deformation (3-61) of perfect crystal to describe thermal expansion.

Here we give a rough estimation about the thermal expansion coefficient defined by

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T} \,, \tag{3-114}$$

where V denotes the volume of the crystal. Because phonons have faster degrees of freedom, they respond much faster than the lattice points to the temperature change. So the lattice can be assumed to stay fixed when phonons reestablish equilibrium with the reservoir characterized by the new temperature. We suppose that the distribution function of phonons corresponding to the increased temperature $T = T_0 + \delta T$ is,

$$f_0 = Q_0^{-1} e^{-\beta H_s(q)}, \tag{3-115}$$

$$f = Q^{-1} e^{-\beta H_s(q)}. \tag{3-116}$$

Assuming that δT is small, the linear expansion of f around f_0 to first order takes the form,

$$f = f_0 \left\{ 1 - (H - \langle H \rangle_0) \delta\beta \right\}. \tag{3-117}$$

We therefore see that phonons absorb heat from the reservoir. It follows from (3-117) that the change in the average phonon energy corresponding to δT is,

$$\delta \langle H_s(q) \rangle_q = -\frac{\delta T}{kT^2} \int f_0 \left\{ H(H - \langle H \rangle_0) \right\} d\Gamma. \tag{3-118}$$

According to (3-101), the increase in the force exerted by phonons is

$$\delta F_{s_i} = -\frac{\delta T}{T} \int f_0 (H - \langle H \rangle_0) \partial_{s_i} H_s(q) d\Gamma. \tag{3-119}$$

We define $C(s)$ as the specific heat of a crystal with fixed configuration $s(x)$,

$$C(s) = -\frac{1}{kT^2} \int f_0 \left\{ H(H - \langle H \rangle_0) \right\} d\Gamma, \tag{3-120}$$

with which we rewrite (3-119) as

$$\delta F_{s_i} \approx -\frac{\delta T}{T} \frac{V_{ijk}(s)}{V_{ij}(s)} \int f_0 (H - \langle H \rangle_0) V_s(q) d\Gamma \approx -\frac{1}{2} \frac{\delta T}{T} \frac{V_{ijk}(s)}{V_{ij}(s)} C_V, \tag{3-121}$$

where we replace $C(s)$ by C_V, the specific heat at fixed volume V, if the crystal is homogeneous. It follows from (3-120) that the approximate increase in the driving force of lattice deformation is,

$$\delta F_{s_l} \approx \gamma_{ijl} C_V \delta T \;. \tag{3-122}$$

In a rough approximation, we suppose that this increase in the force is balanced by a homogeneous elastic deformation in the lattice configuration. Consequently the thermal expansion coefficient is roughly expressed as,

$$\alpha \approx \frac{\gamma C_V}{VK} \tag{3-123}$$

in which γ is an abbreviation for γ_{ijl} and K is the value of the elastic modulus $\bar{C}_{\alpha\beta\mu\nu}$ of a homogeneous and isotropic perfect crystal.

The expression (3-122) agrees with the traditional expression for thermal expansion in solid physics. We therefore show that the deformation equation can indeed help us understand the macroscopic properties of a perfect crystal. Moreover, expression (3-123) is obtained from the equation of deformation with many approximations such as homogeneity. We therefore expect that we could get more information of thermal expansion from the detailed investigation of the deformation equation (3-61).

3.4 Summary

In this chapter, we introduced the basic concepts of the formulation of the statistical mechanics of a complex solid. The current theory capitalizes on the essential difference between a crystal and a fluid, i.e. atoms in a crystal are associated with a lattice. To capture the presence of a lattice, we associated with each atom <u>two classes of variables</u>: the displacement s_i of the corresponding lattice point from its nominal position and the relative atomic displacement q_i. Because there are only three absolute degrees of freedom per atom, these six variables are related by constraints. We then invoked a BO-like Ansatz, acting as a constraint here, to construct a constrained distribution function for lattice points, integrating out the "fast" vibrational (phonon) degrees of freedom. The derived effective Liouville equation for the distribution function of lattice points has a similar form as the Boltzmann transport equation. We can then determine the equilibrium condition as well as calculating the elastic constant.

Now that we have successfully incorporated the lattice into the theory through constrained distribution function, we wish to take into consideration more complexities that characterize a complex crystal such as point defects. The task ahead is then to formulate the statistical mechanics of a crystal with point defects based on the ideas developed for a perfect crystal.

CHAPTER IV

STATISTICAL MECAHNICS OF CRYSTAL WITH VACANCIES AND INTERSTITIALS

In a perfect crystal with N atoms as described in Chapter 3.3, every atom is associated with a lattice point. Each atom is described by six variables $\{\boldsymbol{s}_i, \boldsymbol{q}_i\}$, but there are three constraints between $\boldsymbol{s}_i$ and $\boldsymbol{q}_i$. The constraints are imposed through equation (3-27)

$$H(s,q) = H(s) + H_s(q),$$

where the dependence of $H_s(q)$ on s is treated as parametric. Based on (3-27), we construct the constrained form of the distribution function (3-30)

$$f_c(s,q) = f(s)\, f_s(q),$$

which is the basic equation underlying the statistical mechanics of a perfect crystal.

In terms of degrees of freedom and constraints, a crystal is perfect in the sense that the degrees of freedom equal the number of constraints. Since the absolute degrees of freedom are always determined by the number of atoms, we envision that it is the modification of constraints that results in the formation of defects. Along this line of thought, we first consider point defects, primarily vacancies and self-interstitials.

4.1 Statistical mechanics of a crystal with only vacancies

4.1.1 Formation of vacancies

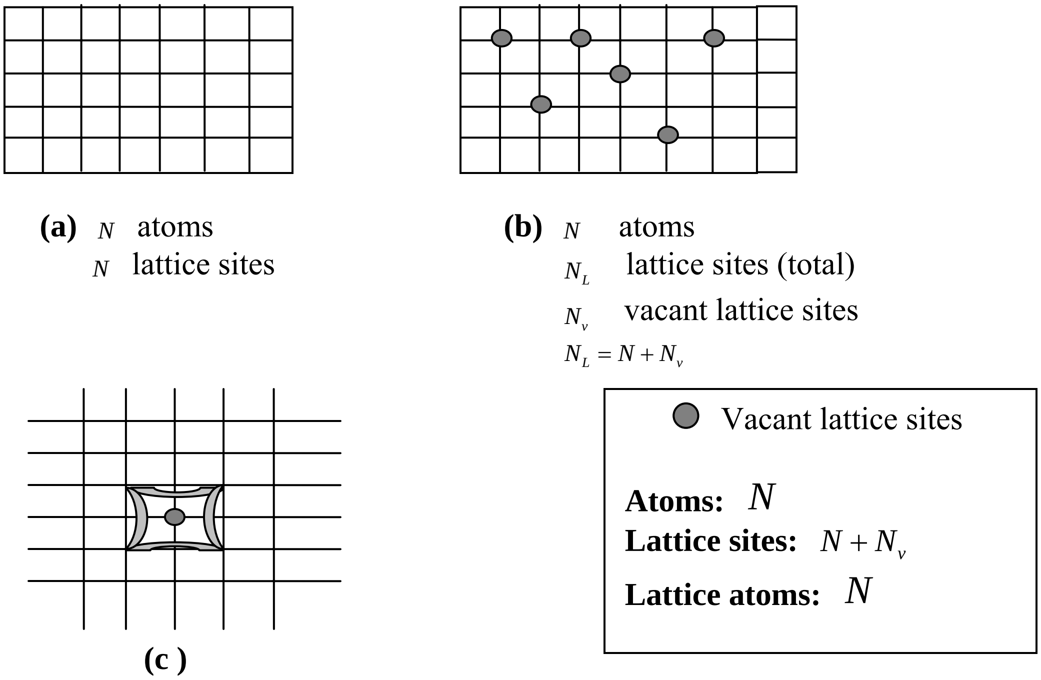
In the case of a perfect crystal, there is no need to distinguish between infinite crystal and finite crystal. To study defects, however, we consider a crystal with finite size which is still large enough to ignore surface effects. Moreover, it is assumed that the shape does not matter throughout the formulation.

A crystal containing N_L lattice sites and $N < N_L$ atoms includes $N_v = N_L - N << N$ vacant lattice sites called vacancies. The formation of a crystal with vacancies is demonstrated in Figure 4.1.

(1) Figure 4.1 (a) shows a perfect crystal containing N atoms and N lattice sites.

(2) Atoms are removed from the bulk of the perfect crystal and put on the surface (Figure 4.1 (b)). The bulk is extended with new lattice sites generated, compared to the perfect crystal in Figure 4.1 (a). The crystal now has N_L lattice sites among which $N_v = N_L - N << N$ are vacant.

(3) Atoms displace from the corresponding perfect lattice sites due to the existence of vacancies as shown in Figure 4.1(c). In other words, the atomic configuration relaxes from the configuration Figure 4.1(b) until new equilibrium state is established.



(a) N atoms
N lattice sites

(b) N atoms
N_L lattice sites (total)
N_v vacant lattice sites
$N_L = N + N_v$

(c)

Figure 4.1 Formation of vacancies

Note that the number of atoms is always conserved throughout the process. The existence of vacancies, however, induces deformation in the crystal demonstrated by Figure 4.1 (c). In the following sections, we shall first derive the equations of deformation for the crystal with vacancies. From the equation of deformation, we calculate the equilibrium concentrations of vacancies as well as the elastic constant.

4.1.2 Liouville equation for the crystal with only vacancies

If all of N_L lattice sites in Figure 4.1 (b) were occupied by atoms, the crystal would be perfect. As shown in Chapter 3.3, we can associate with the lattice points in a perfect crystal a distribution function which satisfies the Liouville equation (3-32)

$$\frac{\partial f(s)}{\partial t} + \left\{ f(s), H'(s) \right\} = 0 \,,$$

where $H'(s)$ is the effective total energy of the perfect crystal expressed by (3-34),

$$H'(s) = H(s) + \frac{1}{\beta}\ell n Q_{ph}(s).$$

For a perfect crystal with N_L lattice points, the effective total energy is denoted by $H'(\{s_i\}_{N_L})$, and the distribution function is denoted by $f(\{s_i\}_{N_L})$. According to (3-34), the expression for $H'(\{s_i\}_{N_L})$ is,

$$\begin{aligned} H'(\{s_i\}_{N_L}) &= H(\{s_i\}_{N_L}) + \frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_{N_L}) \\ &= \sum_{i=1}^{N_L}\frac{1}{2}m\dot{s}_i^2 + V(\{s_i\}_{N_L}) + \frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_{N_L}), \end{aligned} \tag{4-1}$$

where $V(\{s_i\}_{N_L})$ refers to the interaction between the N_L lattice points and $\ell n Q_{ph}(\{s_i\}_{N_L})$ is the Helmholtz energy of phonons in a fixed lattice configuration of a perfect crystal with N_L atoms. For convenience, let $V'(\{s_i\}_{N_L})$ represent the effective potential of lattice points defined by,

$$V'(\{s_i\}_{N_L}) = V(\{s_i\}_{N_L}) + \frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_{N_L}). \tag{4-2}$$

Equation (4-1) is then rewritten as,

$$H'(\{s_i\}_{N_L}) = \sum_{i=1}^{N_L}\frac{1}{2}m\dot{s}_i^2 + V'(\{s_i\}_{N_L}). \tag{4-3}$$

The Liouville equation (3-32) for the perfect crystal with N_L lattice points is expressed in terms of $H'(\{s_i\}_{N_L})$ and $f(\{s_i\}_{N_L})$ as,

$$\frac{\partial f(\{s_i\}_{N_L})}{\partial t} + \left\{ f(\{s_i\}_{N_L}), H'(\{s_i\}_{N_L}) \right\} = 0 \tag{4-3}$$

We now distinguish between two types of lattice sites, depending on whether or not the associated atoms are to be removed. One is the lattice site to become vacancy when the associated atom is removed. The other has atoms vibrating around. We will use the term "lattice atom" to denote the lattice sites that have atoms even after vacancies are created. We then follow the method in Chapter 3.3. The system we use as the reference is the nominal lattice of a perfect crystal with N_L lattice sites. The position of a "lattice atom" is then described by its displacement $s_i\left(i=1...N\right)$ relative to its nominal position $R_i^0\left(i=1...N\right)$. For the description of the lattice sites that become vacancies, it is more convenient to describe their positions by coordinates $R^v{}_k\left(k=1...N_v\right)$ measured from a single origin. So the corresponding momenta conjugate to $R^v{}_k\left(k=1...N_v\right)$ are,

$$p^v{}_k = m\dot{R}_k^v \quad . \tag{4-4}$$

Note that the mass of an atom m is here because we still have atoms at all $N_L = N + N_v$ sites.

If the crystal with N_L sites were perfect (no vacancies), then $s_i\left(i=1...N\right)$ and $R^v{}_k\left(k=1...N_v\right)$ would be independent variables. The effective energy $H'(\left\{s_i\right\}_{N_L})$ is written in terms of $s_i\left(i=1...N\right)$ and $R^v{}_k\left(k=1...N_v\right)$ as,

$$\begin{aligned} H'(\left\{s_i\right\}_{N_L}) &= H'(\left\{s_i\right\}_N, \left\{R^v{}_k\right\}_{N_v}) \\ &= \sum_{i=1}^{N}\frac{1}{2}m\dot{s}_i^2 + V'(\left\{s_i\right\}_N) + \sum_{k=1}^{N_v}\frac{1}{2}m\dot{R}_k^2 + V'(\left\{R^v{}_k\right\}_{N_v}) + V_c'(\left\{s_i\right\}_N, \left\{R^v{}_k\right\}_{N_v}), \end{aligned} \tag{4-5}$$

where $V_c'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ represents the interaction among the two classes of atoms in our perfect crystal with N_L sites. For $H'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ in (4-5), the Liouville equation (4-3) becomes,

$$\frac{\partial f(\{s_i\}_N, \{R^v{}_k\}_{N_v})}{\partial t} + \left\{ f(\{s_i\}_N, \{R^v{}_k\}_{N_v}), H'(\{s_i\}_N, \{R^v{}_k\}_{N_v}) \right\} = 0 . \qquad (4\text{-}6)$$

When we actually remove N_v atoms, the crystal has only N atoms and therefore only $3N$ absolute degrees of freedom. Despite this fact, we still associate $3N_L$ variables $(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ with the crystal in order to capture the deformation driven by vacancies. If these $3N_L$ variables were independent, the Liouville equation for the system is expressed by (4-6) with $H'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ described by (4-5). Now that the crystal has only $3N$ absolute degrees of freedom, we must impose $3N_v$ constraints on $\{s_i\}_N$ and $\{R^v{}_k\}_{N_v}$ in order to reduce the total degrees of freedom from $3N_L$ back to $3N$. We see therefore the difference between the descriptions of vacancies and the lattice sites to become vacancies in a perfect crystal is:

The $\{R^v{}_k\}_{N_v}$ *of vacancies are constrained variables. The* $\{R^v{}_k\}_{N_v}$ *of the lattice sites to become vacancies, on the other hand, are independent variables in a perfect crystal.*

To find the equation of constraints, we observe that the vacancy migration (redistribution) occurs at a faster time scale than lattice deformation. In other words, the $R^v{}_k (k = 1,..N_v)$ are the faster variables while $s_i (i = 1,..N)$ are the slower one. Based on this observation, we impose the constraints on the form of $H'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ in (4-5) so that it is written as,

$$H'_c(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = H'(\{s_i\}_N) + H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}), \tag{4-7}$$

where

$$H'(\{s_i\}_N) = \sum_{i=1}^{N} \frac{1}{2} m\dot{s}_i^2 + V'(\{s_i\}_N) \tag{4-8}$$

$$H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}) = \sum_{k=1}^{N_v} \frac{1}{2} m\dot{R}_k^{v2} + V'(\{R^v{}_k\}_{N_v}) + V_c'(\{s_i\}_N, \{R^v{}_k\}_{N_v}). \tag{4-9}$$

The key point here is that the dependence of the energy of vacancies $H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})$ on $\{s_i\}_N$ is treated as parametric. According to (4-7), we construct the constrained form of distribution function $f_c(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ which must obey the separation ansatz:

$$f_c(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = f(\{s_i\}_N) f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}), \tag{4-10}$$

where $f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})$ is the distribution function for vacancies in a fixed lattice configuration while the $f(\{s_i\}_N)$ describes the state of the lattice points.

The Liouville equation (4-6) together with the equations of constraints (4-7) and (4-10) form the basic equations for a crystal with vacancies. Vacancies are associated with a distribution function $f_{\{s_i\}_N}(\{R_k\}_{N_v})$, *while* $f(\{s_i\}_N)$ *enables one to obtain the description of lattice deformation.*

We now solve the equation (4-6) augmented by (4-7) and (4-10). The procedure is similar as how we separate the fast and slow variables in a perfect crystal. Based on the assumption that vacancies establish equilibrium in each ‘fixed’ lattice configuration, we first write down the Liouville equation for $f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})$,

$$\frac{\partial f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})}{\partial t}+\left\{f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}),H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})\right\}=0\,. \tag{4-11}$$

Inserting the separation ansatz (4-10) into Liouville equation (4-6), integrating over the phase space of vacancies $d\Gamma_v = d\{R^v{}_k\}_{N_v}\, d\{p^v{}_k\}_{N_v}$ with the help of (4-11), one obtains,

$$\frac{\partial f(\{s_i\}_N)}{\partial t}+\left\{f(\{s_i\}_N),H'(\{s_i\}_N)+\frac{1}{\beta}\ell n Q_v(\{s_i\}_N)\right\}=0\,, \tag{4-12}$$

where $Q_v(\{s_i\}_N)$ is the partition function for N_v vacancies expressed by

$$Q_v(\{s_i\}_N)=\int \exp\left[-\beta H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})\right]d\Gamma_v\,. \tag{4-13}$$

Here the parameter β is introduced during the averaging process of vacancies, and is expressed as $\beta = 1/kT$ where k is Boltzmann’s constant and T is the Kelvin temperature. The $\frac{1}{\beta}\ell n Q_v(\{s_i\}_N)$ will be later interpreted as the Helmholtz energy of vacancies in the ‘fixed’ lattice configuration.

Equation (4-12) shows that the existence of vacancies provides an extra potential $\frac{1}{\beta}\ell n Q_v(\{s_i\}_N)$ to the lattice points. Let $H_L(\{s_i\}_N)$ denote the effective Hamiltonian of lattice points in a crystal with vacancies defined by,

$$H_L(\{s_i\}_N)=H'(\{s_i\}_N)+\frac{1}{\beta}\ell n Q_v(\{s_i\}_N)\,. \tag{4-14}$$

It follows that the effective canonical equations for the lattice points become,

$$\begin{aligned} \dot{s}_i &= \partial_{p_{s_i}} H_L(\{s_i\}_N) \\ \dot{p}_{s_i} &= -\partial_{s_i} H_L(\{s_i\}_N) \quad (i = 1, \ldots N) \end{aligned} . \tag{4-15}$$

Equations (4-15) are the effective microscopic dynamic equations for the lattice points in a crystal with vacancies. If there are no vacancies, i.e. $N_v = 0$, equation (4-14) is reduced to $H'(\{s_i\}_N)$ which is just the effective total energy for the perfect crystal with N atoms.

Thus, by adding constraints in the “lattice space”, vacancies are naturally incorporated into the theory. We explore next the relationship between constraints and formation of interstitials.

4.2 Statistical mechanics of a crystal with only interstitials

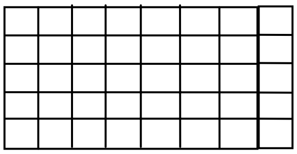
4.2.1 Formation of interstitials

A crystal containing N atoms and $N_L < N$ lattice sites includes $N_{in} = N - N_L < N$ interstitials. The formation of a crystal with interstitials is demonstrated in *Figure 4.2*:

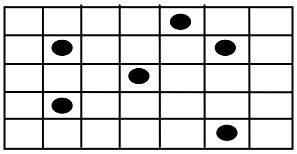
(1) *Figure 4.2 (a)* shows a perfect crystal containing N atoms and N lattice sites.

(2) Atoms are removed from the surface of the perfect crystal (*Figure 4.2 (a)*) and put inside the bulk. The volume of the bulk diminishes. The crystal now has $N_L < N$ lattice sites. There are $N_{in} = N - N_L$ atoms occupying the interstitial space among the lattice sites as shown by *Figure 4.2 (b).*

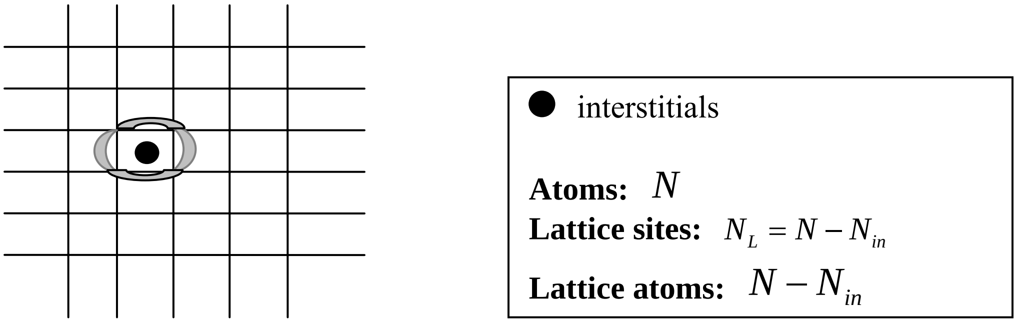
(3) The existence of interstitials induces deformation as shown in Figure *4.2 (c).*



(a) N atoms
N lattice sites



(b) N atoms
N_L lattice sites



● interstitials

Atoms: N
Lattice sites: $N_L = N - N_{in}$
Lattice atoms: $N - N_{in}$

(c)

Figure 4.2 Formation of interstitials

4.2.2 Liouville equation for a crystal with only interstitials

If the N atoms made up a perfect crystal, we could describe it by two classes of variables $\{s_i\}_N$ and $\{q_i\}_N$ as shown in Chapter3.3. The perfect crystal can be associated with a distribution function $f(\{s_i\}_N, \{q_i\}_N)$ which satisfies the Liouville equation

$$\frac{\partial f(\{s_i\}_N, \{q_i\}_N)}{\partial t} + \left\{ f(\{s_i\}_N, \{q_i\}_N), H(\{s_i\}_N, \{q_i\}_N) \right\} = 0\,, \tag{4-16}$$

augmented by equations of constraints

$$H(\{s_i\}_N, \{q_i\}_N) = H(\{s_i\}_N) + H_{\{s_i\}_N}(\{q_i\}_N)\,, \tag{4-17}$$

$$f_c(\{s_i, q_i\}_N) = f(\{s_i\}_N)\, f_{\{s_i\}_N}(\{q_i\}_N)\,, \tag{4-18}$$

where

$$H(\{s_i\}_N, \{q_i\}_N) = \sum_{i=1}^{N} \frac{1}{2} m\dot{s}_i^2 + \sum_{i=1}^{N} m\dot{s}_i\, \dot{q}_i + \sum_{i=1}^{N} \frac{1}{2} m\dot{q}_i^2 + V(\{s_i\}_N, \{q_i\}_N)\,, \tag{4-19}$$

$$H(\{s_i\}_N) = \sum_{i=1}^{N} \frac{1}{2} m\dot{s}_i^2 + V(\{s_i\}_N)\,, \tag{4-20}$$

$$H_{\{s_i\}_N}(\{q_i\}_N) = \sum_{i=1}^{N} m\dot{s}_i\, \dot{q}_i + \sum_{i=1}^{N} \frac{1}{2} m\dot{q}_i^2 + V_s(\{q_i\}_N)\,. \tag{4-21}$$

For convenience, we shall refer to the system of $\{s_i\}_N$ as "lattice space" and the system of $\{q_i\}_N$ as "atomic space". The "atomic space" has fast variables $\{q_i\}_N$ and is assumed to establish equilibrium state before lattice deformation. The distribution function of the "atomic space" $f_{\{s_i\}_N}(\{q_i\}_N)$ in (4-18) therefore satisfies the following Liouville equation,

$$\frac{\partial f_{\{s_i\}_N}(\{q_i\}_N)}{\partial t} + \left\{ f_{\{s_i\}_N}(\{q_i\}_N), H_{\{s_i\}_N}(\{q_i\}_N) \right\} = 0\,. \tag{4-22}$$

It then follows from (4-16)-(4-22) that the effective Liouville equation for the "lattice space" of a perfect crystal with N atoms is

$$\frac{\partial f(\{s_i\}_N)}{\partial t} + \left\{ f(\{s_i\}_N), H(\{s_i\}_N) + \frac{1}{\beta} \ell n Q_{ph}(\{s_i\}_N) \right\} = 0\,, \tag{4-23}$$

where $\frac{1}{\beta} \ell n Q_{ph}(\{s_i\}_N)$ is interpreted as the Helmholtz energy of phonons in a fixed lattice configuration.

We now distinguish between two types of atoms: one is the atom that vibrates around a lattice site and is referred to as the "lattice atom"; the other is the atom to become an interstitial. For the description of "lattice atoms", we follow the method introduced in Chapter 3.3. The system we use as the reference is the nominal lattice of a perfect crystal containing N atoms. The position of a "lattice atom" is then described by two variables: $s_i\left(i=1...N_L\right)$ and $q_i\left(i=1...N_L\right)$: the $s_i\left(i=1...N_L\right)$ describes the displacement of the corresponding lattice site from its nominal position R_i^0 ; the $q_i\left(i=1...N_L\right)$ describes the relative atomic displacement from the lattice site. For the description of atoms that become interstitials, it is more convenient to describe their positions by coordinates ${r^{in}}_l\left(l=1...N_{in}\right)$ measured from a single origin. The corresponding momenta conjugate to ${r^{in}}_l\left(l=1...N_{in}\right)$ are,

$$ {p^{in}}_l = m\dot{r}_l^{in} \quad . \tag{4-24}$$

The "atomic space" is now described by $\left(\left\{q_i\right\}_{N_L},\left\{{r^{in}}_l\right\}_{N_{in}}\right)$.

In terms of new variables, the energy of the "atomic space" $H_{\{s_i\}_N}(\left\{q_i\right\}_N)$ is now denoted by $H_{\{s_i\}_N}(\left\{q_i\right\}_{N_L},\left\{{r^{in}}_l\right\}_{N_{in}})$ expressed as,

$$\begin{aligned} H_{\{s_i\}_N}(\left\{q_i\right\}_{N_L},\left\{{r^{in}}_l\right\}_{N_{in}}) &= H_{\{s_i\}_N}(\left\{q_i\right\}_N) \\ &= H_{\{s_i\}_N}(\left\{{r^{in}}_l\right\}_{N_{in}}) + H_{\{s_i\}_N}(\left\{q_i\right\}_{N_L}) + V_{\{s_i\}_N}(\left\{q_i\right\}_{N_L},\left\{{r^{in}}_l\right\}_{N_{in}})^{,} \end{aligned} \tag{4-25}$$

where

$$ H_{\{s_i\}_N}(\left\{{r^{in}}_l\right\}_{N_{in}}) = \sum_{l=1}^{N_{in}}\frac{1}{2}m\left(\dot{r}^{in}\right)_l^2 + \sum_{i=1}^{N}\sum_{l=1}^{N_{in}} m\dot{s}_i\,\dot{r}_l^{in} + V_{\{s_i\}_N}(\left\{{r^{in}}_l\right\}_{N_{in}}), \tag{4-26}$$

$$ H_{\{s_i\}_N}(\left\{q_i\right\}_{N_L}) = \sum_{i=1}^{N_L}\frac{1}{2}m\dot{q}_i^2 + \sum_{j=1}^{N}\sum_{i}^{N_L} m\dot{s}_j\dot{q}_i + V_{\{s_i\}_N}(\left\{q_i\right\}_{N_L}), \tag{4-27}$$

and $V_{\{s_i\}_N}(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ represents the interaction between the two types of atoms in the "atomic space". The distribution function $f_{\{s_i\}_N}(\{q_i\}_N)$ is rewritten as $f_{\{s_i\}_N}(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ and the Liouville equation (4-16) is rewritten as,

$$\frac{\partial f_{\{s_i\}_N}(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})}{\partial t}+\left\{f_{\{s_i\}_N}(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}}),H_{\{s_i\}_N}(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})\right\}=0 \qquad (4\text{-}28)$$

Note that the "atomic space" always has $3N$ degrees of freedom because there are N atoms.

If all N atoms were "lattice atoms", the crystal would be perfect (no interstitials) with $3N$ *independent* constraints *simultaneously* imposed on the "atomic space". In other words, all the lattice points $\{s_i\}_N$ are effectively frozen on the same time scale.

We see therefore that the number of total degrees of freedom is determined by the number of atoms. Any crystal containing N atoms *has* $3N$ degrees of freedom. *The number of independent constraints, on the other hand, is determined by the number of "lattice atoms". In a perfect crystal, all the atoms are "lattice atoms", so that the number of the degrees of freedom is equal to the number of independent constraints.*

When we actually have N_{in} interstitials, however, there are only N_L "lattice atoms" and therefore only $3N_L$ independent constraints. In other words, there are $3N_{in}$ constraints *released* when N_{in} interstitials are generated. In order to capture the deformation induced by interstitials, however, we still associate the atomic space $(\{q_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ with $3N$ constraints. If these constraints were all independent, i.e. they were simultaneously imposed on the "atomic space", the atomic energy would be

$H_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}})$ expressed in (4-25) and the Liouville equation would be described by (4-28). Now that there are only $3N_L$ independent constraints, we must restrict the form of $H_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}})$ in order to reduce the total number of independent constraints from $3N$ to $3N_L$. We observe that:

(1) Phonons vibrate on a time scale much smaller than both diffusion of interstitials and lattice deformation. In other words, both interstitials and lattice points are effectively frozen while phonons establish equilibrium state.

(2) The diffusion of interstitials, on the other hand, is on a time scale faster than lattice deformation but slower than phonons. As a result, interstitials are effectively frozen on the time scale of phonons, but free on the time scale of lattice deformation.

(3) Lattice points are effectively frozen with respect to both phonons and interstitials.

Based on this observation, the state of phonons is first described with respect to 'frozen' interstitials. In other words, there are $3N_{in}$ constraints first imposed on $\{q_i\}_{N_L}$ while phonons establish equilibrium state. These $3N_L$ constraints are effectively released on the scale of lattice deformation, however, because interstitials are now 'free' while the lattice $\{s_i\}_{N_L}$ is effectively frozen. Thus on the time scale of the lattice, we are only dealing with $3N_L$ constraints imposed upon interstitials $\{r^{in}{}_l\}_{N_{in}}$ while interstitials establish equilibrium state.

Based on this physical picture, we restrict the form of $H_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}})$ in (4-25) by writing it as,

$$H_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}}) = H_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) + H_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L}), \tag{4-29}$$

where

$$H_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) = \sum_{l=1}^{N_{in}} \frac{1}{2} m \left(\dot{r}^{in}\right)_l^2 + \sum_{i=1}^{N} \sum_{l=1}^{N_{in}} m \dot{s}_i \dot{r}_l^{in} + V_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}), \tag{4-30}$$

$$\begin{aligned} H_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L}) &= \sum_{i=1}^{N_L} \frac{1}{2} m \dot{q}_i^2 + V_{\{s_i\}_N}(\{q_i\}_{N_L}) + V_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}}) \\ &\quad + \sum_{j=1}^{N_L} \sum_{i}^{N_L} m \dot{s}_j \dot{q}_i + \sum_{l=1}^{N_{in}} \sum_{i}^{N_L} m \left(\dot{r}_l^{in}\right) \dot{q}_i \end{aligned} . \tag{4-31}$$

The lower index $\{r^{in}{}_l\}^s{}_{N_{in}}$ in (4-29) represents the instantaneous configuration of interstitials in a fixed lattice configuration $\{s_i\}_{N_L}$. *The key point here is that the dependence of phonon energy* $H_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})$ *on interstitials* $\{r^{in}{}_l\}^s{}_{N_{in}}$ *is first treated as parametric, and then the dependence of interstitials on the lattice configuration* $\{s_i\}_{N_L}$ *is treated as parametric*. As a result, although we still associate $3N$ constraints with the "atomic space" $(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}})$, we are only dealing with $3N_L$ independent constraints on the time scale of lattice deformation.

For the expression of $H_{\{s_i\}_N}(\{q_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}})$ in (4-29), we construct the constrained form of distribution function for the "atomic space" which obey the separation ansatz

$$f_{\{s_i\}_N}(\{r^{in}{}_l\}_{N_{in}}, \{q_i\}_{N_L}) = f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L}), \tag{4-32}$$

where $f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})$ is the distribution function of phonons in a fixed configuration of interstitials while $f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})$ describes the states of interstitials in a fixed lattice configuration.

The Liouville equation (4-28) together with the equations of constraints (4-29) and (4-32) form the basic equations for the " atomic space" of a crystal with interstitials. The motion of phonons is captured by $f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})$. The state of interstitials is described by $f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})$ from which we obtain the dynamics of interstitials.

We now solve equation (4-28) augmented by (4-29) and (4-32) in the "atomic space" by applying the separation of fast and slow variables. The two time scales involved in the "atomic space" are the scale of phonons and the scale of the diffusion of interstitials. Phonons have faster variables, and are assumed to establish equilibrium in each 'fixed' configuration of interstitials. The distribution function of phonons $f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})$ satisfies the Liouville equation,

$$\frac{\partial f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})}{\partial t}+\left\{ f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L}), H_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})\right\}=0\,. \tag{4-33}$$

Substituting the separation ansatz (4-32) into Liouville equation (4-28), integrating over the phase space of phonons Γ_{ph} with the help of (4-33), one obtains

$$\frac{\partial f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})}{\partial t}+\left\{ f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}), H_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})+\frac{1}{\beta}\ell n Q_{ph}(\{r^{in}{}_l\}^s{}_{N_{in}})\right\}=0\,, \tag{4-34}$$

Where $Q_{ph}(\{r^{in}{}_l\}^s{}_{N_{in}})$ is the partition function for phonons expressed by

$$Q_{ph}(\{r^{in}{}_l\}^s{}_{N_{in}})=\int \exp\left[-\beta H_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N_L})\right] d\Gamma_{ph}\,. \tag{4-35}$$

Here the parameter β is introduced during the averaging process of vacancies, and is expressed as $\beta = 1/kT$ where k is Boltzmann's constant and T is the Kelvin temperature. The $\frac{1}{\beta}\ell n Q_{ph}(\left\{r^{in}{}_{l}\right\}^{s}{}_{N_{in}})$ will be interpreted as the Helmholtz energy of phonons in the 'fixed' configuration of interstitials.

Equation (4-34) shows that phonons provide an extra potential $\frac{1}{\beta}\ell n Q_{ph}(\left\{r^{in}{}_{l}\right\}^{s}{}_{N_{in}})$ to the interstitials. Let $H^{in}{}_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}})$ denote the effective Hamiltonian of interstitials in a fixed lattice configuration defined by,

$$H^{in}{}_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}) = H_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}) + \frac{1}{\beta}\ell n Q_{ph}(\left\{r^{in}{}_{l}\right\}^{s}{}_{N_{in}}) \,. \tag{4-36}$$

It follows that the effective canonical equations for interstitials become,

$$\begin{aligned} \dot{r}^{in}_{l} &= \partial_{p^{in}{}_{l}} H^{in}{}_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}) \\ \dot{p}^{in}_{l} &= -\partial_{r^{in}{}_{l}} H^{in}{}_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}) \quad (l = 1, \ldots N_{in}) \end{aligned} \tag{4-37}$$

The effective Liouville equation for the atomic space of a crystal with interstitials is now,

$$\frac{\partial f_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}})}{\partial t} + \left\{ f_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}), H^{in}{}_{\{s_i\}_{N_L}}(\left\{r^{in}{}_{l}\right\}_{N_{in}}) \right\} = 0 \,. \tag{4-38}$$

Now we take into account the "lattice space" in order to derive the dynamic equation for lattice points. Interstitials diffuse on a time scale smaller than the lattice deformation. Thus the N_L lattice points are effectively frozen while interstitials establish equilibrium state. The total energy of the crystal containing N_L "lattice atoms" and N_{in} interstitials is denoted by $H(\left\{s_i\right\}_{N_L}, \left\{r^{in}{}_{l}\right\}_{N_{in}})$ is expressed in a constrained form as,

$$H(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}}) = H(\{s_i\}_{N_L}) + H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}), \tag{4-39}$$

where

$$H(\{s_i\}_{N_L}) = \sum_{i=1}^{N_L} \frac{1}{2} m\dot{s}_i^2 + V(\{s_i\}_{N_L}), \tag{4-40}$$

and $H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})$ is expressed by (4-36). The crystal is then associated with a distribution function $f(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ which satisfies the Liouville equation,

$$\frac{\partial f(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})}{\partial t} + \left\{ f(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}}), H(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}}) \right\} = 0. \tag{4-41}$$

Based on the constrained form of $H(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ in (4-39), the $f(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}})$ must obey the following separation ansatz:

$$f(\{s_i\}_{N_L},\{r^{in}{}_l\}_{N_{in}}) = f(\{s_i\}_{N_L}) f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}). \tag{4-42}$$

We now solve the equation (4-41) augmented by equations of constraints (4-39) and (4-42) by applying the separation of fast and slow variables. The two time scales involved are the time scale for diffusion of interstitials and the time scale for lattice deformation. Because interstitials have faster variables, they are assumed to establish equilibrium state in each ‘fixed’ lattice configuration. The distribution function of interstitials therefore satisfies the following Liouville equation,

$$\frac{\partial f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})}{\partial t} + \left\{ f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}), H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) \right\} = 0. \tag{4-43}$$

Inserting the separation ansatz (4-42) into Liouville equation (4-41), integrating over the phase space of interstitials Γ_{in} with the help of (4-43), one obtains,

$$\frac{\partial f(\{s_i\}_{N_L})}{\partial t}+\left\{f(\{s_i\}_{N_L}),H(\{s_i\}_{N_L})+\frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N_L})\right\}=0\,, \tag{4-44}$$

where $Q_{in}(\{s_i\}_{N_L})$ is the partition function for interstitials expressed by

$$Q_{in}(\{s_i\}_{N_L})=\int\exp\left[-\beta H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})\right]d\Gamma_{in}\,. \tag{4-45}$$

The integration is carried over the phase space of interstitials $d\Gamma_{in}=\{dr^{in}{}_l dp^{in}{}_l\}_{N_{in}}$. Here the parameter β is introduced during the averaging process of interstitials, and is expressed as $\beta=1/kT$ where k is Boltzmann's constant and T is the Kelvin temperature. The $\frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N_L})$ will be later interpreted as the Helmholtz energy of interstitials in a fixed lattice configuration $\{s_i\}_{N_L}$.

Equation (4-44) shows that the existence of interstitials provides an extra potential $\frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N_L})$ to the lattice points. The effective Hamiltonian of lattice points $H_L(\{s_i\}_{N_L})$ in a crystal with interstitials is expressed as,

$$H_L(\{s_i\}_{N_L})=H(\{s_i\}_{N_L})+\frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N_L})\,. \tag{4-46}$$

It follows that the effective canonical equations for the lattice points become,

$$\begin{aligned}\dot{s}_i&=\partial_{p_{s_i}}H_L(\{s_i\}_{N_L})\\ \dot{p}_{s_i}&=-\partial_{s_i}H_L(\{s_i\}_{N_L})\quad(i=1,\ldots N_L)\end{aligned}\,. \tag{4-47}$$

Equations (4-47) are the effective microscopic dynamic equations for the lattice points in a crystal with interstitials. If there are no interstitials, i.e. $N_{in}=0$, the $\frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N_L}$ is reduced to the Helmholtz energy of phonons $\frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_{N_L})$ which suggests that the pressure of phonons will directly act on lattice points. It then follows that the $H_L(\{s_i\}_{N_L})$ in (4-46) is reduced to the effective energy for a perfect crystal with N_L "lattice atoms",

$$H_L(\{s_i\}_{N_L}) = H'(\{s_i\}_{N_L}) = H(\{s_i\}_{N_L}) + \frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_{N_L}) \quad . \tag{4-48}$$

In terms of $H_L(\{s_i\}_{N_L})$, the Liouville equation (4-44) for the N_L lattice points in a crystal with interstitials is rewritten as,

$$\frac{\partial f(\{s_i\}_{N_L})}{\partial t} + \left\{ f(\{s_i\}_{N_L}), H_L(\{s_i\}_{N_L}) \right\} = 0 . \tag{4-49}$$

Starting from (4-49), we can derive the equation of lattice deformation which shall be described in detail in the following sections.

To summarize, we write the complete distribution function for a crystal containing N_L "lattice atoms" and N_{in} interstitials from (4-32) and (4-42) as,

$$f(\{s_i\}_{N_L}, \{r^{in}{}_l\}_{N_{in}}, \{q_i\}_{N_L}) = f(\{s_i\}_{N_L}) f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) f_{\{r^{in}{}_l\}^s_{N_{in}}}(\{q_i\}_{N_L}) . \tag{4-50}$$

The series of Liouville equations for phonons, interstitials and lattice are respectively expressed by

$$\frac{\partial f_{\{r^{in}{}_l\}^s_{N_{in}}}(\{q_i\}_{N_L})}{\partial t} + \left\{ f_{\{r^{in}{}_l\}^s_{N_{in}}}(\{q_i\}_{N_L}), H_{\{r^{in}{}_l\}^s_{N_{in}}}(\{q_i\}_{N_L}) \right\} = 0, \tag{4-51}$$

$$\frac{\partial f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})}{\partial t} + \left\{ f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}), H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}) \right\} = 0 , \tag{4-52}$$

$$\frac{\partial f(\{s_i\}_{N_L})}{\partial t}+\left\{f(\{s_i\}_{N_L}),H_L(\{s_i\}_{N_L})\right\}=0\,. \tag{4-53}$$

The above equations provide the complete descriptions of a crystal with interstitials.

In equilibrium state, interstitials also vibrate around their equilibrium positions. Let $\bar{r}_l$ denote the equilibrium position of an interstitial. We write the position of an interstitial as

$$r^{in}{}_l=\bar{r}_l+q^{in}{}_l,(l=1,..N_{in})\,, \tag{4-54}$$

where $q^{in}{}_l$ denotes the relative displacement of an interstitial with respect to its equilibrium position $\bar{r}_l$. With (4-54), we associate with an interstitial with two variables $\bar{r}_l$ and $q^{in}{}_l$. The effective energy of interstitials $H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})$ in (4-36) is expressed in terms of $\bar{r}_l$ and $q^{in}{}_l$ as,

$$\begin{aligned}H^{in}{}_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})&=H^{in}{}_{\{s_i\}_{N_L}}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})\\&=\sum_{l=1}^{N_{in}}\frac{1}{2}m\dot{\bar{r}}_l^2+\sum_i m\dot{\bar{r}}_l\dot{q}_l^{in}+\sum_i\frac{1}{2}m\left(\dot{q}_l^{in}\right)^2+V'(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})\end{aligned} \tag{4-55}$$

where

$$V'(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})=V(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})+\frac{1}{\beta}\ell nQ_{ph}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})\,.$$

Again, we apply the technique developed in Chapter3.2. If $\bar{r}_l$ and $q^{in}{}_l$ were independent from each other, we could construct a distribution function $f^*{}_{\{s_i\}_{N_L}}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})$ that satisfies the Liouville equation,

$$\frac{\partial f^*{}_{\{s_i\}_{N_L}}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})}{\partial t}+\left\{f^*{}_{\{s_i\}_{N_L}}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}}),H^{in}{}_{\{s_i\}_{N_L}}(\{\bar{r}_l\}_{N_{in}},\{q^{in}{}_l\}_{N_{in}})\right\}=0 \tag{4-56}$$

The $\overline{r}_l$ and $q^{in}{}_l$ are not independent, however, because they must satisfy equation (4-54). We then invoke the fact that $q^{in}{}_l$ and $\overline{r}_l$ are degrees of freedom operating on different time scales. The $\left\{\overline{r}_l\right\}_{N_{in}}$ are the slower variables while $\left\{q^{in}{}_l\right\}_{N_{in}}$ are the faster ones. We therefore impose $3N_{in}$ constraints on the expression of $H^{in}{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}},\left\{q^{in}{}_l\right\}_{N_{in}})$ in (4-55) as,

$$H^{in}{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}},\left\{q^{in}{}_l\right\}_{N_{in}}) = H^{in}{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}}) + H^{in}{}_{\{\overline{r}_l\}^s{}_{N_{in}}}(\left\{q^{in}{}_l\right\}_{N_{in}}), \tag{4-57}$$

where we use $\left\{\overline{r}_l\right\}^s{}_{N_{in}}$ to denote the equilibrium configuration of interstitials in a fixed lattice configuration. In (4-57) the dependence of $H^{in}{}_{\{\overline{r}_l\}^s{}_{N_{in}}}(\left\{q^{in}{}_l\right\}_{N_{in}})$ on $\left\{\overline{r}_l\right\}^s{}_{N_{in}}$ is treated as parametric which will act as a form of constraint that reduces the number of degrees of freedom from $6N_{in}$ to $3N_{in}$ for interstitials. Based on the constrained form of $H(\left\{\overline{r}_l\right\}_{N_{in}},\left\{q^{in}{}_l\right\}_{N_{in}})$ in (4-55), we construct the distribution function $f^*{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}},\left\{q^{in}{}_l\right\}_{N_{in}})$ which must obey the separation ansatz:

$$f^*{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}},\left\{q^{in}{}_l\right\}_{N_{in}}) = f^*{}_{\{s_i\}_{N_L}}(\left\{\overline{r}_l\right\}_{N_{in}})\, f^*{}_{\{\overline{r}_l\}^s{}_{N_{in}}}(\left\{q^{in}{}_l\right\}_{N_{in}}), \tag{4-58}$$

where the dependence of $f^*{}_{\{\overline{r}_l\}^s{}_{N_{in}}}(\left\{q^{in}{}_l\right\}_{N_{in}})$ on $\left\{\overline{r}_l\right\}^s{}_{N_{in}}$ is again treated as parametric. With the $f^*{}_{\{\overline{r}_l\}^s{}_{N_{in}}}(\left\{q^{in}{}_l\right\}_{N_{in}})$, we are able to describe the vibration of interstitials around their equilibrium positions.

Thus, we demonstrate that by releasing constraints in the “atomic space”, interstitials are naturally included into the formulation.

To summarize, we showed that the system of interstitials or vacancies can be regarded as a “gas”. As a result, one can refer to the well developed theory for gas and apply them separately to the system of interstitials and vacancies. An advantage of the above formulation is that it could apply to system of interacting point defects.

4.3 Discussions on some defect complexities

Vacancies or interstitials can exist in pairs or forming clusters in a crystal which further complicates the formulation. We now use vacancies as an example to briefly discuss the case when defects form pairs.

If the system of vacancies is a ‘monoatomic gas’, it means that all vacancies are constrained by the “lattice atoms” at the same time. In other words, in the lattice space there are $3N_v$ constraints imposed <u>simultaneously</u> on the gas of vacancies. The distribution function for the ‘monoatomic’ gas of vacancies is described by equation (4-11).

When two vacancies form a molecule, the ‘gas’ is ‘diatomic’ containing $N_v{}^d = 3N_v/2$ molecules. As a result, half of the $3N_v$ degrees of freedom become the internal degrees of freedom of molecules. It means that in a ‘diatomic gas’ the $3N_v$ constraints are imposed on two different time scales: on the time scale of the translation of molecules, there are $3N_v/2$ constraints first imposed on the internal degrees of freedom of the vacancy molecule; while on the time scale of lattice deformation, there are only $3N_v/2$ constraints imposed on the molecules where the internal degrees of freedom have already been averaged out.

For diatomic gas, it's more suitable to describe a molecule in terms of the center of mass and the relative distance between two vacancies that form a molecule. The position and the corresponding momenta of the center of mass of a molecule is expressed as,

$$R^c{}_n = \frac{\left(R^v{}_1\right)_n + \left(R^v{}_2\right)_n}{2},$$
$$\dot{p}_n^c = 2m\dot{R}_n^c, \qquad (4\text{-}59)$$

where $\left(R^v{}_1\right)_n$ and $\left(R^v{}_2\right)_n$ are respectively the positions of the two vacancies that form the n^{th} molecules. The relative distance between two vacancies is,

$$d_n = \left(R^v{}_1\right)_n - \left(R^v{}_2\right)_n, \qquad (4\text{-}60)$$

The internal degrees of freedom of a molecule are fast variables, and the motion of the center of the mass of a molecule is the slower one. We therefore write down the the constrained form of the energy of the vacancies as,

$$H_{\{s_i\}_N}(\left\{R^v{}_k\right\}_{N_v}) = H_{\{s_i\}_N}(\left\{R^c{}_n\right\}_{N_v/2}) + H_{\left\{R^c{}_n\right\}_{N_v/2}}(\left\{d_n\right\}_{N_v/2}) \qquad (4\text{-}61)$$

where the key point is that the dependence of the internal energy of molecule on $\left\{R^c{}_n\right\}_{N_v/2}$ is treated as parametric. The explicit expressions for the $H_{\{s_i\}_N}(\left\{R^c{}_n\right\}_{N_v/2})$ and $H_{\left\{R^c{}_n\right\}_{N_v/2}}(\left\{d_n\right\}_{N_v/2})$ are not given here. One can refer to such books as *Statistical Physics by Landau and Lifshitz* [1] to derive the expression of energy in terms of the center of the mass and relative distance. Based on (4-61), the constrained form of $f_{\{s_i\}_N}(\left\{R^v{}_k\right\}_{N_v})$ is,

$$f_{\{s_i\}_N}(\left\{R^v{}_k\right\}_{N_v}) = f_{\{s_i\}_N}(\left\{R^c{}_n\right\}_{N_v/2}) f_{\left\{R^c{}_n\right\}_{N_v/2}}(\left\{d_n\right\}_{N_v/2}). \qquad (4\text{-}62)$$

We then apply the technique of separating fast and slow variables to obtain the dynamic equations of vacancy molecules and then the lattice deformation. The internal degrees of freedom are first averaged out with $f_{\{R^c{}_m\}_{N_v/2}}(\{d_n\}_{N_v/2})$ which satisfies,

$$\frac{\partial f_{\{R^c{}_n\}_{N_v/2}}(\{d_n\}_{N_v/2})}{\partial t}+\left\{f_{\{R^c{}_n\}_{N_v/2}}(\{d_n\}_{N_v/2}),H_{\{R^c{}_n\}_{N_v/2}}(\{d_n\}_{N_v/2})\right\}=0\,. \tag{4-63}$$

The result is a driving force exerted on the center of mass of each molecule. The Liouville equation for the molecule is,

$$\frac{\partial f_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2})}{\partial t}+\left\{f_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2}),H_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2})+\frac{1}{\beta}\ell n Q_r(\{R^c{}_n\}_{N_v/2})\right\}=0\,, \tag{4-64}$$

where $Q_r(\{R^c{}_n\}_{N_v/2})$ is the partition function for the internal degrees of freedom of molecules calculated by,

$$Q_r(\{R^c{}_n\}_{N_v/2})=\int\exp\left[-\beta H_{\{R^c{}_n\}_{N_v/2}}(\{d_n\}_{N_v/2})\right]d\Gamma_d\,, \tag{4-65}$$

in which the integration is over the phase space Γ_d for the internal degrees of freedom.

The equation demonstrates that the effective energy for the “diatomic gas” of vacancies is now,

$$H^c{}_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2})=H_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2})+\frac{1}{\beta}\ell n Q_r(\{R^c{}_n\}_{N_v/2})\,, \tag{4-66}$$

and the effective canonical equations for the molecule of vacancies are now,

$$\begin{aligned}&\dot{R}^c_n=\partial_{p^c{}_n}H^c{}_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2})\\&\dot{p}^c_n=-\partial_{R^c{}_n}H^c{}_{\{s_i\}_N}(\{R^c{}_m\}_{N_v/2})\quad(n=1,\dots N_v/2)\end{aligned} \tag{4-67}$$

Ultimately, the Liouville equation for the lattice deformation is,

$$\frac{\partial f(\{s_i\}_N)}{\partial t} + \left\{ f(\{s_i\}_N), H(\{s_i\}_N) + \frac{1}{\beta} \ell n Q_v(\{s_i\}_N) \right\} = 0 \tag{4-68}$$

where the partition function for the vacancies is now expressed by,

$$Q_v(\{s_i\}_N) = \int \exp\left[-\beta H_{\{s_i\}_N}(\{R^c{}_n\}_{N_v/2}) \right] d\Gamma_{v(c)}, \tag{4-69}$$

in which the integration is over the phase space of the center of mass of molecules of vacancies $\Gamma_{v(c)}$. The $\mu_v{}^d(\{s_i\}_N) = \frac{1}{\beta}\frac{\partial \ell n Q_v(\{s_i\}_N)}{\partial N_v{}^d}$ gives the chemical potential of a divacancy molecule in a fixed lattice configuration.

In reality, both di-vacancies and single vacancies exist in a crystal. In other words, the “gas of vacancies” in a crystal is usually a mixture. Having demonstrated that vacancies behave like particles in a fluid, we can then apply the techniques developed for a gas with multi-components [3-5] to the description of vacancies in a crystal.

Summary

The relationship between degrees of freedom, constraints and point defects can be briefly summarized as follows:

(1) The total number of degrees of freedom is solely determined by the number of atoms N. A crystal containing N, whether it is perfect or has defects, has $3N$ degrees of freedom.

(2) The total number of constraints is determined by the number of lattice sites N_L.

(3) The number of “lattice atoms” determines the number of *independent constraints*.

(4) The generation of a vacancy corresponds to an addition of one constraint in the lattice space. In a crystal with N_v vacancies, there are $3N_v$ constraints *imposed in the "lattice space".*

(5) The generation of one interstitial atom corresponds to the release of one constraint in the atomic space. In a crystal with N_{in} interstitials, there are $3N_{in}$ constraints *released in the" atomic space".*

Up to now, by respectively adding or releasing constraints, we successfully incorporated the vacancies and interstitials into the formulation. We then consider a more complicated condition when a crystal has both interstitials and vacancies.

4.4 Liouville equation for a crystal with both vacancies and interstitials

A crystal with both vacancies and interstitials is demonstrated in *Figure. 4.3.*

In a crystal containing N atoms, N_v vacancies and N_{in} interstitials, there are $N_L = N + \left(N_v - N_{in} \right)$ lattice sites. Among the N atoms, there are $N - N_{in}$ "lattice atoms".

(1) If $N_v - N_{in} > 0$, there are more vacancies than interstitials. Consequently, there are more lattice sites than atoms.

(2) If $N_v - N_{in} < 0$, there are more interstitials than vacancies. Consequently, there are more atoms than lattice sites.

(3) If $N_v - N_{in} = 0$, there are the same number of interstitials as vacancies.

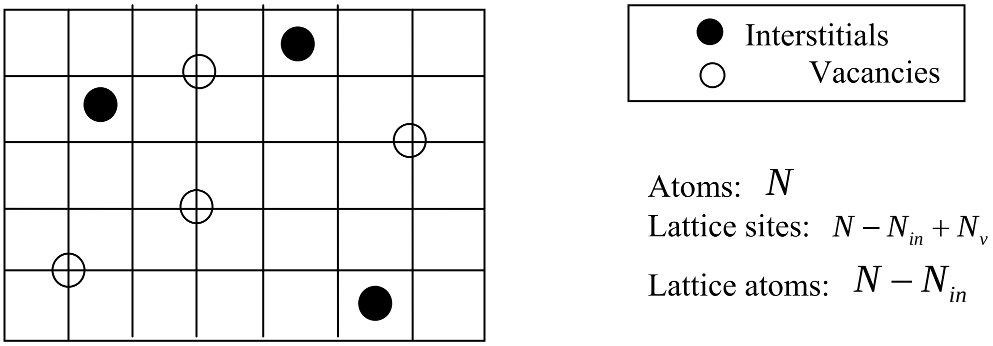


Figure 4.3 Crystal with both vacancies and interstitials

To write down the distribution function for a crystal with both vacancies and interstitials, we invoke that in a crystal with vacancies, the distribution function for the "*lattice space*" with N "lattice atoms" is,

$$f(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = f(\{s_i\}_N)\, f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}) \,.$$

In a crystal with interstitials, on the other hand, the distribution function for the “atomic space” is,

$$f_{\{s_i\}_{N-N_{in}}}(\{q_i\}_{N-N_{in}}, \{r_i\}_{N_{in}}) = f_{\{s_i\}_{N-N_{in}}}(\{r_i\}_{N_{in}})\, f_{\{r_i\}^s_{N_{in}}}(\{q_i\}_{N-N_{in}}) \,.$$

We cannot, however, just combine the above two expressions to get the distribution function for a crystal containing both interstitials and vacancies. The reason is that interstitials are coupled with vacancies and “lattice atoms” in different ways. In the following part, we first discuss two limiting cases:

1. Interstitials and vacancies in the dilute limit

In the dilute limit, vacancies are so far away from interstitials that interstitials cannot distinguish between the “lattice atoms” and vacancies. In other words, all the lattice sites, vacant or not, appear to be on the same time scale with respect to interstitials. As a result, interstitials see $N_L = N - N_{in} + N_v$ “lattice atoms”. *Figure 4.4* shows the vision of “lattice space” in the eyes of interstitials in the dilute limit.

According to the above analysis, we follow the method in Chapter 4.2.2 and write down the constrained form of the distribution function of the “atomic space” as,

$$f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}}, \{q_i\}_{N_L}) = f_{\{s_i\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})\, f_{\{r^{in}{}_l\}^s_{N_{in}}}(\{q_i\}_{N_L}) \,. \qquad (4\text{-}70)$$

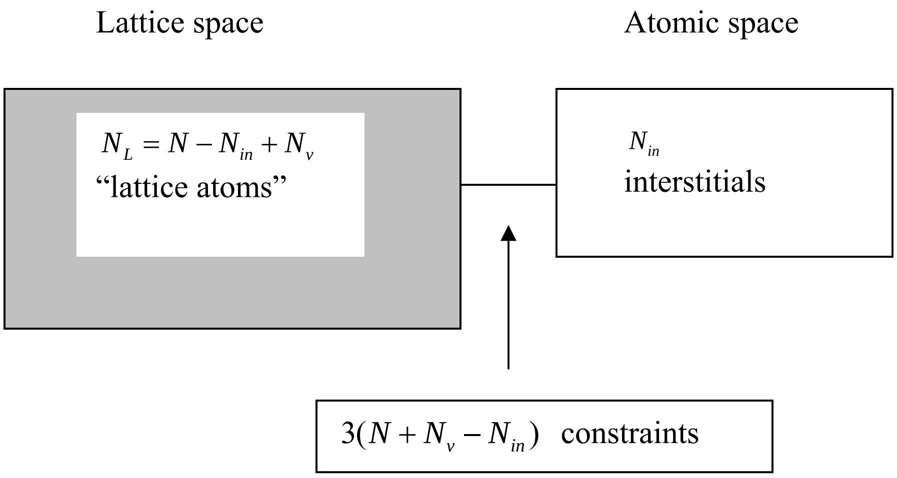


Figure 4.4 The "lattice space" in the eyes of interstitials in the dilute limit

The distribution function for the "lattice space" is $f(\{s_i\}_{N-N_{in}+N_v})$. The complete distribution function for the crystal is therefore:

$$f\left(\{s_i\}_{N-N_{in}+N_v}, \{r^{in}{}_l\}_{N_{in}}, \{q_i\}_{N-N_{in}}\right) = f(\{s_i\}_{N-N_{in}+N_v}) f_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}}) f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N-N_{in}}). \tag{4-71}$$

The Liouville equation for the distribution function of phonons $f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N-N_{in}})$ is,

$$\frac{\partial f_{\{r_i\}^s{}_{N_{in}}}(\{q_i\}_{N_L})}{\partial t} + \left\{ f_{\{r_i\}^s{}_{N_{in}}}(\{q_i\}_{N_L}), H_{\{r_i\}^s{}_{N_{in}}}(\{q_i\}_{N_L}) \right\} = 0. \tag{4-72}$$

With $f_{\{r^{in}{}_l\}^s{}_{N_{in}}}(\{q_i\}_{N-N_{in}})$, phonons are averaged out which provides a driving force to the motion of interstitials. The effective Liouville equation for the interstitials is

$$\frac{\partial f_{\{s_i\}_{N-N_{in}+N_v}}(\{r_i\}_{N_{in}})}{\partial t} + \left\{ f_{\{s_i\}_{N-N_{in}+N_v}}(\{r_i\}_{N_{in}}), H_{\{s_i\}_{N-N_{in}+N_v}}(\{r_i\}_{N_{in}}) + \frac{1}{\beta} \ell n Q_{ph}(\{r_i\}^s{}_{N_{in}}) \right\} = 0, \tag{4-73}$$

where $\frac{1}{\beta}\ell n Q_{ph}(\{r_i\}^s_{N_{in}})$ is the Helmholtz energy of phonons in the fixed configuration of interstitials. From (4-73), the effective energy of interstitials $H^{in}(\{r^{in}{}_l\}_{N_{in}})$ is now,

$$H^{in}(\{r^{in}{}_l\}_{N_{in}}) = H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}}) = H_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}}) + \frac{1}{\beta}\ell n Q_{ph}(\{r^{in}{}_l\}^s_{N_{in}}). \quad (4\text{-}74)$$

The effective canonical equations for interstitials become,

$$\begin{aligned} \dot{r}^{in}_l &= \partial_{p^{in}{}_l} H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}}) \\ \dot{p}^{in}_l &= -\partial_{r^{in}{}_l} H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}}) \qquad (l = 1, \ldots N_{in}) \end{aligned} . \quad (4\text{-}75)$$

With $f_{\{s_i\}_{N-N_{in}+N_v}}(\{r_i\}_{N_{in}})$, the degrees of freedom of interstitials are averaged out which generates a driving force on the lattice deformation. It follows that the ultimate Liouville equation for the lattice space containing $N + N_v - N_{in}$ "lattice atoms" is,

$$\frac{\partial f(\{s_i\}_{N-N_{in}+N_v})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}+N_v}), H^*(\{s_i\}_{N-N_{in}+N_v}) \right\} = 0, \quad (4\text{-}76)$$

where $H^*(\{s_i\}_{N-N_{in}+N_v})$ denotes the effective energy for the whole lattice space defined by,

$$H^*(\{s_i\}_{N-N_{in}+N_v}) = H(\{s_i\}_{N-N_{in}+N_v}) + \frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N-N_{in}+N_v}), \quad (4\text{-}77)$$

in which

$$Q_{in}(\{s_i\}_{N-N_{in}+N_v}) = \int \exp\left[-\beta H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}})\right] d\Gamma_{in}. \quad (4\text{-}78)$$

Equation (4-77) shows that interstitials provide a potential field for the whole lattice space. Let $V^e(\{s_i\}_{N-N_{in}+N_v})$ denote the total potential field of "lattice space" defined by,

$$V^e(\{s_i\}_{N-N_{in}+N_v}) = V(\{s_i\}_{N-N_{in}+N_v}) + \frac{1}{\beta}\ell n Q_{in}(\{s_i\}_{N-N_{in}+N_v}) . \tag{4-79}$$

The expression of $H^*(\{s_i\}_{N-N_{in}+N_v})$ in (4-77) is then rewritten as,

$$H^*(\{s_i\}_{N-N_{in}+N_v}) = \sum_{i=1}^{N} \frac{1}{2} m\dot{s}_i^2 + V^e(\{s_i\}_{N-N_{in}+N_v}) . \tag{4-80}$$

Within the lattice space, however, one needs to distinguish between the "lattice atoms" and the vacancies. Following the method described in Chapter 4.2.2, we describe "lattice atoms" by $s_i\left(i = 1 \ldots N - N_{in}\right)$ and vacancies by $R^v{}_k\left(k = 1 \ldots N_v\right)$. Equation (4-76) is then rewritten in terms of $\{s_i\}_{N-N_{in}}$ and $\left\{R^v{}_k\right\}_{N_v}$ as,

$$\frac{\partial f(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v}), H^*(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v}) \right\} = 0 , \tag{4-81}$$

where

$$\begin{aligned} H^*(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v}) = & \sum_{i=1}^{N-N_{in}} \frac{1}{2} m\dot{s}_i^2 + \sum_{i=1}^{N_v} \frac{1}{2} m\left(\dot{R}_k^v\right)^2 \\ & + V^e(\{s_i\}_{N-N_{in}+N_v}) + V^e(\left\{R^v{}_k\right\}_{N_v}) + V^e(\{s_i\}_{N-N_{in}+N_v}, \left\{R^v{}_k\right\}_{N_v}) \end{aligned} . \tag{4-82}$$

There are only $N - N_{in}$ "lattice atoms", so we impose constraints on the expression of $H^*(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v})$ above,

$$H^*(\{s_i\}_{N-N_{in}}, \left\{R^v{}_k\right\}_{N_v}) = H^*(\{s_i\}_{N-N_{in}}) + H^*{}_{\{s_i\}_{N-N_{in}}}(\left\{R^v{}_k\right\}_{N_v}) , \tag{4-83}$$

where,

$$H^*(\{s_i\}_{N-N_{in}}) = \sum_{i=1}^{N-N_{in}} \frac{1}{2} m\dot{s}_i^2 + V^e(\{s_i\}_{N-N_{in}}) ,$$

$$H^*{}_{\{s_i\}_{N-N_{in}}}(\left\{R^v{}_k\right\}_{N_v}) = \sum_{k=1}^{N_v} \frac{1}{2} m\dot{R}_k^{v2} + V^e(\left\{R^v{}_k\right\}_{N_v}) + V^e(\{s_i\}_N, \left\{R^v{}_k\right\}_{N_v}) . \tag{4-84}$$

The distribution function corresponds to the constrained form of $H^{*}(\{s_i\}_{N-N_{in}},\{R^{v}{}_{k}\}_{N_v})$ in (4-82) is,

$$f(\{s_i\}_{N-N_{in}},\{R^{v}{}_{k}\}_{N_v}) = f(\{s_i\}_{N-N_{in}}) f_{\{s_i\}_{N-N_{in}}}(\{R_k\}_{N_v}) . \tag{4-85}$$

The Liouville equation for the distribution function of vacancies $f_{\{s_i\}_{N-N_{in}}}(\{R_k\}_{N_v})$ is,

$$\frac{\partial f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})}{\partial t} + \left\{ f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v}), H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v}) \right\} = 0 . \tag{4-86}$$

Note that the coupling between vacancies and interstitials is included in the expression of $H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})$.

Ultimately, one obtains the Liouville equation for the $N-N_{in}$ "lattice atoms",

$$\frac{\partial f(\{s_i\}_{N-N_{in}})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}}), H^{*}(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q_v(\{s_i\}_{N_L}) \right\} = 0 , \tag{4-87}$$

where $Q_v(\{s_i\}_{N-N_{in}})$ is the partition function of vacancies in a fixed lattice configuration $\{s_i\}_{N-N_{in}}$,

$$Q_v(\{s_i\}_{N-N_{in}}) = \int \exp\left[-\beta H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v}) \right] d\Gamma_v . \tag{4-88}$$

Equation (4-87) shows that the effective energy of the "lattice atoms" $H_L(\{s_i\}_{N-N_{in}})$ is expressed by,

$$H_L(\{s_i\}_{N-N_{in}}) = H^{*}(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q_v(\{s_i\}_{N-N_{in}}) . \tag{4-89}$$

Note that the driving force from interstitials is included in both the energy of "lattice atoms" $H^{*}(\{s_i\}_{N-N_{in}})$ and the Helmholtz energy of vacancies $\frac{1}{\beta}\ell n Q_v(\{s_i\}_{N-N_{in}})$. We see therefore that in the dilute limit, interstitials are coupled with both vacancies and “lattice atoms”.

2. Interstitials and vacancies are strongly coupled

When interstitials and vacancies are close to each other, their mutual interaction becomes strong and form pairs or clusters. As a result, vacancies and “lattice atoms” appear on different time scales with respect to interstitials. In the limiting case, interstitials see only vacancies and “lattice atoms” become blind to them. It is therefore reasonable to assume that the constraints are first established between vacancies and the “atomic space”. *Figure 4.5* demonstrates the vision of vacancies and “lattice atoms” seen from interstitials when the coupling is strong.

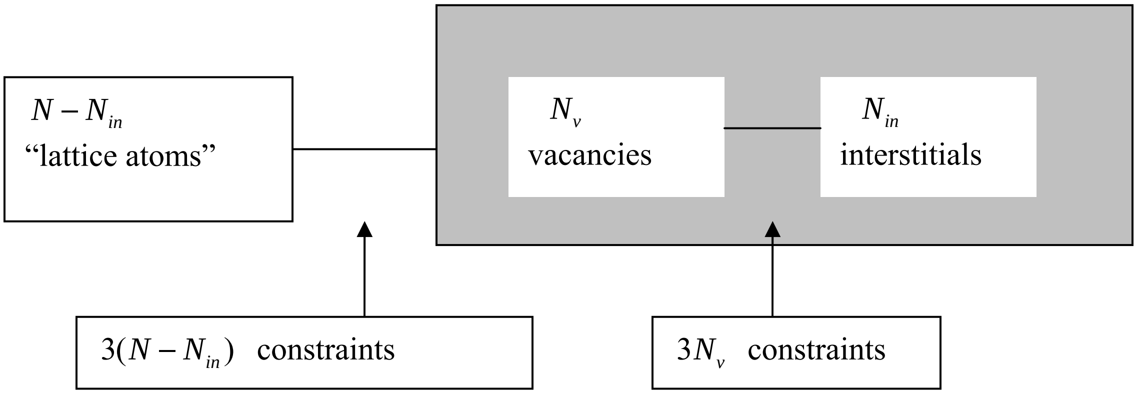


Figure 4.5 Coupling of interstitials with vacancies and “lattice atoms”

Based on this physical picture, the distribution function for the “atomic space” is written as,

$$f_{\{R_k\}^s_{Nv}}(\{r_l\}_{N_{in}}, \{q_i\}_{N_L}) = f_{\{R_k\}^s_{Nv}}(\{r_l\}_{N_{in}})\, f_{\{r_i\}^R_{N_{in}}}(\{q_i\}_{N_L}) . \tag{4-90}$$

In other words, the driving force from interstitials is solely exerted on vacancies. The complete distribution function for the crystal is then,

$$\begin{aligned} & f(\{s_i\}_{N-N_{in}}, ,\{R^v{}_k\}_{N_v}, \{r_i\}_{N_{in}}, \{q_i\}_{N-N_{in}}) \\ & = f(\{s_i\}_{N-N_{in}}) f_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}) f_{\{R^v{}_k\}_{N_v}}(\{r_i\}_{N_{in}}) f_{\{r_i\}_{N_{in}}}(\{q_i\}_{N-N_{in}}) \end{aligned} \tag{4-91}$$

The distribution function for phonons obeys the Liouville equation,

$$\frac{\partial f_{\{r_i\}_{N_{in}}}(\{q_i\}_{N-N_{in}})}{\partial t} + \left\{ f_{\{r_i\}_{N_{in}}}(\{q_i\}_{N-N_{in}}), H_{\{r_i\}_{N_{in}}}(\{q_i\}_{N-N_{in}}) \right\} = 0 \,. \tag{4-92}$$

Phonons are averaged out with $f_{\{r_i\}_{N_{in}}}(\{q_i\}_{N-N_{in}})$ which results in a driving force to the motion of interstitials.

The effective Liouville equation for the interstitials is,

$$\frac{\partial f_{\{R_k\}_{Nv}}(\{r_i\}_{N_{in}})}{\partial t} + \left\{ f_{\{R_k\}_{Nv}}(\{r_i\}_{N_{in}}), H_{\{R_k\}_{Nv}}(\{r_i\}_{N_{in}}) + \frac{1}{\beta} \ell n Q_{ph}(\{r_i\}_{N_{in}}) \right\} = 0 \,. \tag{4-93}$$

The effective energy of interstitials $H^{in}(\{r^{in}{}_l\}_{N_{in}})$ is now expressed as,

$$H^{in}(\{r^{in}{}_l\}_{N_{in}}) = H_{\{R_k\}^s{}_{Nv}}(\{r_i\}_{N_{in}}) + \frac{1}{\beta} \ell n Q_{ph}(\{r_i\}^R{}_{N_{in}}) \,. \tag{4-94}$$

Note that the expression for $H^{in}(\{r^{in}{}_l\}_{N_{in}})$ is different from (4-74), because the motion of interstitials are now constrained only by vacancies instead of the whole lattice space.

The Liouville equation for the system of vacancies and interstitials are then,

$$\frac{\partial f_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}, \{r_i\}_{N_{in}})}{\partial t} + \left\{ f_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}, \{r_i\}_{N_{in}}), H_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}, \{r_i\}_{N_{in}}) \right\} = 0 \,, \tag{4-95}$$

augmented by constraints,

$$H_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v},\{r_i\}_{N_{in}})=H_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})+H^{in}{}_{\{R^{v}{}_{k}\}_{N_v}}(\{r_i\}_{N_{in}})\,,$$

$$f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v},\{r_i\}_{N_{in}})=f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})\,f_{\{R_k\}^{s}{}_{Nv}}(\{r_l\}_{N_{in}})\,. \qquad (4\text{-}96)$$

where $H^{in}{}_{\{R^{v}{}_{k}\}_{N_v}}(\{r_i\}_{N_{in}})$ is expressed in (4-94).

Inserting (4-96) into (4-95) and with the help of (4-93), we obtain the Liouville equation for vacancies,

$$\frac{\partial f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})}{\partial t}+\left\{f_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v}),H(\{R^{v}{}_{k}\}_{N_v})+\frac{1}{\beta}\ell nQ_{in}(\{R^{v}{}_{k}\}_{N_v})\right\}=0\,, \qquad (4\text{-}97)$$

where

$$Q_{in}(\{R^{v}{}_{k}\}_{N_v})=\int\exp\left[-\beta H^{in}{}_{\{R^{v}{}_{k}\}_{N_v}}(\{r^{in}{}_{l}\}_{N_{in}})\right]d\Gamma_{in}\,. \qquad (4\text{-}98)$$

The effective energy of vacancies $H_v(\{R^{v}{}_{k}\}_{N_v})$ is now expressed as,

$$H_v(\{R^{v}{}_{k}\}_{N_v})=H(\{R^{v}{}_{k}\}_{N_v})+\frac{1}{\beta}\ell nQ_{in}(\{R^{v}{}_{k}\}_{N_v})\,. \qquad (4\text{-}99)$$

The effective canonical equations for the vacancies now become,

$$\begin{aligned}\dot{R}^{v}_{k}&=\partial_{p^{v}{}_{k}}H_v(\{R^{v}{}_{k}\}_{N_v})\\ \dot{p}^{v}_{k}&=-\partial_{R^{v}{}_{k}}H_v(\{R^{v}{}_{k}\}_{N_v}) \qquad (k=1,\ldots N_v)\end{aligned}\,. \qquad (4\text{-}100)$$

Ultimately we obtain the Liouville equation for "lattice atoms",

$$\frac{\partial f(\{s_i\}_{N-N_{in}})}{\partial t}+\left\{f(\{s_i\}_{N-N_{in}}),H(\{s_i\}_{N-N_{in}})+\frac{1}{\beta}\ell nQ_v(\{s_i\}_{N-N_{in}})\right\}=0\,, \qquad (4\text{-}101)$$

where the partition function of vacancies is now expressed as,

$$Q_v(\{s_i\}_{N-N_{in}})=\int\exp\left[-\beta H^{v}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})\right]d\Gamma_v\,. \qquad (4\text{-}102)$$

The effective energy of the "lattice atoms" $H_L(\{s_i\}_{N-N_{in}})$ is therefore,

$$H_L(\{s_i\}_{N-N_{in}}) = H(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q_v(\{s_i\}_{N-N_{in}}) . \tag{4-103}$$

In terms of $H_L(\{s_i\}_{N-N_{in}})$, the Liouville equation for the "lattice atoms" is,

$$\frac{\partial f(\{s_i\}_{N-N_{in}})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}}), H_L(\{s_i\}_{N-N_{in}}) \right\} = 0 . \tag{4-104}$$

We see therefore that when the vacancies and interstitials form pairs, the effect of interstitials is only included in the energy of vacancies. Interstitials do not directly exert driving force on "lattice atoms". Instead, they affect the motion of "lattice atoms" through vacancies.

We observe from the above two limit cases that in the eyes of interstitials, there are two "types" of vacancies: one is so far away that it appears on the same time scale of "lattice atoms"; the other is so close that the motion of interstitials is completely constrained by these vacancies. The first type of vacancies is treated as if they were "lattice atoms" with respect to interstitials. We can therefore write down the distribution function for a crystal with both weakly and strongly coupled interstitials and vacancies.

$$\underbrace{\left[f(\{s_i\}_{N-N_{in}}) f_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v{}^1}) \right]}_{(a)} \underbrace{\left[f_{\{s_i\}_{N-N_{in}+N_v{}^1}}(\{R^v{}_k\}_{N_v{}^2}), \{r_i\}_{N_{in}}) f_{\{R^v{}_k\}_{N_v{}^2}}(\{r^{in}{}_l\}_{N_{in}}) \right]}_{(b)} \underbrace{f_{\{r^{in}{}_l\}_{N_{in}}}(\{q_i\}_{N-N_{in}+N_v{}^1})}_{(c)} \tag{4-105}$$

where N_v^1 is the number of vacancies that are far from interstitials, and N_v^2 is the number of vacancies that are strongly coupled with interstitials. In the expression of the distribution function:

(a) is the complete distribution function for the "lattice space" containing $N - N_{in} + N_v^1$ lattice sites which all appear to be "lattice atoms" with respect to interstitials . Within this "lattice space", one further distinguishes vacancies from "lattice atoms";

(b) is the distribution function for strongly coupled vacancies and interstitials;

(c) is the distribution function for phonons.

Thus, we demonstrate that we can gradually incorporated more complexities into the formulation by different modification of constraints. Fig.4.6 summarizes our previous investigations of the modifications of constraints and different types of point defects.

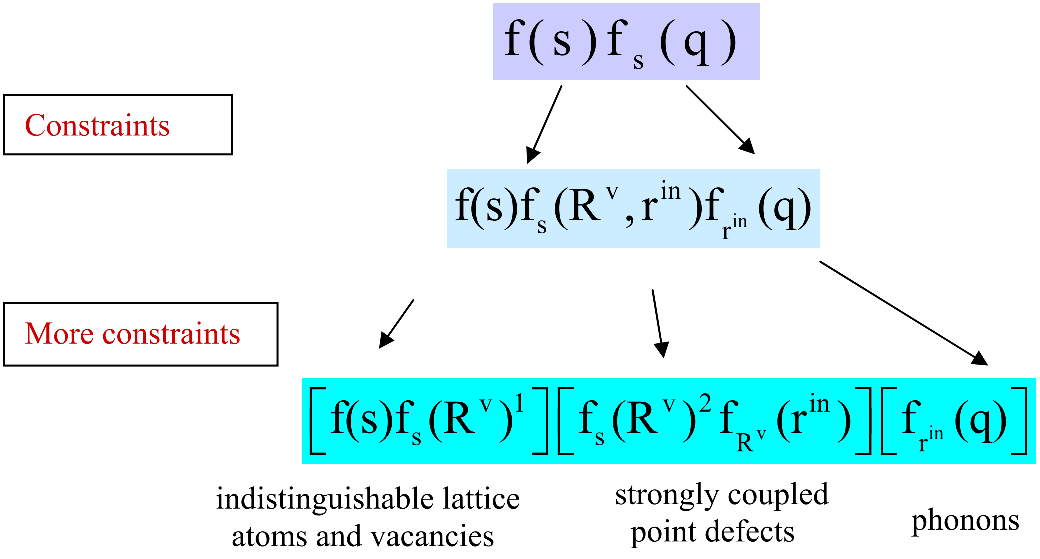


Fig 4.6 Point defects and modification of constraints

Whatever the relationship between interstitials and vacancies, the ultimate Liouville equation for the lattice atoms is,

$$\frac{\partial f(\{s_i\}_{N-N_{in}})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}}), H_L(\{s_i\}_{N-N_{in}}) \right\} = 0 . \tag{4-106}$$

The explicit expression for $H_L(\{s_i\}_{N-N_{in}})$ depends on the detail relationship between interstitials and vacancies. Since we have demonstrated that the system of vacancies and interstitials is like a gas, we can apply the well developed theories of fluids to vacancies and interstitials.

4.5 Elastic deformation of a crystal with point defects

4.5.1 Equation of deformation of a crystal with point defects

The basic equation for the derivation of equation of deformation of the lattice is the Liouville equation for the "lattice atoms" applicable to all kinds of crystals with point defects:

$$\frac{\partial f(\{s_i\}_{N-N_{in}})}{\partial t} + \left\{ f(\{s_i\}_{N-N_{in}}), H_L(\{s_i\}_{N-N_{in}}) \right\} = 0 . \tag{4-107}$$

From (4-107), we apply the technique of coarse graining to obtain the macroscopic description of lattice deformation. The general procedure is similar to that described in the perfect crystal. There are some important modifications, however, due to the existence of point defects.

Let $\hat{x}$ be the continuous coordinate in the space in which the reference perfect crystal with $N_L = N - N_{in}$ "lattice atoms" are defined. We assume that there exists a displacement field described by a continuous function $\overline{s}(\hat{x})$, so that the displacement of a "lattice atom" at $\hat{x} = R_i$ can be written as

$$s_i = s_i' + \overline{s}(R_i) , \quad i = 1, \ldots N - N_{in} , \tag{4-108}$$

where s_i' is the relative displacement of a "lattice atom" with respect to the displacement field $\overline{s}(\hat{x})$. The $\overline{s}(R_i)$ can be written in terms of δ functions as,

$$\bar{s}(R_i) = \int \bar{s}(\hat{x})\delta(\hat{x} - R_i)d\hat{x} \tag{4-109}$$

The displacement density for a crystal with point defects is defined in terms of δ functions as:

$$s(\hat{x}) = \sum_{i=1}^{N-N_{in}} s_i \delta(\hat{x} - R_i) \tag{4-110}$$

$$s'(\hat{x}) = \sum_{i=1}^{N-N_{in}} s_i{}' \delta(\hat{x} - R_i)\,, \tag{4-111}$$

where $s(\hat{x})$ represents the displacement density and $s'(\hat{x})$ denotes the relative displacement density. It follows from equations (4-108)-(4-111) that

$$s(\hat{x}) = s'(\hat{x}) + n(\hat{x})\bar{s}(\hat{x})\,, \tag{4-112}$$

where $n_L(\hat{x})$ is the density of “lattice atoms” defined by,

$$n_L(\hat{x}) = \sum_{i=1}^{N-N_{in}} \delta(\hat{x} - R_i)\,. \tag{4-113}$$

The displacement field $\bar{s}(\hat{x})$ will later be interpreted as the systematic deformation of lattice in a crystal containing N atoms, N_v vacancies and N_{in} interstitials.

With (4-108), the displacement of a lattice atom is described by variables $s_i{}'$ plus a function $\bar{s}(\hat{x})$ which shall be evaluated at the lattice site. The $s_i{}'$ and $\bar{s}(R_i)$, however, are not independent, because they must satisfy equation (4-108). Let $H_L(\{s'_i\}_{N-N_{in}}, \bar{s})$ and $f(\{s'_i\}_{N-N_{in}}, \bar{s})$ respectively denote the effective Hamiltonian $H_L(\{s_i\}_{N-N_{in}})$ and corresponding distribution function $f(\{s_i\}_{N-N_{in}})$ expressed in terms of $s_i{}'$ and $\bar{s}$. If there were no constraints, the $f(\{s'_i\}_{N-N_{in}}, \bar{s})$ would satisfy the Liouville equation,

$$\frac{\partial f(\{s'_i\}_{N-N_{in}},\bar{s})}{\partial t}+\left\{f(\{s'_i\}_{N-N_{in}},\bar{s}),H_L(\{s'_i\}_{N-N_{in}},\bar{s})\right\}=0\,. \tag{4-114}$$

Equation (4-114), however, is not directly applicable because each "lattice atom" has only three degrees of freedom. Constraints must be therefore imposed on s_i' and $\bar{s}(R_i)$. To find constraints, we observe that $\bar{s}(x)$ is a smooth function which varies slowly and s_i' has the physical meaning of fluctuation with respect to the $\bar{s}(x)$. The s_i' is therefore the faster variables and the $\bar{s}(x)$ is the slower one. Based on the separation of the fast-slow variables, we impose the following constraints:

$$H_L(\{s'_i\}_{N-N_{in}},\bar{s})=H_L(\bar{s})+H^L{}_{\bar{s}}(\{s'_i\}_{N-N_{in}})\,, \tag{4-115}$$

where the detailed expression for $H_L(\bar{s})$ and $H^L{}_{\bar{s}(\bar{x})}(\{s'_i\}_{N-N_{in}})$ depend on the detailed information of the existence of point defects. The key point here is that the dependence of $H^L{}_{\bar{s}(\bar{x})}(\{s'_i\}_{N-N_{in}})$ on $\bar{s}(x)$ is treated as parametric. Based on (4-115), we construct the constrained form of the distribution function as,

$$f_c(\{s'_i\}_{N-N_{in}},\bar{s})=f(\bar{s})\,f_{\bar{s}}(\{s'_i\}_{N-N_{in}}) \tag{4-116}$$

Note that although $\bar{s}(x)$ is introduced as a function, it is evaluated at each lattice site.

The $\{s_i'\}$ are faster variables and can establish equilibrium state when the displacement field $\bar{s}(x)$ is effectively fixed. The Liouville equation for $f_{\bar{s}(\bar{x})}(\{s'_i\}_{N-N_{in}})$ is therefore,

$$\frac{\partial f_{\bar{s}}(\{s'_i\}_{N-N_{in}})}{\partial t}+\left\{f_{\bar{s}}(\{s'_i\}_{N-N_{in}}),H^L{}_{\bar{s}}(\{s'_i\}_{N-N_{in}})\right\}=0\,. \tag{4-117}$$

From equations (4-114)-(4-117) we obtain the following *equation of lattice deformation of a crystal with point defects*:

$$\frac{\partial f(\overline{s})}{\partial t}+\frac{\partial f(\overline{s})}{\partial \overline{s}}\dot{\overline{s}}+\frac{\partial f(\overline{s})}{\partial P}\dot{P}=-\frac{\partial}{\partial P}\left[f(\overline{s})\frac{\partial \ell nQ'(\overline{s})}{\partial \overline{s}}\right] \tag{4-118}$$

where $P = m\dot{\overline{s}}$. Here $Q'(\overline{s})$ is the partition function of the system $\{s_i'\}$ expressed by

$$Q'(\overline{s})=\int \exp\left[-\beta H^{L}{}_{\overline{s}}(\{s'_i\}_{N-N_{in}})\right]d\Gamma_{s'}, \tag{4-119}$$

and $\ell nQ'(\overline{s})$ will be interpreted as the Helmholtz function of the system $\{s_i'\}$ in a fixed systematic deformation denoted by $\overline{s}(x)$.

The deformation equation of a crystal with defects is of the same form as the perfect crystal. The essential difference, however, lies in the expression for $\ell nQ'(\overline{s})$. In other words, the driving force to the systematic deformation is dependent on the detailed information of the point defects in a crystal. Table 4.1 lists expressions of $\ell nQ'(\overline{s})$ in various crystals.

Table 4.1 Effective energy of "lattice atoms" in various crystals

Types of crystal	Number of "lattice atoms"	$H^{L}{}_{\overline{s}(\hat{x})}(\{s'_i\}_{N-N_{in}})$
Perfect crystal	N	$H^{L}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)=H_{\overline{s}(\hat{x})}(\{s_i'\}_N)+\frac{1}{\beta}\ell nQ^{ph}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)$ where $Q^{ph}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)=\int\exp\left[-\beta H^{ph}{}_{\{s_i'\}_N}(\{q_i\}_N)\right]d\Gamma_{ph}$
Crystal with only vacancies	N	$H^{L}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)=H'{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)+\frac{1}{\beta}\ell nQ^{v}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)$ where $H'(\{s_i\}_N)=H(\{s_i\}_N)+\frac{1}{\beta}\ell nQ_{ph}(\{s_i\}_N)$ $Q^{v}{}_{\overline{s}(\hat{x})}(\{s_i'\}_N)=\int\exp\left[-\beta H^{v}{}_{\{s_i'\}_{N-N_v}}(\{R^{v}{}_k\}_{N_v})\right]d\Gamma_v$.

Crystal with only interstitials	$N - N_{in}$	$H^{L}{}_{\bar{s}(\hat{x})}(\{s'{}_i\}_{N-N_{in}}) = H_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q^{in}{}_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}})$ where $Q^{in}{}_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N_L}) = \int \exp\left[-\beta H^{in}{}_{\{s_i{}'\}_{N_L}}(\{r^{in}{}_l\}_{N_{in}})\right] d\Gamma_{in}$.
Crystal with weakly coupled interstitials and vacancies	$N - N_{in}$	$H^{L}{}_{\bar{s}(\hat{x})}(\{s_i\}_{N-N_{in}}) = H^{*}{}_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q^{v}{}_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}})$ where $H^{*}(\{s_i\}_{N-N_{in}}) = \sum_{i=1}^{N-N_{in}} \frac{1}{2} m\dot{s}_i^2 + V^e(\{s_i\}_{N-N_{in}})$ $Q_v(\{s_i\}_{N-N_{in}}) = \int \exp\left[-\beta H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v})\right] d\Gamma_v$ where $H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}) = \sum_{k=1}^{N_v} \frac{1}{2} m\dot{R}_k^{v2} + V^e(\{R^v{}_k\}_{N_v}) + V^e(\{s_i\}_N, \{R^v{}_k\}_{N_v}$
Crystal with strongly coupled interstitials and vacancies	$N - N_{in}$	$H^{L}{}_{\bar{s}(\hat{x})}(\{s_i\}_{N-N_{in}}) = H_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}}) + \frac{1}{\beta}\ell n (Q_v)_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}})$ where $Q^{v}{}_{\bar{s}(\hat{x})}(\{s_i{}'\}_{N-N_{in}}) = \int \exp\left[-\beta H^{v}{}_{\{s'{}_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v})\right] d\Gamma_v$, where $H^{v}{}_{\{s'{}_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}) = H(\{R^v{}_k\}_{N_v}) + \frac{1}{\beta}\ell n Q_{in}(\{R^v{}_k\}_{N_v})$ where $Q_{in}(\{R^v{}_k\}_{N_v}) = \int \exp\left[-\beta H^{in}{}_{\{R^v{}_k\}_{N_v}}(\{r^{in}{}_l\}_{N_{in}})\right] d\Gamma_{in}$ $H^{in}(\{r^{in}{}_l\}_{N_{in}}) = H_{\{R_k\}^s{}_{Nv}}(\{r_i\}_{N_{in}}) + \frac{1}{\beta}\ell n Q_{ph}(\{r_i\}^R{}_{N_{in}})$

4.5.2 Absolute equilibrium condition of a crystal with point defects

The equation (4-118) demonstrates two mechanisms that change the distribution function: one is the systematic lattice deformation showed by the streaming term $\frac{\partial f(\overline{s})}{\partial \overline{s}}v + \frac{\partial f(\overline{s})}{\partial P}\dot{P}$; the other is the coupling of the displacement field to the $\{s_i'\}_{N-N_{in}}$ system which generates an internal driving force calculated by $\frac{\partial \ell nQ'(\overline{s})}{\partial \overline{s}}$. When the external force is absent, the condition for the system to establish *absolute equilibrium state* is that both the streaming term and the coupling with $\{s_i'\}$ vanish by themselves,

$$\frac{\partial \ell nQ'(\overline{s})}{\partial \overline{s}} = 0 \tag{4-120}$$

$$\frac{\partial f(\overline{s})}{\partial \overline{s}}v + \frac{\partial f(\overline{s})}{\partial P}\dot{P} = 0. \tag{4-121}$$

From (4-120), we obtain the equilibrium lattice configuration $\overline{s}^0(x)$ that minimizes the Hemholtz energy $\frac{1}{\beta}\ell nQ'(\overline{s})$.

The deformation of a crystal with point defects, however, is more complicated than a perfect crystal. Such factors as the types of defects and the detail ways of coupling between point defects all affect the ultimate lattice deformation. For given types of point defects, the number of point defects is itself a variable. Let N_Δ denote the number of any type of point defects (e.g., $N_\Delta = N_v$ for a crystal with only vacancies). The Helmholtz energy $\ell nQ'(\overline{s})$ of a crystal containing N_Δ point defects is then written as $\ell nQ'(\overline{s}, N_\Delta)$. For a certain lattice configuration $\overline{s}(x)$, the equilibrium value of N_Δ is determined from the condition that the $\ell nQ'(\overline{s}, N_\Delta)$ is a minimum, i.e.,

$$\left(\partial \ell n Q'/\partial N_\Delta\right)_{\bar{s}} = 0 \,. \tag{4-122}$$

The N_Δ that satisfies equation (4-122) is denoted by $N_\Delta{}^0$.

In summary, the conditions for the absolute thermal equilibrium of a crystal with point defects are,

$$\left(\frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial \bar{s}}\right)_{N_\Delta} = 0 \,, \tag{4-123}$$

$$\left(\frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial N_\Delta}\right)_{\bar{s}} = 0 \,. \tag{4-124}$$

4.5.3 Elastic deformation under external force neglecting changes in N_Δ

If one applies suitable external force to a crystal with a certain number of N_Δ point defects, the equilibrium state can be maintained at configuration $\bar{s}(x) \neq \bar{s}^0(x)$. Let us define a force density by,

$$\chi(\bar{s}) = -\frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial \bar{s}} \,. \tag{4-125}$$

Inserting equation (4-125) into (4-118), we obtain for configurations $\bar{s}(x) \neq \bar{s}^0(x)$:

$$\frac{\partial f(\bar{s})}{\partial t} + \frac{\partial f(\bar{s})}{\partial \bar{s}} v + \frac{\partial f(\bar{s})}{\partial P} \dot{P} = \partial_P \left(f(\bar{s}) \chi(\bar{s}) \right), \tag{4-126}$$

$$-\frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial \bar{s}} = \chi(\bar{s}) \,. \tag{4-127}$$

Equation (4-127) suggests that the lattice could attain equilibrium state for configuration $\bar{s}(x) \neq \bar{s}^0(x)$, if an external force

$$F_{ext}(\bar{s}) = -\chi(\bar{s}) = \frac{1}{\beta} \frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial \bar{s}} \tag{4-128}$$

is applied. With (4-128), we construct a new partition function defined by,

$$\ell n Q^*(\bar{s}, N_\Delta) = \ell n Q'(\bar{s}, N_\Delta) + \beta F_{ext}(\bar{s})\bar{s} \tag{4-129}$$

or more generally,

$$\ell n Q^*(\bar{s}, N_\Delta) = \ell n Q'(\bar{s}, N_\Delta) + \int_0^{\bar{s}} \beta F_{ext}(\bar{s}) d\bar{s}\,, \tag{4-130}$$

The equilibrium condition for fixed N_Δ when the external force is present is therefore,

$$\left(\partial \ell n Q^* / \partial \bar{s}\right)_{N_\Delta} = 0 \tag{4-131}$$

Consequently, the lattice could maintain an equilibrium state during a continuous deformation as long as the applied external force satisfies equation (4-128). The deformation that satisfies (4-131) is called the elastic deformation of a crystal with N_Δ point defects.

4.5.4 Chemical potential of point defects

Using similar analysis, under suitable external condition, the crystal can also establish equilibrium state for $N_\Delta \neq N_\Delta{}^0$ in a fixed lattice configuration $\bar{s}(x)$. We introduce the following definition,

$$\frac{\partial \ell n Q'(\bar{s}, N_\Delta)}{\partial N_\Delta} = \beta \mu_\Delta(\bar{s})\,. \tag{4-132}$$

The $\mu_\Delta(\bar{s})$ will be interpreted as the chemical potential of a certain type of point defects. The absolute equilibrium condition (4-124) can be then expressed as,

$$\mu_\Delta(\bar{s}) = 0\,. \tag{4-133}$$

It follows from (4-132) that if there is an input of external energy

$$W_{ext} = -\beta\mu_\Delta(\bar{s})N_\Delta, \tag{4-134}$$

the crystal can maintain its equilibrium even when N_Δ deviates from $N_\Delta{}^0$. With (4-38), we construct a new partition function defined by,

$$\ell n Q^*(\bar{s}, N_\Delta) = \ell n Q'(\bar{s}, N_\Delta) + \beta\mu_\Delta(\bar{s})N_\Delta, \tag{4-135}$$

so that

$$\frac{\partial \ell n Q^*(\bar{s}, N_\Delta)}{\partial N_\Delta} = 0 \tag{4-136}$$

is satisfied for a range of N_Δ.

Figure 4.7 shows the elastic energy of a crystal with point defects as a function of both the number of point defects and the lattice deformation.

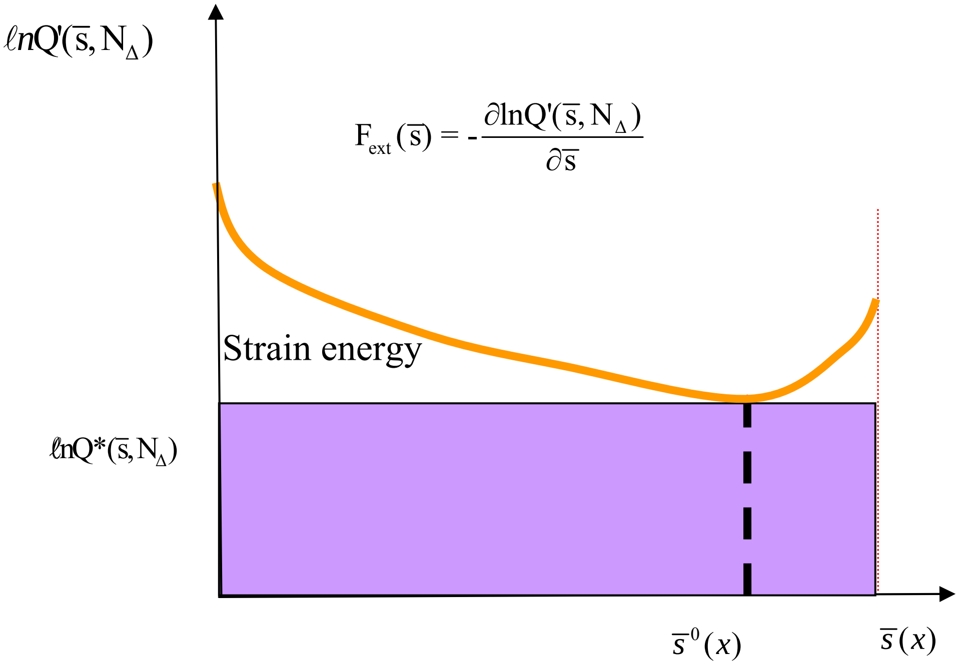


Figure 4.7 (a) Elastic deformation of a crystal with N_Δ point defects under the external force. *Changes in* N_Δ *is neglected. Equilibrium can be established for a range of lattice deformation.*

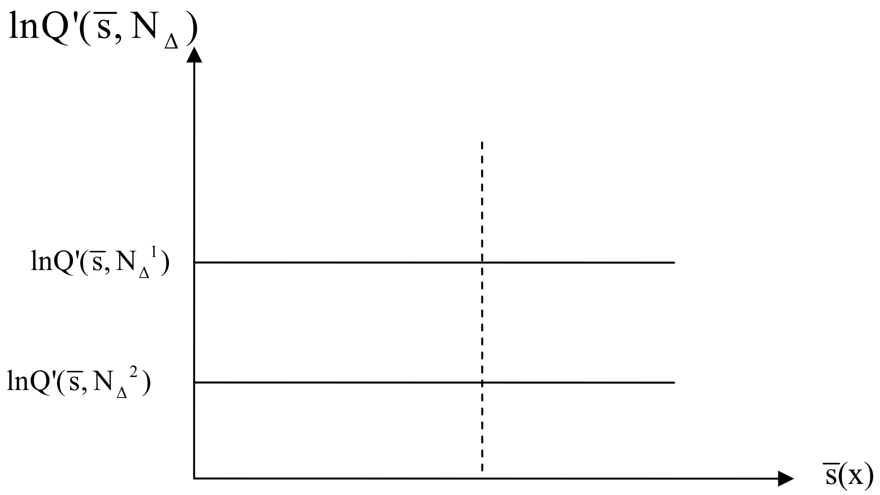


Figure 4.7 1(b) Elastic deformation of a crystal varies with the number of point defects N_Δ is compared.

4.5.5 Grand Helmholtz energy with both N_Δ and $\bar{s}(x)$ as variables

Combining (4-129) with (4-135), we construct a grand partition function that includes both chemical potential and strain:

$$\ell nQ^*(\bar{s}, N_\Delta) = \ell nQ'(\bar{s}, N_\Delta) + \beta\mu(\bar{s})N_\Delta + \int_0^{\bar{s}} \beta F_{ext}(\bar{s}, N_\Delta)d\bar{s} \ . \tag{4-137}$$

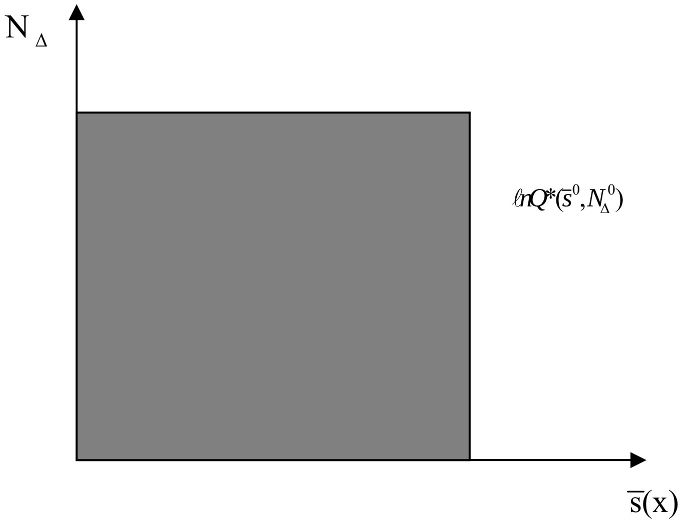


Figure 4.8 Elastic deformation with N_Δ and $\bar{s}(x)$ as variables. *Equilibrium is established for a range of* N_Δ *and lattice deformation* $\bar{s}(x)$.

The equilibrium conditions then become,

$$\left(\frac{\partial \ell n Q^*(\overline{s}, N_\Delta)}{\partial \overline{s}}\right)_{N_\Delta} = 0, \tag{4-138}$$

$$\left(\frac{\partial \ell n Q^*(\overline{s}, N_\Delta)}{\partial N_\Delta}\right)_{\overline{s}} = 0. \tag{4-139}$$

We write the (4-137) in terms of the densities of quantities as,

$$\int \Omega dx = \int \beta\left(\Omega' + \mu_\Delta(\overline{s}) n_\Delta + \left(\nabla \cdot \sigma\right) s\right) dx \tag{4-140}$$

where the densities are defined as following,

$$\ell n Q^*(\overline{s}, N_\Delta) = \int \Omega(x) dx; \tag{4-141}$$

$$\ell n Q'(\overline{s}, N_\Delta) = \int \Omega'(x) dx, \tag{4-142}$$

$$N_\Delta = \int n_\Delta(x) dx, \tag{4-143}$$

$$F_{ext}(\overline{s}) = \int \nabla \cdot \sigma(\overline{s}) dx \tag{4-144}$$

The $\ell n Q'(\overline{s})$ is calculated as,

$$\ell n Q'(\overline{s}, N_\Delta) = \left\langle H^L{}_{\overline{s}}(\{s_i'\}, N_\Delta)\right\rangle - TS(\overline{s}, N_\Delta), \tag{4-145}$$

where $\left\langle H^L{}_{\overline{s}}(s_i')\right\rangle$ denotes the average energy of the crystal and $S(\overline{s}, N_\Delta)$ is the entropy.

We now introduce the energy density $h_{\overline{s}}'(x)$ and entropy density $S_{\overline{s}}(x)$ by

$$\left\langle H^L{}_{\overline{s}}(\{s_i'\}, N_\Delta)\right\rangle = \int h_{\overline{s}}'(x) dx, \tag{4-146}$$

$$S(\overline{s}, N_\Delta) = \int S_{\overline{s}}(x) dx. \tag{4-147}$$

Inserting (4-146) and (4-147) into (4-140) and integrating by parts, we obtain the first law of thermodynamics for a deformed crystal with point defects,

$$\Omega(x) = \beta\left(h_{\overline{s}}' - TS_{\overline{s}}(x) + \mu_\Delta(\overline{s}) n_\Delta + \sigma \nabla \overline{s}\right) \tag{4-148}$$

The $\nabla \overline{s}$ is the strain tensor $e(x)$ in continuum mechanics,

$$e(x) = \nabla \overline{s}(x)\,. \tag{4-149}$$

Equation (4-148) is rewritten in terms of $e(x)$ as,

$$\Omega(x) = \beta\left(h' - TS_{\overline{s}}(x) + \mu(\overline{s})n_{\Delta} + \sigma e\right) \tag{4-150}$$

4.5.6 Elastic constant of a crystal with point defects

Note that the stress tensor σ which entering the equation (4-150) is the external stress tensor which is a function of $\overline{s}(x)$ as well as N_{Δ}. According to its definition (4-128), the external force can be explicitly expressed as,

$$\begin{aligned} F_{ext}(\overline{s}) &= -\int f_{\overline{s}}(\{s_i'\})\partial_{\overline{s}} H^{L}{}_{\overline{s}}(\{s'_i\}, N_{\Delta})d\Gamma_{s'} + N_{\Delta}\partial_{\overline{s}}\beta\mu_{\Delta}(\overline{s}) \\ &= -\int f_{\overline{s}}(\{s_i'\})\partial_{\overline{s}} H^{L}{}_{\overline{s}}(\{s'_i\}, N_{\Delta}{}^{0})d\Gamma_{s'} \end{aligned} \tag{4-151}$$

Although the expression of $H^{L}{}_{\overline{s}}(\{s'_i\}_N, N_{\Delta}{}^{0})$ depends on the detail information of point defects, it can be generally written as the sum of two terms,

$$H^{L}{}_{\overline{s}}(\{s'_i\}, N_{\Delta}{}^{0}) = H_{\overline{s}}(\{s'_i\}) + G_{\overline{s}}(N_{\Delta}{}^{0}, \{s'_i\})\,, \tag{4-152}$$

where the $H_{\overline{s}(\bar{x})}(\{s'_i\})$ represents the energy of "lattice atoms" without coupling with defects, while the $G_{\overline{s}}(N_{\Delta}{}^{0}, \{s'_i\})$ is the remaining energy which is a function of $N_{\Delta}{}^{0}$. With (4-152), the external force (4-151) is written as,

$$F_{ext}(\overline{s}) = \int f_{\overline{s}}(s_i')\partial_{\overline{s}} H_{\overline{s}}(\{s'_i\})d\Gamma_{s'} + \int \frac{1}{\beta} f_{\overline{s}}(s_i')\partial_{\overline{s}} G_{\overline{s}}(N_{\Delta}{}^{0}, \{s'_i\})d\Gamma_{s'}\,,$$

which can be further written in terms of chemical potential,

$$F_{ext}(\overline{s}) = \int f_{\overline{s}}(\{s_i'\})\partial_{\overline{s}} H'_{\overline{s}}(\{s_i'\})d\Gamma_{s'} + N_{\Delta}{}^{0}\int f_{\overline{s}}(\{s_i'\})\partial_{\overline{s}}\mu_{\Delta}(\overline{s}, \{s'_i\})d\Gamma_{s'}\,. \tag{4-153}$$

Equation (4-153) demonstrates that there are two factors contributing to the value of external force: one is the force needed to change the internal energy of the lattice described by ,

$$F_{ext}^{L}(\overline{s}) = \int f_{\overline{s}}(s_i')\partial_{\overline{s}}H'_{\overline{s}}(s_i')d\Gamma_{s'}, \tag{4-154}$$

and the other is the force needed to balance the force from point defects denoted by

$$F_{ext}^{\Delta}(\overline{s}) = {N_\Delta}^{0}\int f_{\overline{s}}(\{s_i'\})\partial_{\overline{s}}\mu_\Delta(\overline{s},\{s'_i\})d\Gamma_{s'}. \tag{4-155}$$

It means that the magnitude of external force needed for the same amount of elastic deformation varies with the number of point defects N_Δ. Table 4.2 lists some expressions for $G_{\overline{s}}({N_\Delta}^{0},\{s'_i\})$.

Table 4.2 Expressions of $G_{\overline{s}(x)}({N_\Delta}^{0},\{s'_i\})$ for various crystals

Types of crystal	N_Δ	Number of "lattice atoms"	$G_{\overline{s}(\hat{x})}(N_\Delta,\{s'_i\}_N)$
Perfect crystal	$N_\Delta = 0$	N	$G_{\overline{s}(x)}(\{s'_i\}_N) = \frac{1}{\beta}\ell n {Q^{ph}}_{\overline{s}(x)}(\{s_i'\}_N)$ where ${Q^{ph}}_{\overline{s}(x)}(\{s_i'\}_N) = \int \exp\left[-\beta {H^{ph}}_{\{s_i'\}_N}(\{q_i\}_N)\right]d\Gamma_{ph}$
Crystal with only vacancies	N_v	N	$G_{\overline{s}(x)}(N_v,\{s'_i\}_N) = \frac{1}{\beta}\ell n {Q^{v}}_{\overline{s}(x)}(\{s_i'\}_N)$ where ${Q^{v}}_{\overline{s}(x)}(\{s_i'\}_N) = \int \exp\left[-\beta {H^{v}}_{\{s_i'\}_{N-N_v}}(\{{R^v}_k\}_{N_v})\right]d\Gamma_{v}$.
Crystal with only interstitials	N_{in}	$N - N_{in}$	$G_{\overline{s}(x)}(N_{in},\{s'_i\}_{N-N_{in}}) = \frac{1}{\beta}\ell n {Q^{in}}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}})$ where ${Q^{in}}_{\overline{s}(x)}(\{s_i'\}_{N_L}) = \int \exp\left[-\beta {H^{in}}_{\{s_i'\}_{N_L}}(\{{r^{in}}_l\}_{N_{in}})\right]d\Gamma_{in}$.

Crystal with weakly coupled interstitials and vacancies	N_v, N_{in}	$N-N_{in}$	$G^{L}{}_{\overline{s}(x)}(N_v, N_{in}, \{s_i\}_{N-N_{in}})$ $= \frac{1}{\beta}\ell n Q^{in}{}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q^{v}{}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}})$ where $Q^{in}{}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}})$ $= \frac{\int \exp\left[-\beta H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}})\right] d\Gamma_{in}}{N-N_{in}+N_v}(N-N_{in})$ $Q_v(\{s_i\}_{N-N_{in}}) = \int \exp\left[-\beta H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v})\right] d\Gamma_v$ $H^{*}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v})$ $= \sum_{k=1}^{N_v} \frac{1}{2} m \dot{R}_k^{v2} + V^{e}(\{R^{v}{}_k\}_{N_v}) + V^{e}(\{s_i\}_N, \{R^{v}{}_k\}_{N_v})$
Crystal with strongly coupled interstitials and vacancies	N_v, N_{in}	$N-N_{in}$	$G^{L}{}_{\overline{s}(x)}(N_v, N_{in}, \{s_i\}_{N-N_{in}}) = \frac{1}{\beta}\ell n Q^{v}{}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}})$ where $Q^{v}{}_{\overline{s}(x)}(\{s_i'\}_{N-N_{in}}) = \int \exp\left[-\beta H^{v}{}_{\{s'_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v})\right] d\Gamma_v$, where $H^{v}{}_{\{s'_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v}) = H(\{R^{v}{}_k\}_{N_v}) + \frac{1}{\beta}\ell n Q_{in}(\{R^{v}{}_k\}_{N_v})$ where $Q_{in}(\{R^{v}{}_k\}_{N_v}) = \int \exp\left[-\beta H^{in}{}_{\{R^{v}{}_k\}_{N_v}}(\{r^{in}{}_l\}_{N_{in}})\right] d\Gamma_{in}$ $H^{in}(\{r^{in}{}_l\}_{N_{in}}) = H_{\{R_k\}^{s}{}_{Nv}}(\{r_i\}_{N_{in}}) + \frac{1}{\beta}\ell n Q_{ph}(\{r_i\}^{R}{}_{N_{in}})$

It follows from (4-154) that the external stress is expressed as

$$\sigma(x) = \overline{\tau}(x) - \overline{\tau}^{\Delta}(x) \qquad (4\text{-}156)$$

where the stress tensors $\overline{\tau}(x)$ and $\overline{\tau}^{\Delta}(x)$ are defined by

$$F^{L}_{ext}(\overline{s}) = \int \nabla \cdot \overline{\tau}(x) dx, \qquad (4\text{-}157)$$

$$F_{ext}^{\Delta}(\overline{s}) = \int \nabla \cdot \overline{\tau}^{\Delta}(x, N_{\Delta}{}^{0})dx . \qquad (4\text{-}158)$$

Note that the first stress tensor is directly related to the atomic stress tensor, while the second one is associated with the driving force from defects. In a simple case when the point defects are homogeneously distributed, the $\overline{\tau}^{\Delta}(x, N_{\Delta}{}^{0})$ is reduced to a scalar which defines the intrinsic pressure induced by point defects,

$$p_{\Delta}^{0} = \frac{1}{3}\sum_{\alpha} \overline{\tau}_{\alpha\alpha}^{\Delta} = n_{\Delta}^{0} p^{\Delta} . \qquad (4\text{-}159)$$

where n_{Δ}^{0} denotes the equilibrium concentration of point defects. Equation (4-156) is then rewritten as

$$\sigma_{\alpha\beta} = \overline{\tau}_{\alpha\beta} - n_{\Delta}^{0} p^{\Delta} \delta_{\alpha\beta} . \qquad (4\text{-}160)$$

The external stress is a function of the lattice deformation as is shown by its definition (4-128). To describe the relationship between the stress and strain, we introduce the definition of elastic constant $C_{\alpha\beta\mu\nu}$ by,

$$\sigma_{\alpha\beta} = C_{\alpha\beta\mu\nu} e^{\mu\nu} \qquad (4\text{-}161)$$

where $C_{\alpha\beta\mu\nu}$ is calculated as,

$$C_{\alpha\beta\mu\nu} = \partial_{e^{\alpha\beta}} \partial_{e^{\mu\nu}} \ell n Q'(\overline{s}(\widehat{x}), N_{\Delta}) = \partial_{e^{\mu\nu}} \left(\overline{\tau}_{\alpha\beta} - n_{\Delta}^{0} p^{\Delta} \delta_{\alpha\beta} \right). \qquad (4\text{-}162)$$

The elastic constant $C_{\alpha\beta\mu\nu}$ here is called isothermal elastic modulus. If we introduce a coefficient $\overline{C}_{\alpha\beta\mu\nu}$ defined by

$$\overline{C}_{\alpha\beta\mu\nu} = \partial_{e^{\mu\nu}} \overline{\tau}_{\alpha\beta} , \qquad (4\text{-}163)$$

the elastic modulus $C_{\alpha\beta\mu\nu}$ is then related with $\overline{C}_{\alpha\beta\mu\nu}$ through the relation

$$C_{\alpha\beta\mu\nu} = \bar{C}_{\alpha\beta\mu\nu}\left(1 - \frac{n_{\Delta}^{0} p^{\Delta} \delta_{\alpha\beta}}{\bar{C}_{\alpha\beta\mu\nu} e_{\mu\nu}}\right). \tag{4-164}$$

The $\bar{C}_{\alpha\beta\mu\nu}$ in (4-163) is interpreted as the elastic modulus of the nominal perfect crystal. We therefore see from equation (4-164) that at finite temperature, the elastic modulus of a crystal with point defects is modified by the existence of defects.

4.6 Summary

We see in this chapter that point defects modify the overall constraints in a perfect crystal. Interstitials are generated when constraints are released in the "atomic space", while vacancies are formed when constraints are imposed in the "lattice space". The total number of degrees of freedom is always conserved for a crystal with N atoms. Further modifications of constraints result in more complicated formations of point defects which result in different lattice deformation.

Point defects bring extra intrinsic time scales in a crystal. Using the technique developed in Chapter III, we introduce a hierarchical development across time/length scales by identifying fast and slow variables. A hierarchy of constrained distribution function is derived by applying BO-like approximations. Ultimately, we obtain dynamic equations for each type of point defects. It is demonstrated that these point defects behave like particles in a fluid on the corresponding time scales. It is therefore justified to apply the methods developed for fluids in chapter one to every intrinsic time scale existing in a crystal.

However, dynamics in a solid is distinguished from a fluid in that dynamics on various intrinsic time scales are coupled together. In the next chapter, we investigate the non-equilibrium dynamics of a complex crystal. We shall also demonstrate that through the methods in Chapter IV, the BO-like approximations which act as our constraints to reduce the number of variables can be relaxed a bit by considering the coupling among the time scales.

Appendix

Expressions of chemical potential of point defects and "lattice atoms" in various types of crystals

The expression of the chemical potential for point defects, however, is dependent on the detailed coupling between the defects and the "lattice atoms". In the following part, we give out the expression for the chemical potential of vacancies, interstitials and "lattice atoms" in a crystal:

(1) Perfect crystal with N atoms

Number of atoms: N;

Number of lattice points: N;

Number of "lattice atoms": N;

The effective energy of the crystal is,

$$H_L(\{s_i\}_N) = H(\{s_i\}_N) + \frac{1}{\beta}\ell n Q_{ph}(\{s_i\}_N) \tag{A-1}$$

Define,

$$\mu_L{}^0(\{s_i\}_N) = \frac{\partial H(\{s_i\}_N)}{\partial N}, \tag{A-2}$$

and the chemical potential of atomic degrees of freedom in a fixed lattice configuration is,

$$\mu_{ph}{}^0(\{s_i\}_N) = \frac{\partial H_{\{s_i\}_N}(\{q_i\}_N)}{\partial N}. \tag{A-3}$$

Then the chemical potential for the "lattice atoms" is defined as,

$$
\begin{aligned}
\mu_L(\{s_i\}_N) &= \frac{\partial H_L(\{s_i\}_N)}{\partial N} \\
&= \partial_N\left[\mu_L{}^0(\{s_i\}_N)N + \mu_{ph}{}^0(\{s_i\}_N)N\right] \\
&= \mu_L{}^0 + \mu_{ph}{}^0 + N\partial_N\left[\mu_{ph}{}^0(\{s_i\}_N)\right] \\
&= \mu_L{}^p
\end{aligned}
\tag{A-4}
$$

(2) Crystal with only vacancies

Number of atoms: N ;

Number of lattice points: $N + N_v$;

Number of "lattice atoms": N ;

The effective energy of the crystal is,

$$H_L(\{s_i\}_N) = H'(\{s_i\}_N) + \frac{1}{\beta}\ell n Q^{N_v}(\{s_i\}_N) \tag{A-5}$$

The chemical potential of vacancies in a fixed lattice configuration is,

$$\mu_v{}^0(\{s_i\}_N) = \frac{\partial H_{\{s_i\}_N}(\{R_k\}_{N_v})}{\partial N_v} \tag{A-6}$$

Then we have,

$$H_L(\{s_i\}_N) = \mu_L{}^p(\{s_i\}_N)N + \mu_v{}^0(\{s_i\}_N)N_v \tag{A-7}$$

So the chemical potential of vacancies is,

$$\frac{\partial H_L(\{s_i\}_N)}{\partial N_v} = \mu_v{}^0(\{s_i\}_N) \tag{A-8}$$

and the chemical potential of the "lattice atoms" is,

$$\begin{aligned}\mu_L(\{s_i\}_N) &= \frac{\partial H_L(\{s_i\}_N)}{\partial N}\\ &= \partial_N\left[\mu_L{}^p(\{s_i\}_N)N + \mu_v{}^0(\{s_i\}_N)N_v\right]\\ &= \mu_L{}^p + N_v\partial_N\left[\mu_v{}^0(\{s_i\}_N)\right]\end{aligned} \tag{A-9}$$

We see therefore that due to the coupling between the lattice atoms and vacancies, the chemical potential of "lattice atoms" is modified due to the existence of vacancies. When there are no vacancies, the chemical potential of the "lattice atoms" is reduced to that of the "lattice atoms" in a perfect crystal.

(3) Crystal with only interstitials

The chemical potential of interstitials in a fixed lattice configuration is,

$$\mu_{in}{}^0(\{s_i\}_{N-N_{in}}) = \frac{\partial H^{in}{}_{\{s_i\}_{N-N_{in}}}(\{r^{in}{}_l\}_{N_{in}})}{\partial N_{in}}. \tag{A-10}$$

$$\begin{aligned}H_L(\{s_i\}_{N-N_{in}}) &= H(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q^{N_{in}}(\{s_i\}_{N-N_{in}})\\ &= (N-N_{in})\mu_L{}^0 + \mu^{in}(\{s_i\}_{N-N_{in}})N_{in}\end{aligned} \tag{A-11}$$

So the effective chemical potential of interstitials in a crystal is,

$$\mu^{in} = \frac{\partial H_L(\{s_i\}_{N-N_{in}})}{\partial N_{in}} = -\mu_L{}^0 + \mu_{in}{}^0. \tag{A-12}$$

The effective chemical potential of the "lattice atoms" is,

$$\begin{aligned}\mu_L(\{s_i\}_{N-N_{in}}) &= \frac{\partial H_L(\{s_i\}_{N-N_{in}})}{\partial(N-N_{in})}\\ &= \partial_{N-N_{in}}\left[(N-N_{in})\mu_L{}^0 + \mu_{in}{}^0(\{s_i\}_{N-N_{in}})N_{in}\right].\\ &= \mu_L{}^0 - \mu_{in}{}^0 + N_{in}\partial_{N-N_{in}}\left[\mu_{in}{}^0(\{s_i\}_{N-N_{in}})\right]\end{aligned} \tag{A-13}$$

(4) Crystal with weakly coupled interstitials and vacancies

The effective chemical potential of interstitials in a fixed lattice configuration (including vacancies) is,

$$\mu_{in}{}^{0}(\{s_i\}_{N-N_{in}+N_v}) = \frac{\partial H^{in}{}_{\{s_i\}_{N-N_{in}+N_v}}(\{r^{in}{}_l\}_{N_{in}})}{\partial N_{in}} \tag{A-14}$$

The lattice space has an effective energy,

$$\begin{aligned} H'(\{s_i\}_{N-N_{in}+N_v}) &= H(\{s_i\}_{N-N_{in}+N_v}) + \frac{1}{\beta}\ell n Q^{N_{in}}(\{s_i\}_{N-N_{in}+N_v}) \\ &= (N - N_{in} + N_v)\mu_L{}^{0} + \mu^{in}(\{s_i\}_{N-N_{in}+N_v})N_{in} \end{aligned} \tag{A-15}$$

$$\mu^{in}(\{s_i\}_{N-N_{in}+N_v}) = \frac{H'(\{s_i\}_{N-N_{in}+N_v})}{\partial N_{in}} = -\mu_L{}^{0} + \mu_{in}{}^{0} \tag{A-16}$$

$$\mu_L{}'(\{s_i\}_{N-N_{in}+N_v}) = \frac{H'(\{s_i\}_{N-N_{in}+N_v})}{\partial\left(N - N_{in} + N_v\right)} = \mu_L{}^{0} - \mu_{in}{}^{0} + N_{in}\frac{\partial \mu^{in}(\{s_i\}_{N-N_{in}+N_v})}{\partial\left(N - N_{in} + N_v\right)}\,. \tag{A-17}$$

The effective energy of the vacancies is,

$$\begin{aligned} H'_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v}) &= H_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v}) + \mu^{in}(\{R^{v}{}_k\}_{N_v})N_{in} \\ &= \mu_v{}^{0}(\{s_i\}_{N-N_{in}})N_v + N_{in}N_v\partial_{N_v}\mu^{in}(\{R^{v}{}_k\}_{N_v}) \end{aligned}, \tag{A-18}$$

and we obtain the effective chemical potential for the vacancies,

$$\begin{aligned} \mu^{v}(\{s_i\}_{N-N_{in}}) &= \frac{\partial H'_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_k\}_{N_v})}{\partial N_v} \\ &= \mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{s_i\}_{N-N_{in}+N_v}) \end{aligned} \tag{A-19}$$

We see therefore that the number of interstitials also affects the chemical potential of the vacancies. The effective energy of the "lattice atoms" is,

$$\begin{aligned} H_L(\{s_i\}_{N-N_{in}}) &= H'(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q^{N_v}(\{s_i\}_{N-N_{in}}) \\ &= (N-N_{in})\mu_L' + \mu^v(\{s_i\}_{N-N_{in}})N_v \end{aligned} , \qquad \text{(A-20)}$$

and we obtain the effective chemical potential for the "lattice atoms",

$$\begin{aligned} \mu_L(\{s_i\}_{N-N_{in}}) &= \frac{\partial H_L(\{s_i\}_{N-N_{in}})}{\partial(N-N_{in})} \\ &= \mu_L' + N_v \partial_{N-N_{in}}\left[\mu^v(\{s_i\}_{N-N_{in}})\right] \\ &= \mu_L{}^0 - \mu_{in}{}^0 + N_{in}\partial_{(N-N_{in}+N_v)}\mu^{in}(\{s_i\}_{N-N_{in}+N_v}) + N_v\partial_{N-N_{in}}\left[\mu^v(\{s_i\}_{N-N_{in}})\right] \end{aligned} \qquad \text{(A-21)}$$

(5) Crystal with strongly coupled interstitials and vacancies

The effective chemical potential of interstitials in a fixed vacancy configuration is,

$$\mu_{in}(\{R_k\}_{N_v}) = \frac{\partial H^{in}{}_{\{R_k\}^s{}_{N_v}}(\{r^{in}{}_l\}_{N_{in}})}{\partial N_{in}} \qquad \text{(A-22)}$$

The effective energy of vacancies in a fixed lattice configuration is therefore,

$$\begin{aligned} H^v{}_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}) &= H_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v}) + \frac{1}{\beta}\ell n Q_{in}(\{R^v{}_k\}_{N_v}) \\ &= \mu_v{}^0(\{s_i\}_{N-N_{in}})N_v + \mu_{in}(\{R_k\}^s{}_{N_v})N_{in} \end{aligned} , \qquad \text{(A-23)}$$

The chemical potential of interstitials in a fixed vacancy configuration is therefore,

$$\mu_{in}(\{R_k\}^s{}_{N_v}) = \frac{\partial H^v{}_{\{s_i\}_{N-N_{in}}}(\{R^v{}_k\}_{N_v})}{\partial N_{in}} \qquad \text{(A-24)}$$

The effective total energy is,

$$H_L(\{s_i\}_{N-N_{in}}) = H(\{s_i\}_{N-N_{in}}) + \frac{1}{\beta}\ell n Q_v''(\{s_i\}_{N-N_{in}}) . \qquad \text{(A-25)}$$

We therefore obtain the effective chemical potential of the vacancies,

$$\begin{aligned}\mu^{v}(\{s_i\}_{N-N_{in}}) &= \frac{\partial H^{v}{}_{\{s_i\}_{N-N_{in}}}(\{R^{v}{}_{k}\}_{N_v})}{\partial N_v} \\ &= \mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{R^{v}{}_{k}\}^{s}{}_{N_v})\end{aligned} \tag{A-26}$$

The effective chemical potential of “lattice atoms” is,

$$\begin{aligned}\mu_L(\{s_i\}_{N-N_{in}}) &= \frac{\partial H_L(\{s_i\}_{N-N_{in}})}{\partial (N-N_{in})} \\ &= \mu_L{}^{0} + N_v\partial_{N-N_{in}}\left[\mu^{v}(\{s_i\}_{N-N_{in}})\right] \\ &= \mu_L{}^{0} + N_v\partial_{N-N_{in}}\left[\mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{R^{v}{}_{k}\}^{s}{}_{N_v})\right]\end{aligned} \tag{A-27}$$

The effective chemical potential of interstitials is,

$$\begin{aligned}\mu_{in}(\{s_i\}_{N-N_{in}}) &= \frac{\partial H_L(\{s_i\}_{N-N_{in}})}{\partial N_{in}} \\ &= \partial_{N_{in}}(N-N_{in})\left\{\mu_L{}^{0} + N_v\partial_{N-N_{in}}\left[\mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{R^{v}{}_{k}\}^{s}{}_{N_v})\right]\right\} \\ &= -\mu_L{}^{0} + N_v\partial_{N-N_{in}}\left[\mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{R^{v}{}_{k}\}^{s}{}_{N_v})\right] \\ &\quad +(N-N_{in})N_v\partial_{N_{in}}\partial_{N-N_{in}}\left[\mu_v{}^{0}(\{s_i\}_{N-N_{in}}) + N_{in}\partial_{N_v}\mu^{in}(\{R^{v}{}_{k}\}^{s}{}_{N_v})\right]\end{aligned} \tag{A-28}$$

CHAPTER V

FORMULATION OF NONEQUILIBRIUM DYNAMICS IN A CRYSTAL

5.1 Philosophy underlining the nonequilibrium formulation

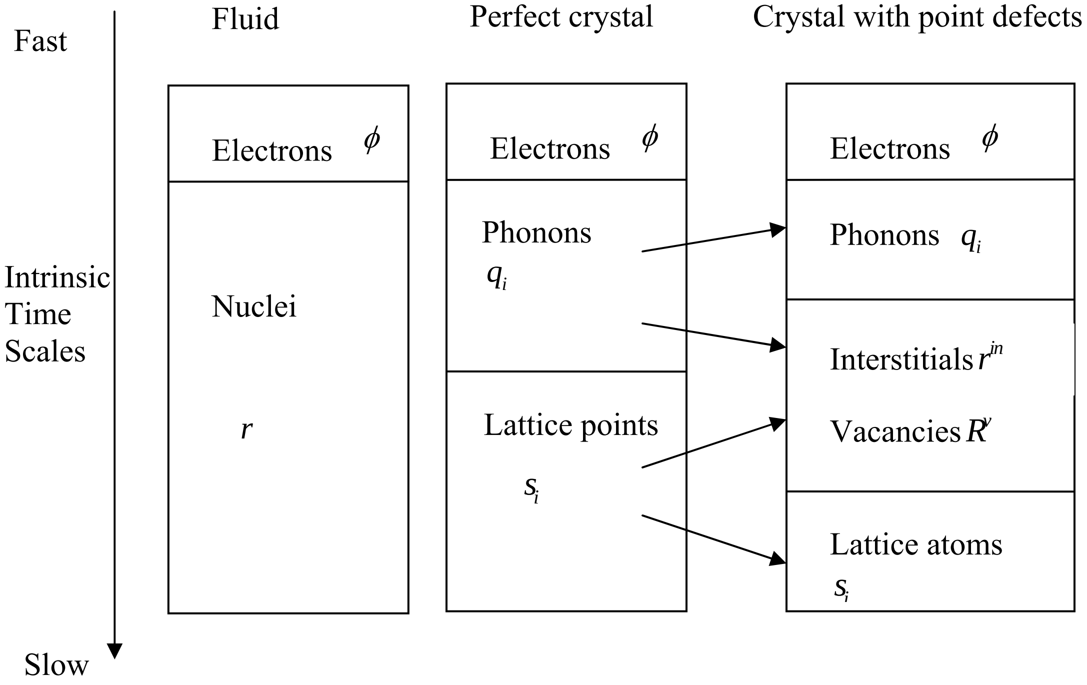


Figure 5.1 Intrinsic time scales in a fluid and crystal (no external force). *There are only two intrinsic time scales in a fluid: those correspond to typical velocities of electrons and nuclei. In crystals, on the other hand, nuclei are associated with a lattice. Each nucleus is therefore associated with two classes of variables:* s_i *and* q_i*. The six variables are related by constraints. As demonstrated in Chapter 3, we introduce a hierarchical development across time scales by identifying fast and slow variables. First, the BO approximation allows us to integrate out the "fast" electron degrees of freedom with the nuclei being fixed. Then, we invoke a BO-like Ansatz to construct a constrained distribution function for lattice points, integrating out the "fast" phonon degrees of freedom. Next we consider point defects (vacancies and interstitials) which modify overall constraints. Thus, we derive a successive series of constrained distribution functions and Liouville equations for each scale, from the quantum world to the macroscopic, that exists in a complex crystal. Note that when there are external forces, the identification of fast and slow variables may be reversed for point defects and "lattice atoms".*

We have up to now demonstrated that there exists a hierarchy of intrinsic time scales that are absent in a fluid (Figure 5.1).

At each individual intrinsic time scale, the respective entity (electrons, nuclei, etc) behaves like a fluid. Going to Figure 5.1, for example, on the fastest time scale, electron fluxes occur in response to external forces or thermodynamic forces (e.g. gradient of temperature) arising from the inhomogeneities in the system. Similarly, there can be phonon fluxes, vacancy fluxes, lattice- point fluxes, etc. We therefore invoke the coarse graining applied in fluid (Chapter II) in order to obtain the fluxes and transport equations. As shown in Figure 5.2, the coordinate space a fluid occupies is divided into cells. Two length scales are then introduced: the microscopic scale ($\{r_i(t)\}$) and the coarse grained coordinate space ($\{x_\alpha(t)\}$).The macroscopic dynamics is assumed to be described in the coarse grained space ($\{x_\alpha(t)\}$).

In a similar way, we apply coarse graining to each individual intrinsic time scale (Figure.5.3). For example, on the fastest scale, the space occupied by electrons is divided into cells. Electrons are assumed to first establish equilibrium in each cell, and then the whole system of electrons gradually approaches a uniform state. Based on the coarse graining, one can construct a nonequilibrium distribution function for electrons using the same technique described for fluids (for electrons, one should be dealing with a quantum density matrix, not a classical distribution function). Thereafter, we could derive the flux of electrons driven by external forces or thermodynamic forces. Note that because the distribution function of electrons is introduced based on the BO-like approximation, the fluxes of electrons are calculated as if the nuclei are frozen. Similarly, one can construct nonequilbrium distribution functions for phonons, point defects and “lattice atoms”. We therefore expect a hierarchy of constrained nonequilibrium distribution functions:

$$f(\{s_i\}_{N-N_{in}})\, f_{\{s_i\}_{N-N_{in}+N_v{}^1}}(\{R^v{}_k\}_{N_v{}^2}), \{r_i\}_{N_{in}})\, f_{\{r^{in}{}_l\}_{N_{in}}}(\{q_i\}_{N-N_{in}+N_v{}^1}), \tag{5-1}$$

where each individual distribution function assumes a nonequilibrium fluid-like form.

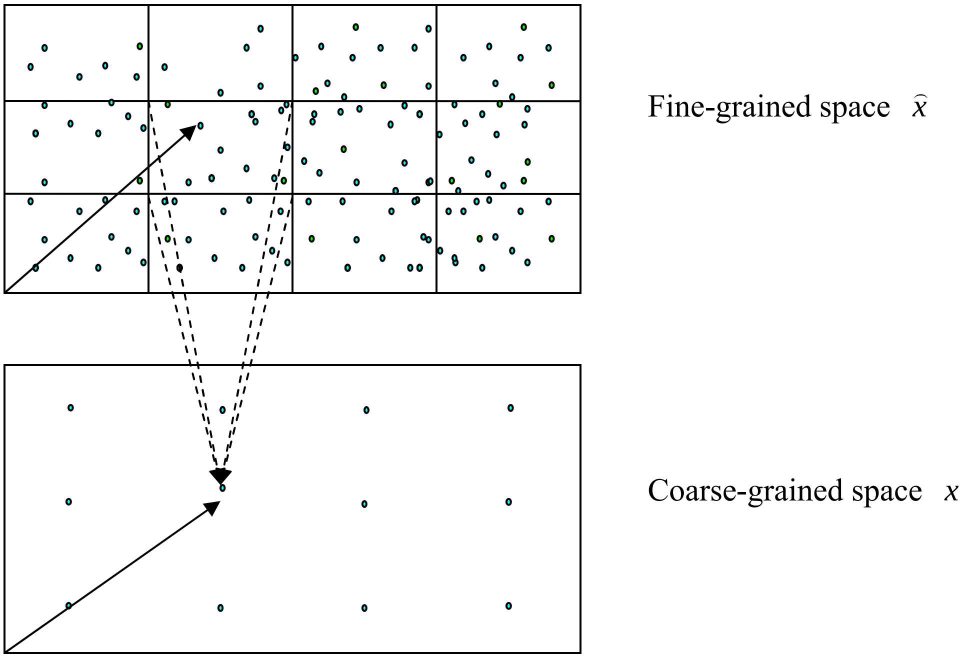


Figure 5.2 Coarse graining in an inhomogeneous fluid. *The coordinate space $\widehat{x}$ occupied by a fluid is divided into cells (the coordinate space $\widehat{x}$ is also called as the fine grained space). In each cell, the fluid can be seen as homogeneous. The coordinate of the center of mass of a cell is denoted as x. This coordinate space x is called the coarse grained coordinate space. It is then assumed that a nonequilibrium fluid approaches equilibrium through two stages: equilibrium is first established for each cell, and then the whole system gradually approaches a uniform state.*

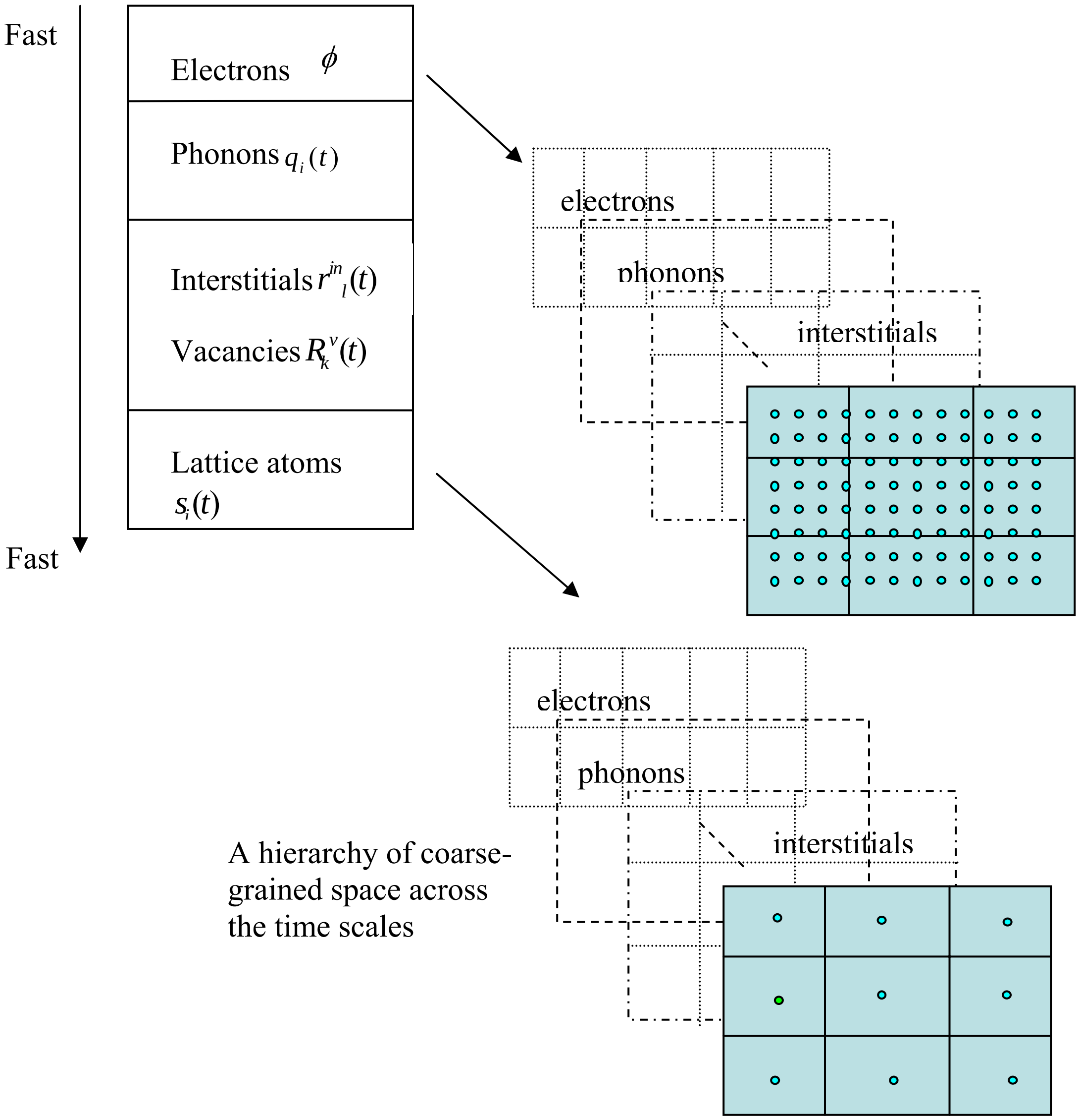


Figure 5.3 Coarse graining in a complex crystal. *The system on each intrinsic time scale behaves like a fluid. The coarse graining demonstrated in Figure 5.2 is applied on every intrinsic time scale. As a result, we obtain a hierarchy of coarse grained space across the time scales.*

What distinguishes the nonequilibrium transport of solid from a fluid, however, is the coupling among different intrinsic time scales (Figure5.4). For example, the stress-strain relationship on the slowest time scale can drive the motion of vacancies; the migration of electrons affects the motion of phonons, vacancies, etc. Thus, after we obtain the constrained nonequilbrium distribution function (5-1), we need to further take into consideration the coupling among time scales. Note that through the constrained distribution function, we have taken into account the influence of fast variables on slow variables. For example, the free energy of phonons acts as an extra potential to the lattice points as demonstrated by equation (3-34); the pressure of phonons drives the deformation of lattice shown by equation (3-36) and (3-37). The effect of slower time scale on the fast time scale, on the other hand, has not been considered and will be discussed in detail this chapter.

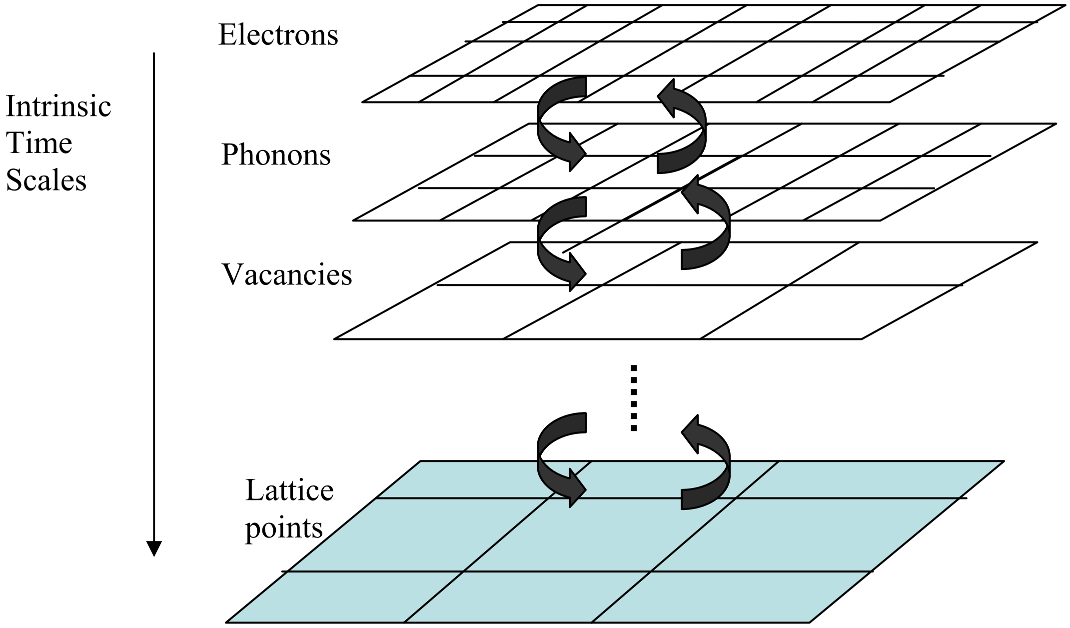


Figure 5.4 Intrinsic time scales in a complex crystal are couple together. *After the coarse graining, we have to take into account of the coupling effect. The coupling is two directional: dynamics of faster time scales influence the motion on slower time scales; on the other hand, the transport on slower time scales may also drive the motion on faster time scales.*

Based on the above physical picture of the nonequilibrium dynamics in a complex crystal, the context of this chapter is organized in the following way: the fluid-like transport at each individual intrinsic time scale is addressed first; then the coupling among different time scales is taken into consideration; finally we apply the developed formulation to the description of Herring creep.

5.2 Fluid-like transport on each intrinsic time scale

In this section, we construct the nonequilibrium distribution function by applying the technique described in Chapter II for the description of the nonequilibrium fluid. The coupling among the scales is temporarily ignored. As a demonstration, we formulate the transport of vacancies in a fixed lattice configuration. The formulations of the nonequilibrium transport driven by thermodynamic forces on every intrinsic time scale follow similar procedures.

5.2.1 Microscopic transport equations of vacancies in a crystal

5.2.1.1 Basic equations

Here we briefly summarize some basic equations for the descriptions of vacancies in a crystal. One could refer the Chapter IV for details on the expressions and equations.

The Liouvile equation for vacancies in the fixed lattice configuration is expressed by (4-11),

$$\frac{\partial f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})}{\partial t}+\left\{f_{\{s_i\}_N}(\{R^v{}_k\}_{N_v}),H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})\right\}=0\,, \tag{5-2}$$

where the $H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})$ is the effective total energy of vacancies on a fixed lattice configuration expressed according to (4-9),

$$H'_{\{s_i\}_N}(\{R^v{}_k\}_{N_v})=H_{\{s_i\}_{N_L}}(\{R^v{}_k\}_{N_v})+\frac{1}{\beta^{ph}}\ell n Q^{ph}{}_{\{s_i\}_{N_L}}(\{R^v{}_k\}_{N_v})\,, \tag{5-3}$$

where the $\frac{1}{\beta^{ph}} \ell n Q^{ph}{}_{\{s_i\}_{N_L}} (\{R^v{}_k\}_{N_v})$ is the Helmholtz energy of phonons in a fixed configuration of both vacancies and "lattice atoms". For clarity, we denote $H'{}_{\{s_i\}_N} (\{R^v{}_k\}_{N_v})$ by $H^v{}_{\{s_i\}_{N_L}} (\{R^v{}_k\}_{N_v})$ and the effective canonical equations of vacancies are,

$$\begin{aligned} \dot{R}^v_k &= \partial_{p^v{}_k} H^v{}_{\{s_i\}_{N_L}} (\{R^v{}_k\}_{N_v}) \\ \dot{p}^v_k &= -\partial_{R^v{}_k} H^v{}_{\{s_i\}_{N_L}} (\{R^v{}_k\}_{N_v}) \quad (k = 1, \dots N_v) \end{aligned} . \tag{5-4}$$

Equation (5-4) demonstrates that vacancies behave like real particles described by its coordinate $R^v{}_k$ and corresponding momenta $p^v{}_k$. In other words, vacancies are treated as pseudo-particles in a way similar to holes in the valence bands of a semiconductor.

5.2.1.2 The local form of conservation equations

Let $\hat{x}$ be the continuous coordinate in the space in which the nominal lattice is defined. In this coordinate space, we introduce the density of vacancies as,

$$n^v(\hat{x}) = \sum_k \delta(\hat{x} - R_k{}^v) . \tag{5-5}$$

In a similar way, the momentum and energy density are expressed by

$$g^v(\hat{x}) = \sum_k p_k{}^v \delta(\hat{x} - R_k{}^v) . \tag{5-6}$$

The effective energy of vacancies in a crystal in (5-3) is expressed as,

$$H^v{}_{\{s_i\}_N} (\{R^v{}_k\}_{N_v}) = \sum_{k=1}^{N_v} \frac{1}{2} m \dot{R}_k^{v2} + V'(\{R^v{}_k\}_{N_v}) + V'(\{s_i\}_N, \{R^v{}_k\}_{N_v}) , \tag{5-7}$$

where,

$$V'(\{R^v{}_k\}_{N_v}) = V(\{R^v{}_k\}_{N_v}) + \frac{1}{\beta^{ph}}\ell n Q_{ph}(\{R^v{}_k\}_{N_v}), \tag{5-8}$$

$$V'(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = V(\{s_i\}_N, \{R^v{}_k\}_{N_v}) + \frac{1}{\beta^{ph}}\ell n Q_{ph}(\{s_i\}_N, \{R^v{}_k\}_{N_v}). \tag{5-9}$$

In cluster expansion, $V'(\{R^v{}_k\}_{N_v})$ and $V'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ can be approximated as,

$$V'(\{R^v{}_k\}_{N_v}) = \frac{1}{2}\sum_k \left\{ \sum_{k\neq l} V'\left(R_{kl}{}^v\right) \right\} + \frac{1}{6}\sum_i \left\{ \sum_{k\neq l}\sum_{m\neq k,l} V'\left(R_{kl}{}^v, R_{km}{}^v, R_{lm}{}^v\right) \right\} + \ldots$$

$$V'(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = \frac{1}{2}\sum_k \left\{ \sum_{k\neq i} V\left(d_{ki}\right) \right\} + \frac{1}{6}\sum_i \left\{ \sum_{k\neq l}\sum_{i\neq j} V\left(d_{ki}, d_{li}, R_{kl}\right) \right\} + \ldots \tag{5-10}$$

where $R_{kl}{}^v$ is the distance between two vacancies, d_{ki} is the distance between the k^{th} vacancy and i^{th} “lattice atom”. For demonstration, we will truncate the cluster expansion of energy at the pair interactions, so the $V'(\{R^v{}_k\}_{N_v})$ and $V'(\{s_i\}_N, \{R^v{}_k\}_{N_v})$ are approximated as,

$$V'(\{R^v{}_k\}_{N_v}) = \frac{1}{2}\sum_k \left\{ \sum_{k\neq l} V'\left(R_{kl}{}^v\right) \right\},$$

$$V'(\{s_i\}_N, \{R^v{}_k\}_{N_v}) = \frac{1}{2}\sum_k \left\{ \sum_{k\neq i} V\left(d_{ki}\right) \right\}. \tag{5-11}$$

We thus introduce an energy density of vacancies as,

$$\begin{aligned} h^v(\hat{x}) = {} & \sum_k \frac{1}{2} m \dot{R}_k^{v2} \delta(\hat{x} - R_k{}^v) \\ & + \frac{1}{2}\sum_k \left\{ \sum_{k\neq l} V\left(R_{kl}{}^v\right) \right\} \delta(\hat{x} - R_k{}^v) + \frac{1}{2}\sum_k \left\{ \sum_{k\neq i} V\left(d_{ki}\right) \right\} \delta(\hat{x} - R_k{}^v) \end{aligned} \tag{5-12}$$

For purpose of clarity, we shall use $n_v(\hat{x}), g_v(\hat{x})$, $h_v(\hat{x})$ to denote the microscopic forms of the particle density, momentum density and energy density of vacancies defined by (5-5), (5-6) and (5-12). We now differentiate these densities with time on the time scale of vacancies. With the help of canonical equations (5-4), we obtain the following equations:

$$\frac{\partial n_v(\hat{x})}{\partial t} = -\nabla \cdot j_v(\hat{x}) , \tag{5-13}$$

$$\frac{\partial g_v(\hat{x})}{\partial t} = -\nabla \cdot \tau_v(\hat{x}) + \sum_k \frac{\partial V'(\{s_i\}_N , \{R^v{}_k\}_{N_v})}{\partial R^v{}_k} \delta(\hat{x} - R_k{}^v) , \tag{5-14}$$

$$\frac{\partial h_v(\hat{x})}{\partial t} = -\nabla \cdot j_h{}^v(\hat{x}) , \tag{5-15}$$

where we introduce corresponding fluxes defined by,

$$j_v(\hat{x}) = \sum_k \dot{R}_k{}^v \delta(\hat{x} - R_k{}^v) , \tag{5-16}$$

$$\tau_v(\hat{x}) = \sum_k \left[m\dot{R}_k{}^v \dot{R}_k{}^v + \frac{1}{2}\sum_{k \neq l} R_{kl}{}^v F_{ij} \right] \delta(\hat{x} - R_k{}^v) , \tag{5-17}$$

$$j_h{}^v(\hat{x}) = \sum_k \left[\frac{p^v{}_k p^v{}_k}{2m} + \frac{1}{2}\sum_{l \neq k} V\left(R^v{}_{kl}\right) I + \frac{1}{2}\sum_{k \neq l} R^v{}_{kl} F^v{}_{kl} \right] \cdot \frac{p^v{}_k}{m} \delta(\hat{x} - R^v{}_k) . \tag{5-18}$$

where I denotes the unit tensor and $F^v{}_{kl}$ represents the interacting force exerted by the lth vacancy on the kth vacancy,

$$F^v{}_{kl} = -\frac{\partial V'\left(R^v{}_{lk}\right)}{\partial R^v{}_k} = \frac{\partial V'\left(R_{lk}{}^v\right)}{\partial R^v{}_l} . \tag{5-19}$$

The $j_v(\hat{x})$, $\tau_v(\hat{x})$, and $j_h{}^v(\hat{x})$ are respectively the microscopic vacancy flux, stress tensor, and the energy flux.

We then assume that there is a velocity field $\upsilon^v(x)$ of vacancies, so that the momenta of a vacancy at $\hat{x} = R^v{}_k$ can be written as,

$$p^v{}_k = p^v{}_k{}' + m\upsilon^v(R^v{}_k) \tag{5-20}$$

where $p^v{}_k{}'$ is the relative momenta of a vacancy with respect to the velocity field $\upsilon^v(\hat{x})$. The $\upsilon^v(R^v{}_k)$ can be written in terms of δ functions as,

$$\upsilon^v(R^v{}_k) = \int \upsilon^v(\hat{x})\delta(\hat{x} - R^v{}_k)d\hat{x} \tag{5-21}$$

The relative momentum density for vacancies is therefore defined as,

$$g'(\hat{x}) = \sum_{k=1}^{N_v} p'^v{}_k\, \delta(\hat{x} - R^v{}_k)\,, \tag{5-22}$$

It follows from equations (5-20)-(5-22) that

$$g^v(\hat{x}) = g^v{}'(\hat{x}) + n_v(\hat{x})\upsilon^v(\hat{x})\,. \tag{5-23}$$

Insert (5-20) into the expression of densities (5-5)-(5-7) and fluxes (5-16)-(5-18), we obtain (we drop $(\hat{x})$ in the following equations for clarity and use the prime variables to denote quantities in the relative moving frame)

$$n_v = n_v{}', \tag{5-24}$$

$$g^v = g^v{}' + mn_v{}'\upsilon^v, \tag{5-25}$$

$$h^v = h^v{}' + \upsilon^v \cdot g^v{}' + \frac{1}{2}mn^v\left(\upsilon^v\right)^2, \tag{5-26}$$

$$j^v = j^v{}' + n_v{}'\upsilon^v, \tag{5-27}$$

$$\tau^v = \tau^v{}' + 2\upsilon^v g^v{}' + mn^v{}'\upsilon^v\upsilon^v, \tag{5-28}$$

$$j_h^v = j_h^v{}' + \left(h^v{}' + \upsilon^v \cdot g^v{}' + \frac{1}{2}mn_v\left(\upsilon^v\right)^2\right)\upsilon^v + \frac{1}{2}\left(\upsilon^v\right)^2 g^v{}' + \tau^v{}' \cdot \upsilon^v, \tag{5-29}$$

5.2.2 Fluid-like local equilibrium distribution function and Euler's equations

We then follow the procedure developed for fluids in Chapter II. The local equilibrium distribution function for vacancies is expressed as,

$$f_l^v = \left(Q_l^v\right)^{-1} \exp\left[-\int\left\{\beta_v(\widehat{x})(h_v(\widehat{x}) - \alpha_v(\widehat{x})n_v(\widehat{x})\right\}\right]d\widehat{x}\ , \tag{5-30}$$

where

$$Q_l^v = \exp\left[-\int\left\{\beta_v(\widehat{x})(h_v(\widehat{x}) - \alpha_v(\widehat{x})n_v(\widehat{x})\right\}\right]d\widehat{x} \tag{5-31}$$

We can therefore obtain

$$\left\langle h_v(\widehat{x})\right\rangle_l = \frac{\partial \ell n Q_l^v}{\partial \beta_v(x)}, \tag{5-32}$$

$$\left\langle n_v(\widehat{x})\right\rangle_l = \frac{\partial \ell n Q_l^v}{\partial \alpha_v(x)}\ . \tag{5-33}$$

The $\beta_v(x)$ is called the local temperature on the time scale of vacancies, and $\mu(x) = -\dfrac{\alpha(x)}{\beta(x)}$ is called the local chemical potential. Note that the local chemical potential and local temperature of vacancies are all calculated in a fixed lattice configuration and are therefore functions of $\left\{s_i\right\}_{N_L}$.

The f_l^v in (5-30) is even with respect to time reversal. So in the local equilibrium state, we have,

$$\left\langle j_v{}'\right\rangle_l = 0, \tag{5-34}$$

$$\left\langle j_h^{v}{}'\right\rangle_l = 0, \tag{5-35}$$

and

$$\left\langle \tau_v{}'^{\alpha\beta}\right\rangle_l = 0 \qquad \text{for } \alpha \neq \beta. \tag{5-36}$$

The diagonal elements of τ_v' are generally nonzero, and we use them to define the fluid pressure:

$$p^v = \frac{1}{3}\sum_{\alpha}\left\langle \tau^{\alpha\alpha} \right\rangle_l \tag{5-37}$$

where $\langle\ \rangle_l$ indicates the ensemble average over f_l^v. We then select the systematic velocity as,

$$\upsilon(x) = \frac{\left\langle g(\widehat{x}) \right\rangle}{\left\langle \rho(\widehat{x}) \right\rangle}.$$

Insert (5-34)-(5-37) into the expressions of densities and fluxes (5-24)-(5-29), we obtain (we drop $\langle\ \rangle_l$ and the hat to indicate the average),

$$n_v = n_v', \tag{5-38}$$

$$g^v = mn_v'\upsilon^v, \tag{5-39}$$

$$h^v = h^v{}' + \frac{1}{2}mn^v\left(\upsilon^v\right)^2, \tag{5-40}$$

$$j^v = n_v'\upsilon^v, \tag{5-41}$$

$$\tau^v{}_{\alpha\beta} = p^v\delta_{\alpha\beta} + mn^v{}'\upsilon_\alpha{}^v\upsilon^v{}_\beta, \tag{5-42}$$

$$j_h^v = \left(h^v{}' + \frac{1}{2}mn_v\left(\upsilon^v\right)^2\right)\upsilon^v. \tag{5-43}$$

The result is the Euler's equation of vacancies,

$$\frac{dn_v'}{dt} = -n_v'\nabla\cdot\upsilon^v \tag{5-44}$$

$$\frac{dh_v'}{dt} = -(h_v' + p^v)\nabla\cdot\upsilon^v \tag{5-45}$$

$$\frac{d\upsilon^{v}}{dt} = -\nabla p^{v} \tag{5-46}$$

5.2.3 Fluid-like non-equilibrium distribution function of vacancies

According to the expression of the non-equilibrium distribution function for fluid (2-70) (c.f. Chapter II), the non-equilibrium distribution function for vacancies is written as,

$$f^{v} = Q_{v}^{-1} \exp\left\{ -\sum_{m} \int \left[\lambda^{v}{}_{m}(\hat{x},t) P^{v}{}_{m}(\hat{x}) - \int_{-\infty}^{0} e^{\varepsilon t_{1}} J_{v}{}^{m}(\hat{x},t') \cdot X^{v}{}_{m}(\hat{x},t+t') dt' \right] d\hat{x} \right\} \tag{5-47}$$

where $J_{v}{}^{m}$ is the thermodynamic flux of vacancies and $X^{v}{}_{m}$ is named thermodynamic force for vacancies defined by,

$$J^{0}{}_{v} = j_{h}{}^{v}{}' - \frac{h^{v}{}' + p^{v}}{\rho^{v}} g^{v}{}', \qquad X^{v}{}_{0} = \nabla \beta^{v}(\hat{x}), \tag{5-48}$$

$$J_{v}{}^{1} = \tau^{v}{}' - \left(\frac{\partial p^{v}}{\partial h^{v}{}'} \right)_{n} h^{v}{}' I - \left(\frac{\partial p^{v}}{\partial n^{v}} \right)_{h^{v}{}'} n^{v} I, \qquad X^{v}{}_{1} = -\beta^{v} \nabla \upsilon^{v}, \tag{5-49}$$

$$J^{2}{}_{v} = j^{v}{}' - \frac{1}{m} g^{v}{}', \qquad X^{v}{}_{2} = -\nabla \beta^{v} \mu^{v}. \tag{5-50}$$

The Q_{v} in (5-47) is determined by the normalization of f^{v}. For small $J_{v}{}^{m}$ and $X^{v}{}_{m}$ and we takes the linear approximation to f^{v},

$$f^{v} = f^{v}{}_{l} \left[1 - (B^{v} - \left\langle B^{v} \right\rangle_{l}) \right], \tag{5-51}$$

where

$$B^{v} = -\sum_{m} \int \int_{-\infty}^{0} e^{\varepsilon t'} J_{v}{}^{m}(\hat{x},t') \cdot X^{v}{}_{m}(\hat{x},t+t') d\hat{x} dt'. \tag{5-52}$$

It follows that f^{v} reduces to $f^{v}{}_{L}$ when B^{v} is set equal to zero.

With the approximated nonequilibrium distribution function (5-51), we obtain the relationship between the mean fluxes and the driving force according to (2-77),

$$\left\langle j_v{}^m(\hat{x})\right\rangle = \left\langle j_v{}^m(\hat{x})\right\rangle_l - \sum_n \int L^v{}_{mn}(x,x')\cdot X^v{}_n(x',t)\,dx', \tag{5-53}$$

where $L^v{}_{mn}(x,x')$ is called transport coefficient defined by,

$$L^v{}_{mn}(x,x') = \int_{-\infty}^{0} e^{\varepsilon t'} \left\langle j^v{}_m(\hat{x})\left(J^v{}_n(\hat{x}',t') - \left\langle J^v{}_n(\hat{x}',t')\right\rangle_l\right)\right\rangle_l dt'. \tag{5-54}$$

The form (5-53) shows a nonlocal dependence of the vacancy flux at a point on conditions throughout the surrounding medium, and at earlier times. Assuming further that $X^v{}_n(x',t)$ varies sufficiently slowly that it can be treated as constant, we obtain from (5-54),

$$\left\langle j^v{}_m(\hat{x})\right\rangle = \left\langle j^v{}_m(\hat{x})\right\rangle_l + \sum_n L^v{}_{mn}(x)\cdot X^v{}_n(x,t) \tag{5-55}$$

where the dynamic coefficient of vacancies $L^v{}_{mn}(x)$ is expressed by,

$$L^v{}_{mn}(x) = \int\int_{-\infty}^{0} e^{\varepsilon t}\left(j_v{}^m(\hat{x}), J_v{}^n(\hat{x}',t')\right) dt'\,d\hat{x}', \tag{5-56}$$

In which $\left(j^m(\hat{x}), J^n(\hat{x}',t')\right)$ is a simplified notation for $\left\langle j_m(\hat{x})\left(J_n(\hat{x}',t') - \left\langle J_n(\hat{x}',t')\right\rangle_l\right)\right\rangle_l$ in (5-54). The transport relation (5-55) is the Onsager's law for vacancies expressed in local form.

Ultimately, we obtain for vacancies the nonequilibrium fluxes induced solely from the inhomogeneities on the time scales corresponding to the diffusion of vacancies,

$$j^v = \lambda^v{}_2 \nabla T + L_2{}^v \nabla \frac{\mu^v}{T} \tag{5-57}$$

$$\tau^v = \eta^v \left\{ \frac{\partial \upsilon^v{}_\alpha}{\partial x_\beta} + \frac{\partial \upsilon^v{}_\beta}{\partial x_\alpha} - \frac{2}{3}\delta_{\alpha\beta}\nabla\cdot\upsilon^v \right\} + \xi^v \nabla\cdot\upsilon^v \delta_{\alpha\beta}. \tag{5-58}$$

The Navier-Stoke equation of vacancies is,

$$\frac{\partial \rho_v \upsilon^v{}_\alpha}{\partial t} + \nabla_\beta \left(\rho_v \upsilon^v{}_\alpha \upsilon^v{}_\beta + p^v \delta_{\alpha\beta} \right) = \nabla_\beta \eta_v \left(\frac{\partial \upsilon^v{}_\alpha}{\partial x_\beta} + \frac{\partial \upsilon^v{}_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \upsilon^v \right) + \nabla_\alpha \xi_v \left(\nabla \cdot \upsilon^v \right) \quad (5\text{-}59)$$

where the coefficients are calculated by,

$$\lambda^v{}_2 = -\frac{1}{T^2} \int \int_{-\infty}^{0} e^{\varepsilon t'} (j_v(\widehat{x}), J_v{}^0(\widehat{x}', t')) d\widehat{x}' dt' \quad (5\text{-}60)$$

$$\xi^v = -\frac{1}{T} \int \int_{-\infty}^{0} e^{\varepsilon t} (p_v{}^0(\widehat{x}), p_v{}^0(\widehat{x}', t)) d\widehat{x}' dt \quad (5\text{-}61)$$

$$\eta^v = -\frac{1}{2T} \int \int_{-\infty}^{0} e^{\varepsilon t} (\tau_v{}^0(\widehat{x}), \tau_v{}^0(\widehat{x}', t)) d\widehat{x}' dt . \quad (5\text{-}62)$$

5.3 The coupling among intrinsic time scales

In Chapter 5.2, the transport is only driven by the inhomogeneities on individual time scale existing in a solid. In this section, we take into consideration the coupling among intrinsic time scales on the basis of the fluid-like distribution function for each scale. Note that through the constrained distribution function, the influence of fast variables on slow variables has already been taken into account. For example, in the formulation of vacancies, the driving force from phonons has been included through the effective Hamiltonian of vacancies as demonstrated by equation (5-3). So the focus of this section will be on the effect of slower time scale on the fast time scale. As a demonstration, we construct for vacancies the modified nonequilibrium distribution function that incorporates the coupling among scales such as the long-range stress-strain relationship. Based on the modified distribution function, we derive the equation of Herring creep.

5.3.1 Modified local-equilibrium distribution function incorporating the coupling among intrinsic time scales

When there is a change in the lattice configuration $\{\Delta s_i\}_{N_L}$, a force of $\frac{\partial H'(s)}{\partial s_i}$ is exerted on each "lattice atom". Because vacancies exist only at lattice sites, they are also subjected to the force generated by the change of lattice configuration, just like holes in the valence bands of a semiconductor are subject to a force exerted by an electronic forces. The work done to the vacancies is expressed as,

$$\Delta W_{in} = \sum_{k=1}^{N_v}\sum_{i=1}^{N_L} \frac{\partial H_{\{s\}_{N_L}}(\{R_k{}^v\}_{N_v})}{\partial p^v{}_k}\left(\frac{\partial H'(\{s\}_{N_L})}{\partial s_i}\right). \tag{5-62}$$

On the other hand, the vacancies provide a driving force to lattice deformation. The work done by the vacancies to the lattice atoms is expressed as,

$$\Delta W_{out} = \sum_{k}^{N_v}\sum_{i}^{N_L} \frac{\partial H_{\{s\}_{N_L}}(\{R_k{}^v\}_{N_v})}{\partial R_k{}^v}\left(\frac{\partial H'(\{s\}_{N_L})}{\partial p^s{}_i}\right). \tag{5-63}$$

So the total modification to the energy of vacancies is,

$$\begin{aligned}\Delta W_v &= \Delta W_{in} - \Delta W_{out}\\ &= \sum_{k=1}^{N_v}\sum_{i=1}^{N_L} \frac{\partial H_{\{s\}_{N_L}}(\{R_k{}^v\}_{N_v})}{\partial p^v{}_k}\left(\frac{\partial H'(\{s\}_{N_L})}{\partial s_i}\right) - \sum_{k}^{N_v}\sum_{i}^{N_L} \frac{\partial H_{\{s\}_{N_L}}(\{R_k{}^v\}_{N_v})}{\partial R_k{}^v}\left(\frac{\partial H'(\{s\}_{N_L})}{\partial p^s{}_i}\right)\end{aligned} \tag{5-64}$$

Assuming that the coupling ΔW_v is small, the distribution function of vacancies is constructed as,

$$f^v = Q_v{}^{-1}\exp\left\{-\beta^v\left(H^v - \mu^v N_v + \sum_{k,i}\frac{\partial H_s(R_k{}^v)}{\partial p_k{}^v}\left(\frac{\partial H'(s)}{\partial s_i}\right) + \sum_{k,i}\frac{\partial H_s(R_k{}^v)}{\partial R_k{}^v}\left(\frac{\partial H'(s)}{\partial p^s{}_i}\right)\right)\right\} \tag{5-65}$$

The fluid-like local equilibrium distribution function of vacancies (5-30) is therefore modified as,

$$f_l^v = \left(Q_l^v\right)^{-1} \exp\left[-\int d\hat{x}\beta_v(\hat{x}) \left\{ (h_v'(\hat{x}) - \mu_v(\hat{x}) n_v(\hat{x}) + \frac{1}{m} g_v(\hat{x}) f^s(\hat{x}) + \frac{1}{m} f^v(\hat{x}) g^s(\hat{x}) \right\} \right] \quad (5\text{-}66)$$

where $f^s(\hat{x})$ and $f^v(\hat{x})$ are respectively the force density for the "lattice atoms" and vacancies defined as,

$$f^s(\hat{x}) = \sum_i \frac{\partial H'(\{s_i\})}{\partial s_i} \delta(\hat{x} - R_i)\,, \quad (5\text{-}67)$$

$$f^v(\hat{x}) = \sum_k \frac{\partial H_{\{s_i\}}(\{R^v{}_k\})}{\partial R^v{}_k} \delta(\hat{x} - R^v{}_k)\,; \quad (5\text{-}68)$$

the $g^s(\hat{x})$ is the momentum density of "lattice atoms" defined as,

$$g^s(\hat{x}) = \sum_i^{N_L} m\dot{s}_i \delta(\hat{x} - R_i)\,. \quad (5\text{-}69)$$

When the change in the lattice configuration is small, we treat the coupling of vacancies with the lattice deformation as a perturbation. The modified local equilibrium distribution function (5-66) is then approximated as,

$$f^v{}_l = \left(f^v{}_l\right)^0 \left[1 - (X - \langle X \rangle_l^0)\right] \quad (5\text{-}70)$$

where $\left(f^v{}_l\right)^0$ is the fluid-like local equilibrium distribution function of vacancies (5-30) (without coupling with lattice), $\langle\ \rangle_l^0$ indicates the average over $\left(f^v{}_l\right)^0$ and the X is defined by,

$$X = \beta_v(\hat{x}) \frac{1}{m} g_v(\hat{x}) f^s(\hat{x}) + \beta_v(\hat{x}) \frac{1}{m} f^q(\hat{x}) g^s(\hat{x})\,. \quad (5\text{-}71)$$

Thus we have,

$$f^v{}_l = \left(f^v{}_l\right)^0 \left[1 - \int d\hat{x}' \frac{\beta_v(\hat{x}')}{m} \left(g_v(\hat{x}') - \langle g_v(\hat{x}') \rangle_l^0\right) f^s(\hat{x}') - \frac{\beta_v(\hat{x}')}{m} \left(f^v(\hat{x}') - \langle f^v(\hat{x}') \rangle_l^0\right) g^s(\hat{x}')\right]$$

$$(5\text{-}72)$$

According to (5-39) and (5-42),

$$\langle g_v(\hat{x})\rangle_l^0 = m\upsilon_v(x)\,,\ \ \langle f^v(\hat{x})\rangle_l = \nabla p^v(x) \tag{5-73}$$

As a result, the explicit expression for the modified local equilibrium distribution function of vacancies in a deformed lattice is,

$$f^v{}_l = \left(f^v{}_l\right)^0\left[1-\beta_v(\hat{x})j_v(\hat{x})f^s(\hat{x})-\beta_v(\hat{x})\frac{1}{m}f^v(\hat{x})g^s(\hat{x})\right]. \tag{5-74}$$

Because vacancies move on a time scale faster than “lattice atoms”, they observe an average motion of “lattice atoms”. We therefore assume that $f^s(\hat{x})$ and $g^s(\hat{x})$ can be respectively approximated by their average values $f^s(\hat{x})$ and $g^s(\hat{x})$ calculated with the distribution function of “lattice atoms” $f(s)$. With this assumption, the modified local equilibrium distribution function of vacancies (5-74) is expressed as,

$$f^v{}_l = \left(f^v{}_l\right)^0\left[1-\int d\hat{x}'\beta_v(\hat{x}')j_v(\hat{x}')f^s(\hat{x}')-\beta_v(\hat{x}')\frac{1}{m}f^v(\hat{x}')g^s(\hat{x}')\right]. \tag{5-75}$$

Since the expressions of $f^s(\hat{x})$ and $g^s(\hat{x})$ depend on whether the lattice is in equilibrium or nonequilibrium state, we see from (5-75) that the nonequilibrium distribution function and therefore the transport of vacancies are also affected by the specific state of lattice.

5.3.2 Modified Euler’s equation

After incorporating the coupling among time scales into the distribution function, the average fluxes calculated in (5-34)-(5-37) will be modified. The general expression of fluxes is now,

$$
\begin{aligned}
&\left\langle j_v{}^m(\widehat{x})\right\rangle_l = \left\langle j_v{}^m(\widehat{x})\right\rangle_l^0 \\
&-\int dx'\beta_v(x')\left(\left\langle j_v{}^m(\widehat{x})\,j_v(\widehat{x}')\right\rangle_l^0 f^s(x') - \frac{1}{m}\left\langle j_v{}^m(\widehat{x})\left(f^v(\widehat{x}')-\nabla p^v\right)\right\rangle_l^0 g^s(x')\right)
\end{aligned}
\tag{5-76}
$$

For example, the diffusion flux of vacancies driven by the force field in a lattice is now expressed as,

$$
\left\langle j_v{}'\right\rangle_l = \frac{D_v(x)}{kT(x)} f^s(x), \tag{5-77}
$$

where the coefficient $D_v(x)$ is given by

$$
D_v(x) = \int d\widehat{x}'\left\langle j_v(\widehat{x})\,j_v(\widehat{x}')\right\rangle_l^0 d\widehat{x}'. \tag{5-78}
$$

According to (3-81), we have

$$
f^s(x) = -\nabla\cdot\sigma(x)
$$

where $\sigma(x)$ is the stress field of lattice. The expression (5-77) is rewritten as,

$$
\left\langle \hat{j}_v{}'\right\rangle_l = -\frac{D_v(x)}{kT(x)}\nabla\cdot\sigma(x). \tag{5-79}
$$

As a result, the Euler's equations of vacancies (5-44)-(5-46) are modified with the new expression of fluxes (5-76). The equation for the change of density of vacancies (5-44) is therefore modified as

$$
\frac{dn_v{}'}{dt} = -n_v{}'\nabla\cdot\upsilon^v + \frac{D_v(x)}{kT(x)}\nabla^2\sigma(x), \tag{5-80}
$$

which shows that there are two mechanisms that determine the change of the local densities of vacancies: the transport of vacancies as shown by the term $\nabla\cdot\upsilon^v$, and the deformation of lattice as is shown by $\nabla^2\sigma(x)$.

To calculate the extra force density on the vacancies due to the coupling with lattice, we write,

$$f^{v}(\widehat{x}) = -\nabla \cdot \tau_{v}{}^{f}(\widehat{x}) \tag{5-81}$$

which is substituted into (5-76) to give,

$$\begin{aligned} &\left\langle j_v{}^m(\widehat{x})\right\rangle_l = \left\langle j_v{}^m(\widehat{x})\right\rangle_l^0 \\ &-\int dx'\beta_v(x')\left(\left\langle j_v{}^m(\widehat{x})j_v(\widehat{x}')\right\rangle_l^0 f^s(x') - \left\langle j_v{}^m(\widehat{x})\tilde{\tau}^v(\widehat{x}')\right\rangle_l^0 \dot{E}^s(x')\right) \end{aligned} \tag{5-82}$$

where the $\tilde{\tau}^v(\widehat{x}')$ is the off-diagonal part of the stress density of vacancies and

$$\dot{E}^s(x') = \nabla j^s(x'), \tag{5-83}$$

where $\dot{E}^s$ is the rate of strain of the lattice. Assuming that the lattice atoms are in local equilibrium state and (4-83) becomes,

$$\dot{\bar{E}}^s(x') = \nabla\left\langle j^s(\widehat{x}')\right\rangle_l, \tag{5-84}$$

where $\dot{\bar{E}}^s(x')$ is the average strain rate of lattice. Substituting (5-84) and we obtain the stress of vacancies that includes the coupling with a deforming lattice,

$$\left\langle \tau_v(\widehat{x})\right\rangle = p\vec{I} + \frac{1}{kT(x)}\int d\widehat{x}'\left\langle \tau_v(\widehat{x})\tau_v(\widehat{x}')\right\rangle_l^0 \dot{\bar{E}}^s(x'). \tag{5-85}$$

The change of velocity of vacancies in (5-46) is therefore modified as,

$$\frac{d\upsilon^v}{dt} = -\nabla p^v - \nabla \cdot \left(\eta^v \dot{\bar{E}}^s\right). \tag{5-86-1}$$

where the coefficient η^v is expressed as,

$$\eta^v = \frac{1}{kT(x)}\int dx'\left\langle \tau_v(\widehat{x})\tau_v(\widehat{x}')\right\rangle_l^0 \tag{5-86-2}$$

Equation (5-86-1) demonstrates that even though the “lattice atoms” are in local equilibrium, there is still exists viscosity within the vacancies due to the coupling between the motion of vacancies and the motion of “lattice atoms”.

5.3.3 Modified non-equilibrium distribution function and transport equations

The modification to the nonequilibrium distribution function of vacancies (5-47) is now approximated as,

$$f^{v} = \left(f^{v}\right)^{0}\left[1 - \int d\hat{x}\left(\beta_{v}(\hat{x})\, j_{v}(\hat{x})\, f^{s}(\hat{x}) - \beta_{v}(\hat{x})\frac{1}{m} f^{q}(\hat{x})\, g^{s}(\hat{x})\right)\right] \tag{5-87}$$

where $\left(f^{v}\right)^{0}$ is the non-equilibrium distribution function of vacancies expressed by (5-51),

$$\left(f^{v}\right)^{0} = \left(f^{v}\right)_{l}^{0}\left[1 - (B^{v} - \left\langle B^{v}\right\rangle_{l})\right], \tag{5-88}$$

where B^{v} is expressed in (5-52). In the first approximation, we ignore the coupling between the thermodynamic forces in (5-88) with the lattice deformation, then (5-87) is approximated as,

$$\left(f^{v}\right)^{0} = \left(f^{v}\right)_{l}^{0} + \left(f^{v}\right)_{l}^{0}\left(B^{v} - \left\langle B^{v}\right\rangle_{l}\right) - \left(f^{v}\right)_{l}^{0}\left(\int d\hat{x}\left(\beta_{v}(\hat{x})\, j_{v}(\hat{x})\, f^{s}(\hat{x}) - \beta_{v}(\hat{x})\, f^{v}(\hat{x})\, j^{s}(\hat{x})\right)\right) \tag{5-89}$$

With the modified nonequilibrium distribution function, the complete expression of the flux of vacancies becomes,

$$\left\langle j_{v}(\hat{x})\right\rangle = \lambda^{v}{}_{2}\nabla T + L^{v}{}_{2}\nabla\frac{\mu}{T} + \frac{D_{v}}{kT}\nabla\cdot\sigma \tag{5-90}$$

$$\left\langle \tau_{v}(\hat{x})\right\rangle = \eta_{v}\left\{\frac{\partial \upsilon^{v}{}_{\alpha}}{\partial x_{\beta}} + \frac{\partial \upsilon^{v}{}_{\beta}}{\partial x_{\alpha}} - \frac{2}{3}\delta_{\alpha\beta}\nabla\cdot\upsilon^{v}\right\} + \xi_{v}\nabla\cdot\upsilon^{v}\delta_{\alpha\beta} + \eta_{v}\nabla\upsilon^{s} \tag{5-91}$$

The Navier-Stoke equation of vacancies (5-59) is modified as,

$$\frac{\partial \rho_{v}\upsilon^{v}{}_{\alpha}}{\partial t} + \nabla_{\beta}\left(\rho_{v}\upsilon^{v}{}_{\alpha}\upsilon^{v}{}_{\beta} + p^{v}\delta_{\alpha\beta}\right) = \nabla_{\beta}\eta_{v}\left(\frac{\partial \upsilon_{\alpha}}{\partial x_{\beta}} + \frac{\partial \upsilon_{\beta}}{\partial x_{\alpha}} - \frac{2}{3}\delta_{\alpha\beta}\nabla\cdot\upsilon\right) + \nabla_{\alpha}\xi_{v}\left(\nabla\cdot\upsilon\right) \tag{5-92}$$

where $\upsilon = \dfrac{n_v \upsilon^v + n_L \upsilon^s}{n_v + n_L}$.

If the "lattice atoms" are also in nonequilibrium state, we shall replace $f^s(\hat{x})$ and $j^s(\hat{x})$ with their nonequilibrium expression. We see therefore that the nonequilibrium dynamics of lattice also affects the transport of vacancies through the expression of $\left\langle g^s(\hat{x}) \right\rangle$ and $\left\langle \sigma(\hat{x}) \right\rangle$. For example, in nonequilibrium state,

$$j^s = \lambda^s{}_2 \nabla T + L^s{}_2 \nabla \frac{\mu_L}{T} + \frac{D_s}{kT} \nabla \cdot \sigma, \tag{5-93-1}$$

where the transport coefficients of "lattice atoms" are calculated by,

$$\lambda^s{}_2 = -\frac{1}{T^2} \int \int_{-\infty}^{0} e^{\varepsilon t'} (j_s(\hat{x}), J_s{}^0(\hat{x}', t')) d\hat{x}' dt', \tag{5-93-2}$$

$$L^s{}_2 = -\frac{1}{3T^2} \int d\hat{x}' \left\langle j_s(\hat{x}) j_s(\hat{x}') \right\rangle_l^0 d\hat{x}', \tag{5-93-3}$$

$$D_s(x) = \int d\hat{x}' \left\langle j_s(\hat{x}) j_s(\hat{x}') \right\rangle_l^0 d\hat{x}'. \tag{5-93-4}$$

Insert (5-93) into (5-91) and we have,

$$\begin{aligned} \left\langle \tau_v(\hat{x}) \right\rangle = \eta_v \left\{ \frac{\partial \upsilon^v{}_\alpha}{\partial x_\beta} + \frac{\partial \upsilon^v{}_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \upsilon^v \right\} + \xi_v \nabla \cdot \upsilon^v \delta_{\alpha\beta} \\ + \eta_v \nabla \upsilon^s + \eta_v \lambda^s{}_2 \nabla^2 T + \eta_v L^s{}_2 \nabla^2 \frac{\mu_L}{T} + \frac{\eta_v D_s}{kT} \nabla (\nabla \cdot \sigma) \end{aligned} \tag{5-94-1}$$

where the bulk and shear viscous coefficients are calculated as,

$$\eta^v = \frac{1}{kT(x)} \int d\hat{x}' \left\langle \tau_v(\hat{x}) \tau_v(\hat{x}') \right\rangle_l^0, \tag{5-94-2}$$

$$\xi_v = \frac{1}{3kT(x)} \sum_\alpha \int d\hat{x}' \left\langle \tau_v{}^{\alpha\alpha}(\hat{x}) \tau_v{}^{\alpha\alpha}(\hat{x}') \right\rangle_l^0 \tag{5-94-3}$$

Note that all the transport coefficients of vacancies such as the viscous coefficients in (5-94) are dependent on the lattice configuration. We see therefore that the inhomogeneity in the temperature on the scale of lattice will also lead to the generation of shear stress in the system of vacancies. As a result, we demonstrate that not only the inhomogeneity on the scale of vacancies can induce the transport of vacancies, the long-range stress field as well as any inhomogeneity in the lattice can also drive the transport of vacancies. Generally, entities on fast time scales respond quickly to thermodynamic changes such as gradient of temperature at slow time scales. Following similar procedures, we can formulate the thermal conduction by the transport of phonons which respond to the gradient of temperature much faster than "lattice atoms". Generally, the procedure introduced for the nonequilibrium formulation of vacancies applies to every time scale in a crystal. As a result, we obtain a hierarchy of dynamic equations for each scale, from the quantum world to the macroscopic, which exists in a complex crystal. Because of the use of the modified constrained nonequilibrium distribution function, the derived transport equations are naturally coupled with the dynamics on other scales.

5.3.4 Herring Creep

When a uniaxial force is applied to a crystal, it is discovered that the strain in the crystal is gradually changing with time at a rate that is linearly proportional to the applied stress. The phenomenon is known as Herring Creep. The traditional theoretical explanation for Herring Creep is that the external stress induces mass transport of vacancies within the crystal which results in the change of strain. In this section, we calculate the flux of vacancies induced by external stress and the resulting strain rate with the help of constrained distribution function. Herring creep is a good example to demonstrate the coupling between the long-range stress/strain relationship and the dynamics at fast time scales.

In equation (5-90), we have shown that the addition of external stress will induce a flux of vacancies expressed by,

$$j^v(x) = \frac{D_v^s}{kT}\nabla \cdot \sigma_{ext}(x)\,, \tag{5-95}$$

where D_v^s is a brief notation for the diffusion coefficient of vacancies in a fixed lattice configuration. The total Helmohotz energy of vacancies therefore changes by an amount of

$$\Delta \frac{1}{\beta}\ell n Q^v(s) = j^v(x)\cdot\left(\nabla\cdot\sigma_{ext}(x)\right). \tag{5-96}$$

The Liouville equation of "lattice atoms" is now,

$$\frac{\partial f(\{s_i\}_N)}{\partial t} + \left\{ f(\{s_i\}_N), H'(\{s_i\}_N) + \frac{1}{\beta}\ell n Q_v(\{s_i\}_N) + \int j^v(x)\cdot\left(\nabla\cdot\sigma_{ext}(x)\right)dx \right\} = 0\,, \tag{5-97}$$

which leads to an additional driving force on the "lattice atoms" expressed as,

$$\int \partial_{s_i} j^v(x)\cdot\nabla\cdot\sigma_{ext}(x)dx \simeq \int \frac{D_v^s}{kT} C(\overline{s})\nabla\cdot\sigma_{ext}(x)dx\,, \tag{5-98}$$

where $C(\overline{s})$ is the elastic constant of lattice calculated from (4-162). This extra driving force on the lattice atoms leads to a flux of "lattice atoms" calculated by,

$$\left\langle j(s)\right\rangle \simeq \frac{D_s D_v^s}{kT} C(\overline{s})\nabla\cdot\sigma_{ext}(x)\,. \tag{5-99}$$

where

$$D_s(x) = \int d\widehat{x}'\left\langle j_s(\widehat{x}) j_s(\widehat{x}')\right\rangle_l^0 d\widehat{x}'\,. \tag{5-100}$$

For simplicity and demonstration, we suppose that there is only external uniaxial force along the Z direction, the introduced external stress field is expressed as $F_z(\hat{x})$. Then according to (5-90) the flux of vacancies induced by the external stress is

$$\left\langle j^v(\hat{x})\right\rangle_x = \frac{D_v^s}{kT}\frac{\partial\sigma_{zx}}{\partial x}, \left\langle j^v(\hat{x})\right\rangle_y = \frac{D_v^s}{kT}\frac{\partial\sigma_{zy}}{\partial y}, \left\langle j^v(\hat{x})\right\rangle_z = \frac{D_v^s}{kT}\frac{\partial\sigma_{zz}}{\partial z}. \tag{5-101}$$

According to (5-96) and (5-98), the change in the Helmholtz energy of vacancies due to the flux of vacancies is therefore,

$$\Delta\frac{1}{\beta}\ell n Q^v(s) = \sum_{\lambda=x,y,z}\left\langle j^v(\hat{x})\right\rangle_\lambda \frac{\partial\sigma_{z\lambda}}{\partial\lambda}, \tag{5-102}$$

which leads to the change of driving force on "lattice atoms" expressed by,

$$\Delta f(s_i) = \partial_{s_i}\sum_{\lambda=x,y,z}\left\langle j_s{}^v(\hat{x})\right\rangle_\lambda \frac{\partial\sigma_{z\lambda}}{\partial\lambda}. \tag{5-103}$$

In the first approximation, we consider the effect of the average lattice-strain on the motion of vacancies. The displacements of "lattice atoms" s_i are therefore approximated by their average displacement of $\bar{s}(\hat{x})$ and the components of force (5-103) becomes,

$$\Delta f_x(\bar{s}) = \partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_x \frac{\partial\sigma_{zx}}{\partial x} + \partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_y \frac{\partial\sigma_{zy}}{\partial y} + \partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_z \frac{\partial\sigma_{zz}}{\partial z},$$

$$\Delta f_y(\bar{s}) = \partial_{\bar{s}_y}\left\langle j_s{}^v(\hat{x})\right\rangle_x \frac{\partial\sigma_{zx}}{\partial x} + \partial_{\bar{s}_y}\left\langle j_s{}^v(\hat{x})\right\rangle_y \frac{\partial\sigma_{zy}}{\partial y} + \partial_{\bar{s}_y}\left\langle j_s{}^v(\hat{x})\right\rangle_z \frac{\partial\sigma_{zz}}{\partial z},$$

$$\Delta f_z(\bar{s}) = \partial_{\bar{s}_z}\left\langle j_s{}^v(\hat{x})\right\rangle_x \frac{\partial\sigma_{zx}}{\partial x} + \partial_{\bar{s}_z}\left\langle j_s{}^v(\hat{x})\right\rangle_y \frac{\partial\sigma_{zy}}{\partial y} + \partial_{\bar{s}_z}\left\langle j_s{}^v(\hat{x})\right\rangle_z \frac{\partial\sigma_{zz}}{\partial z}. \tag{5-104}$$

This extra driving force induces a flux of "lattice atoms" calculated as,

$$\left\langle j(\bar{s})\right\rangle_x \simeq D_x(\bar{s})\left(\partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_x \frac{\partial\sigma_{zx}}{\partial x} + \partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_y \frac{\partial\sigma_{zy}}{\partial y} + \partial_{\bar{s}_x}\left\langle j_s{}^v(\hat{x})\right\rangle_z \frac{\partial\sigma_{zz}}{\partial z}\right),$$

$$\left\langle j(\overline{s})\right\rangle_y \simeq D_y(\overline{s})\left(\partial_{\overline{s}_y}\left\langle j_s{}^v(\widehat{x})\right\rangle_x\frac{\partial\sigma_{zx}}{\partial x}+\partial_{\overline{s}_y}\left\langle j_s{}^v(\widehat{x})\right\rangle_y\frac{\partial\sigma_{zy}}{\partial y}+\partial_{\overline{s}_y}\left\langle j_s{}^v(\widehat{x})\right\rangle_z\frac{\partial\sigma_{zz}}{\partial z}\right),$$

$$\left\langle j(\overline{s})\right\rangle_z \simeq D_z(\overline{s})\left(\partial_{\overline{s}_z}\left\langle j_s{}^v(\widehat{x})\right\rangle_x\frac{\partial\sigma_{zx}}{\partial x}+\partial_{\overline{s}_z}\left\langle j_s{}^v(\widehat{x})\right\rangle_y\frac{\partial\sigma_{zy}}{\partial y}+\partial_{\overline{s}_z}\left\langle j_s{}^v(\widehat{x})\right\rangle_z\frac{\partial\sigma_{zz}}{\partial z}\right) \tag{5-105}$$

where $D_x(\overline{s})$, $D_y(\overline{s})$ and $D_z(\overline{s})$ are components of the diffusion constant (5-100).

If we further assume that the external uni-axial stress is only non-uniform along Z direction, (5-105) can be simplified and we find the flux of lattice atoms on the X direction expressed as,

$$\left\langle j(\overline{s})\right\rangle_x \simeq D_x(\overline{s})\left(\partial_{\overline{s}_x}\left\langle j_s{}^v(\widehat{x})\right\rangle_z\right)\frac{\partial\sigma_{zz}}{\partial z}, \tag{5-106}$$

which suggests that the flux of vacancies on the Z direction will also lead to the flux of "lattice atoms" on the X direction. The flux of "lattice atoms" in the Z direction is,

$$\left\langle j(\overline{s})\right\rangle_z \simeq D_z(\overline{s})\left(\partial_{\overline{s}_z}\left\langle j_s{}^v(\widehat{x})\right\rangle_z\right)\frac{\partial\sigma_{zz}}{\partial z}. \tag{5-107}$$

Together with (5-95), we obtain the rate of strain respectively along the Z direction and the X direction.

$$\left\langle \dot{E}\right\rangle_z = \frac{D_z}{kT}\frac{\partial^2\sigma_{zz}}{\partial z^2}$$

$$\left\langle \dot{E}\right\rangle_x \simeq \frac{D_x}{kT}\frac{\partial^2\sigma_{zz}}{\partial z^2}, \tag{5-108}$$

where we introduce general diffusion coefficients of an elastic crystal defined by,

$$D_z = D_z(\overline{s})D^v{}_z C_{zz},$$

$$D_x = D_x(\overline{s})D^v{}_x C_{zx}. \tag{5-109}$$

Note that the general diffusion coefficients of a crystal include the elastic deformation of lattice through the elastic coefficients. Equation (5-108) shows that the inhomogenous stress along one direction could also induce the flux of lattice along other directions.

In linear approximation, (5-108) can be simplified as

$$\left\langle \dot{E} \right\rangle_z \approx \frac{D_z \sigma_{zz}}{kTL^2},$$

where L is the size of the crystal. This equation recovers the well-known phenomenological equation that shows the linear relationship between the strain rate of Herring creep and the applied stress [44]. With expressions (5-109), one can now calculate the diffusion coefficients from atomistic mechanics. Note that the result (5-108) is obtained on the assumption of first-order coupling between the lattice and the motion of vacancies. If we further consider the coupling between the rate of strain and the motion of vacancies, then according to (5-85) there is an extra force density of $\nabla \cdot \left(\eta^v \dot{\bar{E}}^s(x) \right)$ exerted on the vacancies. This extra force will continue to couple with the motion of vacancies which will in turn change the driving force on the lattice. Thus, in higher order approximation, such terms as the $\nabla \cdot \left(\eta^v \dot{\bar{E}}^s(x) \right)$ might also appear. In other words, the rate of strain during creep could be history dependent.

Besides Herring creep, the method developed in this chapter shows potential to be applied to a wide range of non-equilibrium phenomena in more complicated conditions.

5.4 Summary

Due to the existence of muti-intrinsic time scales in a complex crystal, the non-equilibrium dynamics of a complex crystal is much more complicated than a fluid. Generally, there are two mechanisms that contribute to the non-equilibrium dynamics in a complex crystal: the first mechanism is similar to a fluid, i.e. transport driven by thermodynamic forces such as gradient of temperature field; the second mechanism, which is characteristic of a solid, is the coupling among intrinsic time scales existing in a crystal. A successive series of constrained nonequilibrium distribution function is then constructed which is based on the fluid-form of nonequilibrium distribution function but includes the coupling among intrinsic time scales. Ultimately, we can obtain a hierarchy of dynamic equations for each scale that exists in a complex crystal, from the quantum world to the macroscopic. These equations, such as the transport of defects and lattice deformation, are naturally coupled with dynamics on other scales in a way that can be calculated from statistical mechanics. The method is therefore potentially powerful in explaining and describing more complicated non-equilibrium phenomena that happen in a complex solid.

CHAPTER VI

INCLUSION OF DISLOCATOINS

In Chapter 3 we introduced two deformation fields in a lattice of a perfect crystal (c.f. eq.(3-52), (3-53)): the systematic deformation field $\overline{s}(x)$ and the internal deformation field $s'(x)$. The internal deformation field is averaged out in a perfect crystal (c.f. eq.(3-60), (3-61)), analogous to an ideal fluid where there are no internal fluxes. Thus up to now we have only dealt with the systematic deformation of a crystal. In non-equilibrium conditions, however, the internal deformation field may not be averaged out, which leads to the existence of such defects as dislocations. The existence of internal deformation fields introduces an extra time scale into a crystal. Based on our previous formulations, we envision that this "internal deformation field" can act independently and carry dislocations when suitable constraints are imposed. Though some investigations along these lines have been pursued, they have not been completed and are not included in this thesis.

As a conclusion, we demonstrate in this thesis the possibility to construct a comprehensive theory based on the principles of statistical mechanics that begins from atomistic mechanics, derives dynamics of defects and ultimately describes the complicated macroscopic behavior such as plastic deformation of solids. The basic idea underlying the formulation is to associate an atom in a crystal with six degrees of freedom with constraints imposed by the BO-like approximation. The statistical mechanics of a crystal is therefore characterized by a constrained distribution function which captures the existence of lattice. Various types of defects naturally appear in the theory through different modifications of constraints. We then introduced a hierarchical development across time/length scales by identifying fast and slow variables and applying BO-like approximations. As a result, we constructed for a complex crystal a series of constrained distribution functions that enables us to derive coupled dynamical equations for every intrinsic time scale that exists in a crystal.

The current formulation of a crystal is still much simplified and incomprehensive, but it opened a door for the fundamental understanding of the physics underlying the complicated behavior of solids. And we know that a comprehensive theory for solids based on the principles of statistical mechanics is on the way.

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