

Minoru Fujimoto

# Thermodynamics of Crystalline States

*2nd Edition*

 Springer

# Thermodynamics of Crystalline States



Minoru Fujimoto

# Thermodynamics of Crystalline States

Second Edition

 Springer

Minoru Fujimoto  
Department of Physics  
University of Guelph  
Guelph, ON N1G 2W1  
Canada

ISBN 978-1-4614-5084-9      ISBN 978-1-4614-5085-6 (eBook)  
DOI 10.1007/978-1-4614-5085-6  
Springer New York Heidelberg Dordrecht London

Library of Congress Control Number: 2012954672

© Springer Science+Business Media New York 2013

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media ([www.springer.com](http://www.springer.com))

# Preface

Originated from steam engines, in thermodynamics the energy exchange is formulated traditionally for homogeneous states of materials. Applying to condensed matters however, laws of thermodynamics have to be used with respect to the structural detail. Following Kirkwood's *Chemical Thermodynamics*, this book is written for lattice dynamics in crystalline states under the laws of thermodynamics. It is noted that lattice symmetry remains implicit in thermodynamic functions of crystalline states, if assumed as homogeneous. In contrast, deformed crystals with disrupted symmetry are not stable and inhomogeneous, exhibiting *mesoscopic* properties, for which the lattice dynamics should be redefined under thermodynamic principles. I have selected the topics of structural changes, magnetic crystals, and superconducting transitions in this book to discuss these basic thermodynamic processes in crystalline states.

Born and Huang have laid ground for thermodynamics of crystalline states in their book *Dynamical Theory of Crystal Lattices*. However, they considered that order–disorder phenomena was independent from the lattice dynamics, and so excluded it from their book. On the other hand, today new evidence indicates that the problem should be treated otherwise; in fact, the lattice plays a vital role in ordering processes. Accordingly, I was motivated to write about the physics of crystal lattice in the light of Born-Huang's principles, which constitutes my primary objective in this book.

In modern experiments, mesoscopic objects in crystals can be investigated within the timescale of observation, yielding results that appear somewhat unusual, if compared with macroscopic experiments. It is important that thermodynamic relations in mesoscopic states should be described with respect to the timescale of observation. Also significant is that mesoscopic quantities in crystals are driven by internal interactions in nonlinear character. I have therefore discussed thermodynamic quantities with regard to the timescale of observation, including elementary accounts of nonlinear physics to deal with long-range correlations. For the convenience of readers who are not particularly familiar with nonlinear dynamics, Appendix is attached for some useful formula of elliptic functions.

I have rewritten this second edition for advanced students in physics and material science, assuming basic knowledge of traditional thermodynamics and quantum theories. This book is designed for serving as a useful textbook for classroom and seminar discussions. I hope that it will stimulate advanced studies of condensed matter.

I should mention with my sincere appreciation that I have benefited for my writing from numerous discussions with and comments from my colleagues and students. Finally, I thank my wife Haruko for her continuous support and encouragements.

Mississauga, Ontario

Minoru Fujimoto

# Contents

<b>1</b>	<b>Introduction</b> . . . . .	1
1.1	Crystalline Phases . . . . .	1
1.2	Structural Changes . . . . .	4
1.3	New Concepts . . . . .	7
1.3.1	Modulated Phases and Renormalized Coordinates . . . . .	7
1.3.2	Thermodynamic Changes and Nonlinear Dynamics . . . . .	8
1.3.3	Fields within Thermodynamic Boundaries . . . . .	8
1.3.4	Adiabatic Potentials . . . . .	8
1.4	Sampling Modulated States . . . . .	9
	Exercise 1 . . . . .	9
	References . . . . .	10
<b>2</b>	<b>Phonons</b> . . . . .	11
2.1	Normal Modes in a Simple Crystal . . . . .	11
2.2	Quantized Normal Modes . . . . .	14
2.3	Phonon Field and Momentum . . . . .	16
2.4	Thermal Equilibrium . . . . .	18
2.5	Specific Heat of a Monatomic Crystal . . . . .	20
2.6	Approximate Models . . . . .	22
2.6.1	Einstein's Model . . . . .	22
2.6.2	Debye's Model . . . . .	23
2.7	Phonon Statistics Part 1 . . . . .	25
2.8	Compressibility of a Crystal . . . . .	28
	Exercise 2 . . . . .	30
	References . . . . .	31
<b>3</b>	<b>Order Variables and the Adiabatic Potential</b> . . . . .	33
3.1	A One-dimensional Ionic Chain . . . . .	33
3.2	Displacive Variables . . . . .	35
3.3	Born-Oppenheimer's Approximation . . . . .	39



3.4	Equilibrium Crystals and the Bloch Theorem . . . . .	45
3.4.1	Reciprocal Lattice and Renormalized Coordinates . . . .	45
3.4.2	The Bloch Theorem . . . . .	47
3.4.3	Lattice Symmetry and the Brillouin Zone . . . . .	49
3.5	Phonon Scatterings . . . . .	51
3.5.1	Phonon Scatterings in Crystals . . . . .	51
3.5.2	The Born-Huang Relaxation and Soft Modes . . . . .	52
	Exercise 3 . . . . .	53
	References . . . . .	54
<b>4</b>	<b>Mean-Field Theories of Binary Ordering</b> . . . . .	<b>55</b>
4.1	Probabilities in Binary Alloys . . . . .	55
4.2	The Bragg-Williams Theory . . . . .	57
4.3	Becker's Interpretation . . . . .	60
4.4	Ferromagnetic Order . . . . .	62
4.5	Ferromagnetic Transition in Applied Magnetic Field . . . . .	64
	Exercise 4 . . . . .	66
	References . . . . .	66
<b>5</b>	<b>Pseudospin Clusters</b> . . . . .	<b>67</b>
5.1	Pseudospins for Binary Displacements . . . . .	67
5.2	A Tunneling Model . . . . .	70
5.3	Pseudospin Correlations . . . . .	71
5.4	Pseudospin Clusters in Crystals . . . . .	73
5.4.1	Classical Pseudospins in Crystals . . . . .	73
5.4.2	Clusters of Pseudospins . . . . .	74
5.5	Examples of Pseudospin Clusters . . . . .	78
5.5.1	Cubic to Tetragonal Transition in $\text{SrTiO}_3$ . . . . .	78
5.5.2	Monoclinic Crystals of Tris-Sarcosine Calcium Chloride (TSCC) . . . . .	80
	Exercise 5 . . . . .	82
	References . . . . .	82
<b>6</b>	<b>Critical Fluctuations</b> . . . . .	<b>83</b>
6.1	The Landau Theory of Binary Transitions . . . . .	83
6.2	Internal Pinning of Adiabatic Fluctuations . . . . .	87
6.3	Critical Anomalies . . . . .	88
6.4	Observing Anomalies . . . . .	90
6.5	Extrinsic Pinning . . . . .	92
6.5.1	Pinning by Point Defects . . . . .	93
6.5.2	Pinning by an Electric Field . . . . .	93
6.5.3	Surface Pinning . . . . .	94
	Exercise 6 . . . . .	94
	References . . . . .	95

<b>7 Pseudospin Correlations</b> . . . . .	97
7.1 Propagation of a Collective Pseudospin Mode . . . . .	97
7.2 Transverse Components and the Cnoidal Potential . . . . .	101
7.3 The Lifshitz Condition for Incommensurability . . . . .	103
7.4 Pseudopotentials . . . . .	105
Exercise 7 . . . . .	108
References . . . . .	109
<b>8 Soliton Theory of Long-Range Order</b> . . . . .	111
8.1 A Longitudinal Dispersive Mode of Collective Pseudospins . . . . .	111
8.2 The Korteweg–deVries Equation . . . . .	115
8.3 Solutions of the Korteweg–deVries Equation . . . . .	117
8.4 Cnoidal Theorem and the Eckart Potential . . . . .	120
8.5 Condensate Pinning by the Eckart Potentials . . . . .	122
8.6 Born–Huang’s Transitions . . . . .	126
8.7 Topological Mapping of Mesoscopic Fields . . . . .	129
Exercise 8 . . . . .	132
References . . . . .	135
<b>9 Soft Modes</b> . . . . .	137
9.1 The Lyddane–Sachs–Teller Relation . . . . .	137
9.2 Soft Lattice Modes of Condensates . . . . .	141
9.2.1 The Lattice Response to Collective Pseudospins . . . . .	141
9.2.2 Temperature Dependence of Soft-Mode Frequencies . . . . .	144
9.2.3 Cochran’s Model . . . . .	148
9.3 Symmetry Change at $T_c$ . . . . .	151
Exercise 9 . . . . .	153
References . . . . .	154
<b>10 Experimental Studies on Critical Fluctuations</b> . . . . .	155
10.1 Diffuse X-Ray Diffraction . . . . .	155
10.2 Neutron Inelastic Scatterings . . . . .	160
10.3 Light Scattering Experiments . . . . .	164
10.3.1 Brillouin Scatterings . . . . .	165
10.3.2 Raman Scatterings . . . . .	169
10.4 Magnetic Resonance . . . . .	171
10.4.1 Principles of Nuclear Magnetic Resonance and Relaxation . . . . .	173
10.4.2 Paramagnetic Resonance of Impurity Probes . . . . .	175
10.4.3 The Spin Hamiltonian . . . . .	176
10.4.4 Hyperfine Interactions . . . . .	180
10.5 Magnetic Resonance in Modulated Crystals . . . . .	180
10.6 Examples of Transition Anomalies . . . . .	183
References . . . . .	187

<b>11</b>	<b>Magnetic Crystals</b> . . . . .	189
11.1	Microscopic Magnetic Moments in Crystals . . . . .	189
11.2	Paramagnetism . . . . .	193
11.3	Spin–Spin Correlations . . . . .	194
11.4	Spin Clusters and Magnetic Symmetry . . . . .	198
11.5	Magnetic Weiss Field . . . . .	200
11.6	Spin Waves . . . . .	203
11.7	Magnetic Anisotropy . . . . .	204
11.8	Antiferromagnetic and Ferrimagnetic States . . . . .	208
11.9	Fluctuations in Ferromagnetic and Antiferromagnetic States . . . . .	210
11.9.1	Ferromagnetic Resonance . . . . .	211
11.9.2	Antiferromagnetic Resonance . . . . .	212
	Exercise 11 . . . . .	214
	References . . . . .	214
<b>12</b>	<b>Phonon and Electron Statistics in Metals</b> . . . . .	215
12.1	Phonon Statistics Part 2 . . . . .	215
12.2	Conduction Electrons in Metals . . . . .	218
12.2.1	The Pauli Principle . . . . .	218
12.2.2	The Coulomb Interaction . . . . .	220
12.2.3	The Bloch Theorem in Equilibrium Crystals . . . . .	221
12.3	Many-Electron Systems . . . . .	222
12.4	Fermi–Dirac Statistics for Conduction Electrons . . . . .	226
	Exercise 12 . . . . .	226
	References . . . . .	227
<b>13</b>	<b>Superconducting Metals</b> . . . . .	229
13.1	Superconducting States . . . . .	229
13.1.1	Near-Zero Electrical Resistance . . . . .	229
13.1.2	The Meissner Effect . . . . .	231
13.1.3	Thermodynamic Equilibrium Between Normal and Superconducting Phases . . . . .	233
13.2	Long-Range Order in Superconducting States . . . . .	235
13.3	Electromagnetic Properties of Superconductors . . . . .	237
13.4	The Ginzburg–Landau Equation and the Coherence Length . . . . .	244
	Exercise 13 . . . . .	247
	References . . . . .	248
<b>14</b>	<b>Theories of Superconducting Transitions</b> . . . . .	249
14.1	The Fröhlich’s Condensate . . . . .	249
14.2	The Cooper Pair . . . . .	252
14.3	Critical Anomalies and the Superconducting Ground State . . . . .	255
14.3.1	Critical Anomalies and a Gap in a Superconducting Energy Spectrum . . . . .	255

14.3.2	Order Variables in Superconducting States . . . . .	257
14.3.3	BCS Ground States . . . . .	262
14.3.4	Superconducting States at Finite Temperatures . . . . .	266
	Exercise 14 . . . . .	267
	References . . . . .	268
	<b>Appendix</b> . . . . .	269
	<b>Index</b> . . . . .	271

# Chapter 1

## Introduction

The role played by the lattice for symmetry changes in a crystal is a basic subject for discussion in this book. On the other hand, as related to *lattice excitations*, the concept of *order variables* needs to be established in thermodynamics of crystalline states. Normally inactive at elevated temperatures, order variables at lattice sites should be responsive to a symmetry change at a critical temperature. Exhibiting a *singular* behavior, an *adiabatic potential* should also emerge with order variables in finite magnitude with lowering temperature. Well documented experimentally, we should analyze their properties under thermodynamic principles.

In reviewing thermodynamic principles, the present thermodynamics of crystalline states is overviewed in this chapter, emphasizing dynamic roles played by the lattice structure.

### 1.1 Crystalline Phases

Originated from early studies on steam engines, thermodynamics today is a well-established discipline of physics for thermal properties of matter. Specified by a uniform density, a thermodynamic state of a crystal can be described by state functions of temperature and pressure of the surroundings. In contrast, characterized by symmetry of the lattice structure, properties of a *single crystal* are attributed to masses and other physical properties of constituents at lattice points, while symmetry per se cannot be responsible for the physical properties. We realize that structural changes cannot be described by uniform state functions, unless these functions are defined as related with the structural detail. The structural transition is generally *discontinuous* at a critical temperature  $T_c$ , below which even a chemically pure crystal becomes *heterogeneous*, composed of substructures in smaller volume, for example, *domains* in thermal equilibrium. Nevertheless, an external force or field can transform domains from one type to another while

maintaining structural stability. In addition, there are inhomogeneous crystals among various types, which are signified by a *sinusoidal* density, representing *modulated* structure. Following Kirkwood [1] in *Chemical Thermodynamics* we can consider state functions of continuous internal variables in crystalline states in equilibrium with the surroundings.

In *Dynamical Theory of Crystal Lattices*, Born and Huang [2] proposed the principle for lattice stability, laying the foundation of thermodynamics of crystalline states. However, their principle was not quite verified with experimental results, which were not fully analyzed at that time. Today, in spite of many supporting results, their theory is still not considered as sufficiently substantiated.

A crystalline state is very different from a gaseous state of a large number of *free* independent particles. A crystal structure packed with identical constituents is characterized by distinct symmetry; in contrast, fast molecular motion prevails in gaseous states. The *internal energy* of a gas is primarily kinetic energies of constituent particles in free motion, whereas for a crystal, it is intermolecular potential energies in the packed structure. The structural transformation in crystals is a dynamic process, whereas a gas is normally in a single phase, except in condensation process. In addition, a gas confined to a container has a finite volume, whereas external conditions determine a crystal volume. Simplifying by a mathematical conjecture, we can say that surfaces have a little contribution to bulk properties of a sizable crystal. However, a small volume change is inevitable in practical crystals under structural changes.

In thermodynamics, a crystal must always be in contact with the surroundings. Assuming no chemical activity, surfaces are in *physical contact* with the surroundings, exchanging *heat* between them. Joule demonstrated that heat is nothing but energy, although it is of unique type microscopically. Boltzmann considered that heat originates from randomly distributed microscopic energies in the surroundings. On the other hand, excitations in a crystal are primarily lattice vibrations at a given temperature, which are quantum mechanically expressed as *phonons* in random motion. The phonon spectrum is virtually continuous; the *internal energy* of lattice is given by a statistical average of distributed phonon energies. In this context, the lattice symmetry is implicit in thermodynamic functions, as specified by a uniform density in a constant volume.

Equilibrium between two bodies in thermal contact, as characterized by a common *temperature*  $T$ , signifies that there is no net flow of heat across the surfaces. For a combined system of a crystal and its surroundings, the total fluctuating heat is always *dissipative*, so that  $\Delta Q$  is expressed as negative, that is,  $\Delta Q \leq 0$ , implying that any thermal process is fundamentally *irreversible* in nature, as stated by the *second-law* of thermodynamics. Depending on the nature of heat dissipation, such  $\Delta Q$  cannot generally be expressed by a function of temperature and pressure; namely, the *heat quantity*  $Q$  is not a state function. Instead, a function  $S$ , defined by  $\frac{\Delta Q}{T} = \Delta S$ , can be employed as a state function if the *integrating denominator*  $T$  can be found for an infinitesimal  $S$  to be a *total differential*, representing a reversible contact between the crystal and surroundings. Clausius generalized this argument in integral form  $\oint_C \frac{Q}{T} \leq 0$  or  $\oint_C dS \leq 0$  around a closed

curve  $C$  in a *phase diagram*, where the equality sign indicates an idealized case of *reversible* process. Thermal equilibrium can thus be determined by *maximizing* the state function  $S$ , which is known as the *entropy*.

Boltzmann interpreted the entropy  $S$  in terms of *thermodynamic probability*  $g(T)$  at constant pressure to represent a thermal average of randomly distributed microscopic energies in the surroundings, for which he wrote the relation

$$S = k_B \ln g(T), \quad (1.1)$$

where  $k_B$  is the Boltzmann constant. For crystalline states in equilibrium at temperature  $T$ , such a probability is a valid concept if random phonon energies are responsible for the statistical description under a constant volume  $V$ . However, if a small volume change  $\Delta V$  is considered at constant  $T$  and  $p$ , a process at a constant crystal volume  $V$  is not an acceptable assumption for a crystal under constant  $p$ . Hence, Boltzmann's statistical theory is valid only if  $V$  is constant; otherwise, the dynamical system in a crystal is statistically *non-ergodic*.

In thermodynamics, physical properties of a crystal can be represented by the internal energy  $U(p, T)$ , which is varied not only by heat  $\Delta Q$  but also by external work  $W$ , as stated by *the first law of thermodynamics*. Namely,

$$\Delta U = \Delta Q + W. \quad (1.2)$$

A mechanical work  $W$  can change the volume  $V$ , where a structural modification may be induced, for example, by an electric or magnetic field, straining crystals by their forces  $X$ . Considering that such variables  $\sigma_m$  respond to applied  $X$ , the work  $W$  can be expressed as  $W = -\sum_m \sigma_m X$ . It is noted that such  $X$  can be associated with internal interactions with  $\sigma_n$  at different sites  $n$ , signifying *correlations* between internal variables  $\sigma_m$  and  $\sigma_n$ . Such internal correlations can occur *adiabatically* in a crystal, independent of temperature. However, they are weakly temperature dependent in practice, via interactions with phonons. In contrast, the heat energy  $Q$  depends only on the temperature of the surroundings, flowing in and out of a crystal at a constant  $V$ .

Correlated  $\sigma_m$  is generally in collective motion at long wavelength, propagating through an excited lattice. Such motion in a crystal should occur when driven by an *adiabatic potential*  $\Delta U_m$  at the lattice point  $m$ , as will be discussed in Chap. 7. In a *modulated structure*, the propagation can be detected in a standing wave whose period is not necessarily the same as in the lattice. On the other hand, if the correlation energy in short range is expressed in a form  $-J_{mn}\sigma_m\sigma_n$ , where  $J_{mn}$  is a function of the distance between  $\sigma_m$  and  $\sigma_n$ , we can write

$$-\sum_n J_{mn}\sigma_m\sigma_n = -\sigma_m X_m \quad (1.3)$$

which allows us to define the *internal field*  $X_m = \sum_n J_{mn}\sigma_n$  at a site  $m$ . Averaging  $X_m$  and  $\sigma_m$  over all lattice sites, we can define the *mean-field average*  $\langle X_m \rangle$  and  $\langle \sigma_m \rangle$ , respectively. For a nonzero  $\langle \sigma_m \rangle$ , the expression (1.3) can be interpreted as work

performed by a field  $\langle X_m \rangle$  on the  $\langle \sigma_m \rangle$  in mean-field accuracy. On the other hand, by writing (1.3) as  $-\langle \sigma_m \rangle X_{\text{int}}$ ,  $X_{\text{int}}$  can represent another kind of internal field, defined in better accuracy than the mean-field average  $\langle X_m \rangle$ . In this case, attributed to the adiabatic potential  $\Delta U_m$ , we can write  $X_{\text{int}} = -\nabla_m(\Delta U_m)$ , corresponding to the *Weiss field* that was originally proposed for a magnetic crystal.

In the presence of an external field  $X$ , the *effective field* can be defined as  $X + X_{\text{int}} = X'$ , considering  $X'$  as if applied externally. Such a field  $X'$  is usually temperature dependent, as contributed by temperature-dependent  $X_{\text{int}}$ ; hence, we can write  $X' = X'(T)$  under a constant  $p$ . The macroscopic energy relation can therefore be expressed as

$$\Delta U \leq \Delta Q - \Delta(\sigma X') \quad \text{or} \quad \Delta U - T\Delta S + \Delta(\sigma X') \leq 0.$$

Writing the Gibbs potential as  $G = U - TS + \sigma X'$ , we can obtain the inequality

$$\Delta G \leq 0, \tag{1.4}$$

indicating that the minimum of  $G$  determines the equilibrium at constant  $T$  and  $p$ .

In practice, *order variables*  $\sigma_m$  should be identified experimentally; thereby, equilibrium can be determined from the Gibbs function at given  $T$  and  $p$ . On the other hand, the mean-field average  $\langle \sigma_m \rangle = \sigma$ , called *order parameter*, can be utilized for simplifying description. In this case, the Gibbs function can be written as  $G(p, T, \sigma)$ , where the order parameter  $\sigma$  is defined for the range  $0 \leq \sigma \leq 1$ , where 0 and 1 are designated to perfect *disorder* and *order*, respectively. In *spontaneously* ordered crystals, the internal field  $X_{\text{int}}$  can be related to spatially distributed  $\sigma_m$ . For a ferromagnetic crystal, Weiss (1907) postulated that  $X_{\text{int}} \propto (\text{magnetization})$ , which is traditionally called *Weiss' molecular field* in a ferroelectric crystal.

## 1.2 Structural Changes

The structure of an equilibrium crystal is stable, which is however transformable from one stable state to another by applying an external field. In addition, we consider that the order variables  $\sigma_m$  emerging at  $T_c$  in finite magnitude are in collective motion, leading to spontaneous *phase transitions*. Although assumed primarily as independent of the hosting lattice, the correlated order variables modulate translational lattice symmetry. Interpreting this by Newton's action–reaction principle, correlated lattice displacements  $\mathbf{u}_m$  should interact with correlated vectors  $\sigma_m$ . Born and Huang [2] proposed their principle for the lattice to maintain stability with minimum strains, which can be evaluated by minimizing the Gibbs potential. Such a minimizing process can nevertheless be observed as thermal relaxation.

Regarding a transition from a phase 1 to another phase 2 at a critical point  $(p_c, T_c)$ , the Gibbs potential may be written as  $G(p_c, T_c; \sigma_1, \sigma_2)$ , where  $\sigma_1$  and  $\sigma_2$  represent



these phases 1 and 2 which coexist during the transition. Although somewhat imprecise, we write the whole Gibbs potential under an applied field  $X$  as

$$G_{\text{trans}} = G(p_c, T_c; \sigma_1, \sigma_2) - (\sigma_1 + \sigma_2)X.$$

In the noncritical region below  $T_c$ , we consider two Gibbs potentials  $G_1$  and  $G_2$ , coexisting at  $p$  and  $T$ , which are expressed as

$$G_1 = G(p, T) - \sigma_1 X$$

and

$$G_2 = G(p, T) - \sigma_2 X,$$

respectively.

For a *binary transition* characterized by inversion  $\sigma_1 = -\sigma_2$ , we consider fluctuations  $\Delta\sigma_1 = -\Delta\sigma_2$ , and hence,  $\sum_{i=1,2} \left( \frac{\partial G_{\text{trans}}}{\partial \sigma_i} \right)_{p_c, T_c} \Delta\sigma_i = 0$ . Therefore, expanding with respect to  $\Delta\sigma_i$ , the Gibbs potential can be expressed as

$$\Delta G_{\text{trans}} = \frac{1}{2} \sum_{i=1,2} \left( \frac{\partial^2 G_{\text{trans}}}{\partial \sigma_i \partial \sigma_j} \right)_{p_c, T_c} \Delta\sigma_i \Delta\sigma_j + \dots \quad (1.5)$$

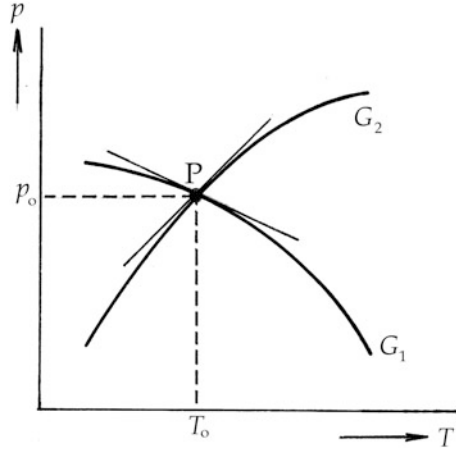
Neglecting higher than second-order terms for small  $\Delta\sigma_i$ , a nonvanishing  $\Delta G_{\text{trans}}$  gives a discontinuity due to the leading term of the second-order in (1.5). On the other hand, if such an inversion does not apply,  $\Delta G_{\text{trans}}$  is dominated by the finite first-order derivative terms; hence, the transition is called the *first-order*, according to the *Ehrenfest's classification*. In the binary case,  $\Delta G_{\text{trans}}$  is dominated by the second-order terms, and hence, the transition is called the *second-order*. It is noted from (1.5) that both the correlations  $\Delta\sigma_i \Delta\sigma_j$  and the second-order derivatives should not vanish for the leading term to come into effect; nonzero correlations are essential, as substantiated by *transition anomalies* observed for the specific heat. Such fluctuations  $\Delta\sigma_i$  should be quantum mechanical in nature, being responsible for the threshold anomalies, while  $\sigma_i$  behave like a *classical vector* at and below  $T_c$ .

The transformation below  $T_c$  is signified by the difference  $\Delta G_{1,2} = G_2 - G_1$ , which is finite at  $X \neq 0$ , however zero if  $X = 0$ . Accordingly,

$$\Delta G_{1,2} = (\sigma_2 - \sigma_1)X. \quad (1.6)$$

For  $X = 0$  and  $X \neq 0$ , the transformations are the second- and the first-order, respectively. In thermodynamics, both the Gibbs potential and order parameter are *extensive variables* by definition, as they are proportional to the corresponding volume. Denoting domain volumes by  $V_1$  and  $V_2$ , the total volume is  $V_1 + V_2 = V$ , which can be assumed as invariant under a constant  $p$ . If so, (1.6) can be determined by either the volume ratio  $V_1/V_2$  or order-parameter ratio  $\sigma_1/\sigma_2$ ; both can be changed by applying  $X$  (see Chap. 4).

**Fig. 1.1** Phase equilibrium in the  $p$ - $T$  diagram. Two curves of Gibbs functions,  $G_1(p, T)$  and  $G_2(p, T)$  cross at a point  $P(p_0, T_0)$ , representing thermal equilibrium between phase 1 and phase 2. If the transition is discontinuous at  $P$ , such Gibbs functions cannot specify the equilibrium sufficiently at  $P$ , requiring another variable such as  $\sigma$ .



**Fig. 1.2 (a)** The second-order phase transition is characterized by two functions  $G_1$  and  $G_2$  that have a common tangent and different curvatures at  $P$  in the  $p$ - $T$  diagram. **(b)** Equilibrium between binary domains specified by  $\sigma_1$  and  $\sigma_2$ , which are separated phases at temperatures below the critical temperature  $T_c$ . Transition anomalies near  $T_c$  are shown schematically by the shaded area.

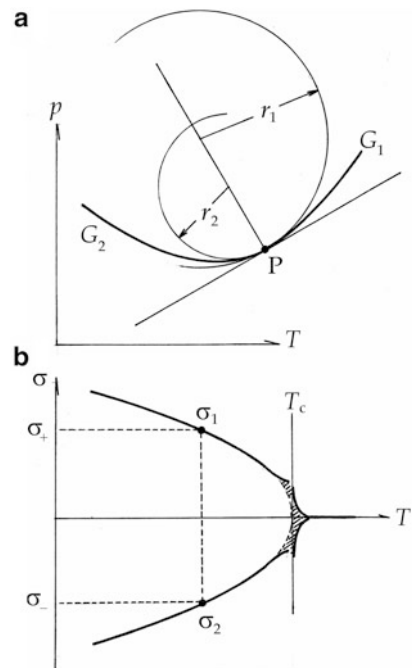


Figure 1.1 shows a phase diagram, where two Gibbs functions of phases  $G_1$  and  $G_2$  are schematically plotted in a  $p$ - $T$  plane. The crossing point  $P(p_0, T_0)$  indicates that a transition occurs between  $G_1$  and  $G_2$  at  $P(p_0, T_0)$ . The transition is generally first-order, because of discontinuity in the perpendicular direction to  $p$ - $T$  plane, although implicit in the two-dimensional  $p$ - $T$  diagram; there is a finite change of curvature at  $P$  as related to  $\Delta G_{\text{trans}}$ . Nevertheless, the discontinuity vanishes, if we ignore fluctuations. Figure 1.2(a) illustrates a continuous binary transition  $G_1 \rightarrow G_2$  at  $T_c$ , assuming that there are no

fluctuations. In the diagram  $\sigma$ - $T$  in Fig. 1.2(b), a continuous transition is sketched by solid lines, which are broadened by fluctuations in the vicinity of  $T_c$ . Below  $T_c$ , the transformation  $\sigma_1 \leftrightarrow \sigma_2$  can take place in the first order, if performed by an external  $X$ . It is noted that such a process under a constant  $p$  condition is not strictly adiabatic, because  $X_{\text{int}}$  is temperature dependent in practical crystals.

## 1.3 New Concepts

In this book, we discuss thermodynamics of crystalline states under the laws of thermodynamics, for which new concepts, such as *renormalized coordinates*, *solitons*, and *fields*, are added to express collective properties of order variables in periodic structure. These are listed in the following.

### 1.3.1 Modulated Phases and Renormalized Coordinates

We describe fluctuations in crystals as arising from quantum-mechanical space-time uncertainties for order variables  $\sigma_i$  that represent classical vectors at all sites of a periodic lattice. Their correlated motion described as propagation in the *continuum field* suited particularly to low excitations of lattice under critical conditions. Associated with sinusoidal lattice displacements  $u_i$ , the related variables  $\sigma_i$  are signified by their displacements and expressed as a sinusoidal field  $\sigma_i = \sigma_o \exp i(\mathbf{k} \cdot \mathbf{r}_i - \omega t_i + \varphi_i)$ , accompanying phase uncertainties  $\Delta\varphi_i$ .

Surfaces are significant for thermal properties of a crystal; however, by ignoring them, we can idealize a crystal as infinite periodic structure, where phases of order variables  $\sigma_i$  fluctuate by  $\Delta\varphi_i$  at a given  $T$ . Such sinusoidal fluctuations are detectable if their *standing waves* are *pinned* by the modulated lattice, visualizing *mesoscopic* fluctuations. (See Chap. 8 for the detail.) The order variable  $\sigma(\mathbf{r}, t) = \sigma(\phi)$  is continuous in space-time or phase  $\phi = \mathbf{k} \cdot \mathbf{r} - \omega t$ , for which one full angular period  $0 \leq \phi \leq 2\pi$  is sufficient instead of a repeated expression. Hence, such a continuous variable  $\sigma(\phi)$  can be utilized for expressing thermodynamic functions in a mesoscopic state.

Expressed in the form  $\sigma = \sigma_o f(\phi)$  incorporated with periodic boundary conditions,  $\sigma_o$  is a finite amplitude and  $\phi = \mathbf{k} \cdot \mathbf{r} - \omega t$  in the range  $0 \leq \phi \leq 2\pi$ . The *spatial phase*  $\phi_s = \mathbf{k} \cdot \mathbf{r}$  in standing waves visualizes distributed mesoscopic phases in the angular range  $0 \leq \phi_s \leq 2\pi$  in a whole crystal without referring to lattice sites. Noted that this definition is similar to a *renormalization group* of order variables in statistical mechanics [3], we shall call  $\phi_s$  and  $(\mathbf{r}, t)$  *renormalized* phase and coordinates, respectively. The Gibbs function in a mesoscopic phase can also be expressed as  $G(\sigma_o, \phi_s)$  in terms of renormalized variables.

### 1.3.2 *Thermodynamic Changes and Nonlinear Dynamics*

Physical properties of matter can change with the responsible dynamical system in equilibrium under isothermal and adiabatic conditions. Small deviations from equilibrium are always restorable in stable crystals, where the dynamical system is *dissipative* and *dispersive* under these conditions. Accordingly, the equation of motion during thermodynamic changes can be *nonlinear*, leading to the modulated lattice structure. While not particularly familiar in traditional physics, we need to deal with the nonlinearity in thermodynamics of crystalline states. *Soliton* theory [4] in nonlinear physics provides with collective motion in an accurate approximation better than the mean-field approach.

### 1.3.3 *Fields within Thermodynamic Boundaries*

For collective motion in crystals, it is convenient to use the *field* concept [5]. The superconducting transition in metals can be discussed with the field concept on condensation of electrons in the reciprocal lattice space. Characterized by *supercurrents* and *Meissner effects*, superconducting phase transitions are more complex than other ordering phenomena, although exhibiting similar specific heat anomalies arising from condensing charge carriers. Fröhlich's field-theoretical model of electron-phonon interaction provides a clear image of condensates to initiate a phase transition, on which the theory of Bardeen, Cooper, and Schrieffer can define order variables. The last three chapters in this book are for superconducting transitions in metals, which can be discussed by analogy of structural changes. Phase changes in crystals are generally associated with adiabatic potentials, where the *nonlinearity* arises from interactions with the lattice.

In this book, dynamical variables in crystals are discussed within thermal boundaries at constant  $T$  and  $p$ , which can be described as isothermal and adiabatic processes in crystals. The former remains the same as in traditional theories, whereas the latter process cannot be separated from the former, showing thermal relaxation to stabilize structure.

### 1.3.4 *Adiabatic Potentials*

Introduced early by Boltzmann and Ehrenfest, the concept of adiabatic invariance should be extended explicitly to crystalline states to deal with long-range correlations, which can be discussed by means of the *internal adiabatic potential* in the lattice. Recognized in practical applications of thermodynamics, it was however not seriously dealt with in most available references. We therefore emphasized its significance for driving condensates for structural order.

## 1.4 Sampling Modulated States

For critical fluctuations, the timescale  $t$  is a significant for sampling experiments of the spatial distribution of  $\sigma$ . For that purpose, the timescale  $t_0$  of sampling should be shorter than the timescale  $t$  of fluctuations. A Gibbs potential, if sampled at a given  $p$ - $T$  condition, should be expressed by a space-time average over  $t_0$ , namely,

$$G_{p,T} = \frac{1}{t_0} \int_0^{t_0} dt \left( \frac{1}{V} \int_V g(\mathbf{r}, t) d^3\mathbf{r} \right), \quad (1.7a)$$

where  $g(\mathbf{r}, t)$  is the density of Gibbs potential in the sampling volume  $V$ . Writing the time average as  $\frac{1}{t_0} \int_0^{t_0} g(\mathbf{r}, t) dt = \langle g(\mathbf{r}, t) \rangle_t$ , (1.7a) can be expressed by

$$G_{p,T} = \frac{1}{V} \int_V \langle g(\mathbf{r}, t) \rangle_t d^3\mathbf{r}. \quad (1.7b)$$

The average density  $\langle g(\mathbf{r}, t) \rangle_t$  over  $t_0$  can be sampled from a specimen of volume  $V$ . It is noted that such a sampling results in a useful information only if  $t > t_0$ . Sampled mesoscopic  $\langle \sigma(\mathbf{r}, t) \rangle_t$  represents  $\sigma(\phi_s)$ , where  $0 \leq \phi_s \leq 2\pi$  and the distributed  $\sigma(\phi_s)$  is explicit, provided that  $t > t_0$ .

### Exercise 1

1. What is the mean-field average? If a physical event at each lattice point is random and independent, the average should always be zero, should it not? There must be some kind of correlations among them in order to have a nonzero average. Discuss this issue.
2. Review Ehrenfest's classification of phase transitions from a standard textbook on thermodynamics. In his definition of second-order transitions, vanishing first-order derivatives and nonzero second-order derivatives of the Gibbs function are necessary. On the other hand, as we mentioned in Sect. 1.2, nonzero correlations  $\Delta\sigma_i\Delta\sigma_j$  among internal variables are required, in addition to Ehrenfest's definition. Is this a conflict? This problem should be discussed to clear this issue before proceeding to the following chapters.
3. In traditional thermodynamics, the Gibbs potential was defined as a function of macroscopic variables. However, macroscopic heat and order parameter are associated with internal variables in a crystal, which are essentially related to thermal and adiabatic averages of fluctuating microscopic variables, respectively. In this context, the Gibbs function defined in this chapter is associated with all sites that may not be identical. Discuss this issue for thermodynamics of heterogeneous matters.

## References

1. J.G. Kirkwood, I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961)
2. M. Born, K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1968)
3. D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987)
4. G.L. Lamb, *Elements of Soliton Theory* (Wiley, New York, 1980)
5. H. Haken, *Quantenfeldtheorie des Festkörpers* (B. G. Teubner, Stuttgart, 1973)

# Chapter 2

## Phonons

Disregarding point symmetry, we can simplify the crystal structure by the space group [1, 2], representing the thermodynamic state in equilibrium with the surroundings at given values of  $p$  and  $T$ . In this approach, the restoring forces secure stability of the lattice, where the masses at lattice points are in harmonic motion. In this case, we realize that their *directional* correlations in the lattice are ignored so that a possible disarrangement in the lattice can cause structural instability.

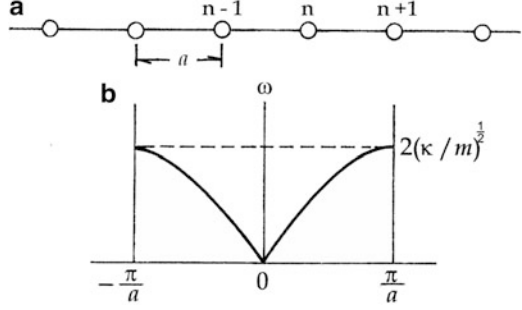
In this chapter, we discuss a harmonic lattice to deal with basic excitations in equilibrium structure. Lattice vibrations in periodic structure are in propagation, specified by frequencies and wavevectors in virtually continuous spectra. Quantum mechanically, on the other hand, the corresponding *phonons* signify the dynamical state in crystals. In strained crystals, as modulated by correlated constituents, low-frequency excitations dominate over the distorted structure, which is however thermally unstable as discussed in this chapter.

### 2.1 Normal Modes in a Simple Crystal

A crystal of chemically identical constituent ions has a rigid periodic structure in equilibrium with the surroundings, which is characterized by *translational symmetry*. Referring to symmetry axes, physical properties can be attributed to the translational invariance, in consequence of energy and momentum conservations among constituents.

Constituents are assumed to be bound together by restoring forces in the lattice structure. Considering a cubic lattice of  $N^3$  identical mass particles in a cubic crystal in sufficiently large size, we can solve the *classical* equation of motion with nearest-neighbor interactions. Although such a problem should be solved *quantum mechanically*, classical solutions provide also a useful approximation. It is noted that the lattice symmetry is unchanged with the nearest-neighbor interactions, assuring

**Fig. 2.1** (a) One-dimensional monatomic chain of the lattice constant  $a$ . (b) A dispersion curve  $\omega$  vs.  $k$  of the chain lattice.



structural stability in this approach. In the harmonic approximation, we have *linear* differential equations, which can be separated into  $3N$  independent equations; this one-dimensional equation describes *normal modes* of  $N$  constituents in collective motion along the symmetry axis  $x$ ,  $y$ , or  $z$  [3]. Denoting the displacement by a vector  $\mathbf{q}_n$  from a site  $n$ , we write equations of motion for the components  $q_{x,n}$ ,  $q_{y,n}$  and  $q_{z,n}$  independently, that is,

$$\ddot{q}_{x,n} = \omega^2 (q_{x,n+1} + q_{x,n-1} - 2q_{x,n}), \quad \ddot{q}_{y,n} = \omega^2 (q_{y,n+1} + q_{y,n-1} - 2q_{y,n}) \quad \text{and} \\ \ddot{q}_{z,n} = \omega^2 (q_{z,n+1} + q_{z,n-1} - 2q_{z,n}),$$

where  $\omega^2 = \kappa/m$  and  $\kappa$  and  $m$  are the mass of a constituent particle and the force constant, respectively. As these equations are identical, we write the following equation for a representative component to name  $q_n$  for brevity:

$$\ddot{q}_n = \omega^2 (q_{n+1} + q_{n-1} - 2q_n), \quad (2.1)$$

which assures lattice stability along any symmetry direction.

Defining the conjugate momentum by  $p_n = m\dot{q}_n$ , the *Hamiltonian* of a harmonic lattice can be expressed as

$$H = \sum_{n=0}^N \left\{ \frac{p_n^2}{2m} + \frac{m\omega^2}{2} (q_{n+1} - q_n)^2 + \frac{m\omega^2}{2} (q_n - q_{n-1})^2 \right\}. \quad (2.2)$$

Each term in the summation represents one-dimensional infinite chain of identical masses  $m$ , as illustrated in Fig. 2.1a.

*Normal coordinates* and *conjugate momenta*,  $Q_k$  and  $P_k$ , are defined with the Fourier expansions

$$q_n = \frac{1}{\sqrt{N}} \sum_{k=0}^{k_N} Q_k \exp(ikna) \quad \text{and} \quad p_k = \sum_{k=0}^{k_N} P_k \exp(ikna), \quad (2.3)$$



where  $a$  is the *lattice constant*. For each mode of  $q_n$  and  $p_n$ , the amplitudes  $Q_k$  and  $P_k$  are related as

$$Q_{-k} = Q_k^*, P_{-k} = P_k^* \quad \text{and} \quad \sum_{n=0}^N \exp i(k - k')na = N\delta_{kk'}, \quad (2.4)$$

where  $\delta_{kk'}$  is *Kronecker's delta*, that is,  $\delta_{kk'} = 1$  for  $k = k'$ , otherwise zero for  $k \neq k'$ .

Using normal coordinates  $Q_k$  and  $P_k$ , the Hamiltonian can be expressed as

$$H = \frac{1}{2m} \sum_{k=0}^{2\pi/a} \left\{ P_k P_k^* + Q_k Q_k^* m^2 \omega^2 \left( \sin^2 \frac{ka}{2} \right) \right\}, \quad (2.5)$$

from which the equation of motion for  $Q_k$  is written as

$$\ddot{Q}_k = -m^2 \omega^2 \sin^2 \frac{ka}{2} Q_k, \quad (2.6)$$

where

$$\omega_k = 2\omega \sin \frac{ka}{2} = 2\sqrt{\frac{\kappa}{m}} \sin \frac{ka}{2}. \quad (2.7)$$

As indicated by (2.7), the  $k$ -mode of coupled oscillators is *dispersive*, which are linearly independent from the other modes of  $k' \neq k$ .  $H$  is composed of  $N$  independent harmonic oscillators, each of which is determined by the normal coordinates  $Q_k$  and conjugate momenta  $P_k$ . Applying Born-von Kármán's boundary conditions to the periodic structure,  $k$  can take discrete values as given by  $k = \frac{2\pi n}{Na}$  and  $n = 0, 1, 2, \dots, N$ . Figure 2.1b shows the dispersion relation (2.7) determined by the characteristic frequency  $\omega_k$ .

With initial values of  $Q_k(0)$  and  $\dot{Q}_k(0)$  specified at  $t = 0$ , the solution of (2.7) can be given by

$$Q_k(t) = Q_k(0) \cos \omega_k t + \frac{\dot{Q}_k(0)}{\omega_k} \sin \omega_k t.$$

Accordingly,

$$q_n(t) = \frac{1}{\sqrt{N}} \sum_{k=0}^{k_N} \sum_{n'=n, n\pm 1} \left[ q_{n'}(0) \cos \{ka(n - n') - \omega_k t\} + \frac{\dot{q}_{n'}(0)}{\omega_k} \sin \{ka(n - n') - \omega_k t\} \right], \quad (2.8)$$

where  $a(n - n')$  represents distances between sites  $n$  and  $n'$  so that we write it as  $x = a(n - n')$  in the following. The crystal is assumed as consisting of a large number of the cubic volume  $L^3$  where  $L = Na$ , if disregarding surfaces.

The periodic boundary conditions can then be set as  $q_{n=0}(t) = q_{n=N}(t)$  at an arbitrary time  $t$ . At a lattice point  $x = na$  between  $n = 0$  and  $N$ , (2.8) can be expressed as

$$q(x, t) = \sum_k [A_k \cos(\pm kx - \omega_k t) + B_k \sin(\pm kx - \omega_k t)],$$

where  $A_k = \frac{q_k(0)}{\sqrt{N}}$  and  $B_k = \frac{\dot{q}_k(0)}{\omega_k \sqrt{N}}$ , and  $x$  is virtually continuous in the range  $0 \leq x \leq L$ , if  $L$  is taken as sufficiently long. Consisting of waves propagating in  $\pm x$  directions, we can write  $q(x, t)$  conveniently in complex exponential form, that is,

$$q(x, t) = \sum_k C_k \exp i(\pm kx - \omega_k t + \varphi_k), \quad (2.9)$$

where  $C_k^2 = A_k^2 + B_k^2$  and  $\tan \varphi_k = \frac{B_k}{A_k}$ . For a three-dimensional crystal, these one-dimensional  $k$ -modes along the  $x$ -axis can be copied to other symmetry axes  $y$  and  $z$ ; accordingly, there are  $3N$  normal modes in total in a cubic crystal.

## 2.2 Quantized Normal Modes

The classical equation of motion of a harmonic crystal is separable to  $3N$  independent normal propagation modes specified by  $k_n = \frac{2\pi n}{aN}$  along the symmetry axes. In quantum theory, the normal coordinate  $Q_k$  and conjugate momentum  $P_k = -i\hbar \frac{\partial}{\partial Q_k}$  are *operators*, where  $\hbar = \frac{h}{2\pi}$  and  $h$  is the Planck constant. For these normal and conjugate variables, there are commutation relations:

$$[Q_k, Q_{k'}] = 0, [P_k, P_{k'}] = 0 \quad \text{and} \quad [P_k, Q_{k'}] = i\hbar \delta_{kk'}, \quad (2.10)$$

and the Hamiltonian operator is

$$H_k = \frac{1}{2m} \left( P_k P_k^\dagger + m^2 \omega_k^2 Q_k Q_k^\dagger \right). \quad (2.11a)$$

Here,  $P_k^\dagger$  and  $Q_k^\dagger$  express *transposed* matrix operators of the complex conjugates  $P_k^*$  and  $Q_k^*$ , respectively.

Denoting the eigenvalues of  $H_k$  by  $\varepsilon_k$ , we have the equation

$$H_k \Psi_k = \varepsilon_k \Psi_k. \quad (2.11b)$$

For real eigenvalues  $\varepsilon_k$ ,  $P_k$  and  $Q_k$  should be *Hermitian* operators, which are characterized by the relations  $P_k^\dagger = P_{-k}$  and  $Q_k^\dagger = Q_{-k}$ , respectively. Defining operators

$$b_k = \frac{m\omega_k Q_k + iP_k^\dagger}{\sqrt{2m\varepsilon_k}} \quad \text{and} \quad b_k^\dagger = \frac{m\omega_k Q_k^\dagger - iP_k}{\sqrt{2m\varepsilon_k}}, \quad (2.12)$$

we can write the relation

$$\begin{aligned} b_k b_k^\dagger &= \frac{1}{2m\varepsilon_k} \left( m^2 \omega_k^2 Q_k^\dagger Q_k + P_k^\dagger P_k \right) + \frac{i\omega_k}{2\varepsilon_k} \left( Q_k^\dagger P_k^\dagger - P_k Q_k \right) \\ &= \frac{H_k}{\varepsilon_k} + \frac{i\omega_k}{2\varepsilon_k} (Q_{-k} P_{-k} - P_k Q_k). \end{aligned}$$

From this relation, we can be derive

$$H_k = \hbar\omega_k \left( b_k^\dagger b_k + \frac{1}{2} \right), \quad \text{if} \quad \varepsilon_k = \frac{1}{2} \hbar\omega_k. \quad (2.13)$$

Therefore,  $H_k$  are commutable with the operator  $b_k^\dagger b_k$ , that is,

$$[H_k, b_k^\dagger b_k] = 0,$$

and from (2.12)

$$[b_{k'}, b_k^\dagger] = \delta_{k'k}, \quad [b_{k'}, b_k] = 0 \quad \text{and} \quad [b_k^\dagger, b_k^\dagger] = 0.$$

Accordingly, we obtain

$$[H_k, b_k^\dagger] = \hbar\omega_k b_k^\dagger \quad \text{and} \quad [b_k, H_k] = \hbar\omega_k b_k.$$

Combining with (2.11b), we can derive the relations

$$H_k \left( b_k^\dagger \Psi_k \right) = (\varepsilon_k + \hbar\omega_k) \left( b_k^\dagger \Psi_k \right) \quad \text{and} \quad H_k (b_k \Psi_k) = (\varepsilon_k - \hbar\omega_k) (b_k \Psi_k),$$

indicating that  $b_k^\dagger \Psi_k$  and  $b_k \Psi_k$  are eigenfunctions for the energies  $\varepsilon_k + \hbar\omega_k$  and  $\varepsilon_k - \hbar\omega_k$ , respectively. In this context,  $b_k^\dagger$  and  $b_k$  are referred to as *creation* and *annihilation* operators for the energy quantum  $\hbar\omega_k$  to add and subtract in the energy  $\varepsilon_k$ ; hence, we can write

$$b_k^\dagger b_k = 1. \quad (2.14)$$

Applying the creation operator  $b_k^\dagger$  on the ground state function  $\Psi_k$   $n_k$ -times, the eigenvalue of the wavefunction  $(b_k^\dagger)^{n_k} \Psi_k$  can be given by  $(n_k + \frac{1}{2})\hbar\omega_k$ , generating a

state of  $n_k$  quanta plus  $\frac{1}{2}\hbar\omega_k$ . Considering a quantum  $\hbar\omega_k$  like a particle, called a *phonon*, such an excited state with  $n_k$  identical phonons is multiply degenerate by *permutation*  $n_k!$ . Hence, the normalized wavefunction of  $n_k$  phonons can be expressed by  $\frac{1}{\sqrt{n_k!}}(b_k^\dagger)^{n_k}\Psi_k$ . The total lattice energy in an excited state of  $n_1, n_2, \dots$  phonons in the normal modes 1, 2, ... can be expressed by

$$U(n_1, n_2, \dots) = U_0 + \sum_k n_k \hbar\omega_k, \quad (2.15a)$$

where  $U_0 = \sum_k \frac{\hbar\omega_k}{2}$  is the total zero-point energy. The corresponding wavefunction can be written as

$$\Psi(n_1, n_2, \dots) = \frac{(b_1^\dagger)^{n_1} (b_2^\dagger)^{n_2} \dots}{\sqrt{n_1! n_2! \dots}} (\Psi_1 \Psi_2 \dots), \quad (2.15b)$$

which describes a state of  $n_1, n_2, \dots$  phonons of energies  $n_1\hbar\omega_{k_1}, n_2\hbar\omega_{k_2}, \dots$ . The total number  $N = n_1 + n_2 + \dots$  cannot be evaluated by the dynamical theory; however, we can determine the value in thermodynamics, as related to the level of thermal excitation at a given temperature.

### 2.3 Phonon Field and Momentum

In a one-dimensional chain of identical mass particles, the displacement mode  $q_k$  is independent from each other's modes, and hence representing normal modes in a three-dimensional crystal. However, this model is only approximate, in that these normal modes arise from the one-dimension harmonic chain model, where mutual interactions between different normal modes are prohibited. For propagation in arbitrary direction, the *vibrating field* offers more appropriate approach than the normal modes, where quantized phonons move in any direction like free particles in the field space.

Setting rectangular coordinates  $x, y, z$  along the symmetry axes of an orthorhombic crystal in classical theory, the lattice vibrations are described by a set of equations

$$\begin{aligned} \frac{p_{x,n_1}^2}{2m} + \frac{\kappa}{2} \left\{ (q_{x,n_1} - q_{x,n_1+1})^2 + (q_{x,n_1} - q_{x,n_1-1})^2 \right\} &= \varepsilon_{x,n_1}, \\ \frac{p_{y,n_2}^2}{2m} + \frac{\kappa}{2} \left\{ (q_{y,n_2} - q_{y,n_2+1})^2 + (q_{y,n_2} - q_{y,n_2-1})^2 \right\} &= \varepsilon_{y,n_2}, \end{aligned} \quad (2.16)$$

and

$$\frac{p_{z,n_3}^2}{2m} + \frac{\kappa}{2} \left\{ (q_{z,n_3} - q_{z,n_3+1})^2 + (q_{z,n_3} - q_{z,n_3-1})^2 \right\} = \varepsilon_{z,n_3},$$

where  $\varepsilon_{x,n_1} + \varepsilon_{y,n_2} + \varepsilon_{z,n_3} = \varepsilon_{n_1 n_2 n_3}$  is the total propagation energy along the direction specified by the vector  $q(n_1, n_2, n_3)$  and  $\kappa$  is the force constant.

The variables  $q_{x,n_1}$ ,  $q_{y,n_2}$ ,  $q_{z,n_3}$  in (2.16) are components of a classical vector  $q(n_1, n_2, n_3)$ , which can be interpreted quantum theoretically as *probability amplitudes* of components of the vector  $q$  in the vibration field. We can therefore write the wavefunction of the displacement field as  $\Psi(n_1, n_2, n_3) = q_{x,n_1} q_{y,n_2} q_{z,n_3}$ , for which these classical components are written as

$$q(x, t) = \sum_{k_x} C_{k_x} \exp i(\pm k_x x - \omega_{k_x} t + \varphi_{k_x}),$$

$$q(y, t) = \sum_{k_y} C_{k_y} \exp i(\pm k_y y - \omega_{k_y} t + \varphi_{k_y}),$$

$$q(z, t) = \sum_{k_z} C_{k_z} \exp i(\pm k_z z - \omega_{k_z} t + \varphi_{k_z}),$$

and hence, we have

$$\Psi(n_1, n_2, n_3) = \sum_k \mathcal{A}_k \exp i\left(\pm \mathbf{k} \cdot \mathbf{r} - \frac{n_1 \varepsilon_{x,n_1} + n_2 \varepsilon_{y,n_2} + n_3 \varepsilon_{z,n_3}}{\hbar} t + \varphi_k\right).$$

Here,  $\mathcal{A}_k = C_{k_x} C_{k_y} C_{k_z}$ ,  $\varphi_k = \varphi_{k_x} + \varphi_{k_y} + \varphi_{k_z}$ , and  $\mathbf{k} = (k_x, k_y, k_z)$  are the amplitude, phase constant, and wavevector of  $\Psi(n_1, n_2, n_3)$ , respectively. Further writing

$$\frac{n_1 \varepsilon_{x,n_1} + n_2 \varepsilon_{y,n_2} + n_3 \varepsilon_{z,n_3}}{\hbar} = \omega_k(n_1, n_2, n_3) = \omega_k, \quad (2.17a)$$

the field propagating along the direction of a vector  $\mathbf{k}$  can be expressed as

$$\Psi(\mathbf{k}, \omega_k) = \mathcal{A}_k \exp i(\pm \mathbf{k} \cdot \mathbf{r} - \omega_k t + \varphi_k), \quad (2.17b)$$

representing a phonon of energy  $\hbar \omega_k$  and momentum  $\pm \hbar \mathbf{k}$ . For a small  $|\mathbf{k}|$ , the propagation in a cubic lattice can be characterized by a constant speed  $v$  of propagation determined by  $\omega_k = v|\mathbf{k}|$ , indicating no *dispersion* in this approximation.

The phonon propagation can be described by the vector  $\mathbf{k}$ , composing a *reciprocal lattice* space, as illustrated in two dimensions in Fig. 2.2 by

$$k_x = \frac{2\pi n_1}{L}, \quad k_y = \frac{2\pi n_2}{L} \quad \text{and} \quad k_z = \frac{2\pi n_3}{L},$$