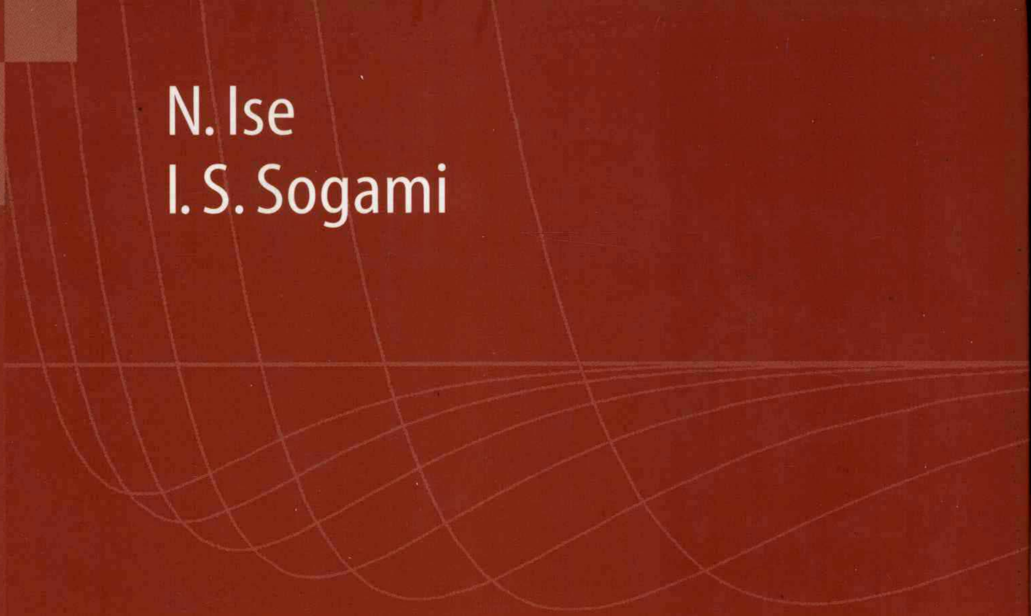
N. Ise
I. S. Sogami



Structure Formation in Solution

Ionic Polymers and Colloidal Particles

Springer

Norio Ise
Ikuo S. Sogami

Structure Formation in Solution

Ionic Polymers and Colloidal Particles

Springer

Norio Ise
Professor Emeritus
Kyoto University
Kyoto, Japan

Ikuo S. Sogami
Kyoto Sangyo University
Kyoto, Japan

DOI 10.1007/b83993
ISBN-10 3-540-25271-1 Springer Berlin Heidelberg New York
ISBN-13 978-3-540-25271-9 Springer Berlin Heidelberg New York
e-ISBN 3-540-27715-3

Library of Congress Control Number: 2005921903

This work is subject to copyright. All rights reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media
springeronline.com

© Springer-Verlag Berlin Heidelberg 2005
Printed in Germany

The use of general descriptive names, registered names, trademarks, 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.

Product liability: The publisher cannot guarantee the accuracy of any information about dosage and application contained in this book. In every individual case the user must check such information by consulting the relevant literature.

The instructions given for carrying out practical experiments do not absolve the reader from being responsible for safety precautions. Liability is not accepted by the authors.

Typesetting: By the Authors
Production: LE-TEX, Jelonek, Schmidt & Vöckler GbR, Leipzig
Coverdesign: design&production, Heidelberg

Printed on acid-free paper 2/YL - 5 4 3 2 1 0

Preface

In this monograph we discuss solutions of ionic polymers and dispersions of electrically charged colloidal particles. These substances dynamically dissociate and associate into macroions and counterions in polar solvents such as water. Thus, they have two facets: they behave as electrolytes like NaCl and as high polymers.

The outstanding feature of these systems is the electrostatic interaction between solutes. This interaction is of long-range nature and results in various phenomena, which has been unknown for non-ionic polymer solutions. The colloidal particles help us analyze ionic polymer solutions, which are not easy to understand. When the particles are large enough, they can be "seen" under the microscope. As will be shown in Chap. 4, Brownian motion, crystallization, lattice defects, lattice vibration and so on can be visualized by using colloidal particles. Such direct information of colloidal systems can provide powerful suggestions to our understanding of "invisible" ionic polymers in solutions and condensed matter in general as well. In this monograph, we discuss recent investigations on the structure formation of ionic polymers and colloidal particles at low concentrations and its related topics.

In gases, the distribution of molecules and atoms is "random", whereas geometric regularity characterizes solid crystals. In liquids and solutions, a short-range order exists, but a longer intermediate order is also possible. A long-range order in the form of clusters has been reported to exist over 50 years for colloidal systems and about 20 years for ionic polymers. This general phenomenon has its origin in the interactions between solutes and appears to correspond to thermodynamic equilibrium. Fundamental understanding of this ubiquitous phenomenon is an outstanding scientific challenge.

In Chap. 1, we first consider the general features of the structure of ionic polymer solutions and of the interactions therein as well as the principles of the methods to be applied. We then proceed, in Chap. 2, to the discussion of existing theoretical frameworks such as the Debye-Hückel theory of strong electrolytes [Debye PJW, Hückel E (1923) Physik Z 24:185] and the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of the interactions between colloidal particles [Verwey EJW, Overbeek JThG (1948) Theory of the stability of lyophobic colloids. Elsevier, New York]. On the basis of these theoretical foundations, recent experimental observations are reviewed. We deal with flexible ionic polymer solutions in Chap. 3 and colloidal dispersions in Chap. 4, in which agreement with and discrepancy from the existing theories are dissected. In Chap. 5 the Kikuchi-Kossel method for the structural analysis of colloidal crystals is considered. In Chap. 6, a mean field theory for spherical macroions is derived, and a long-range attraction is shown to exist, in addition to the purely repulsive interaction presented by the DLVO theory, between similarly charged macroions. Discussion is given in Chap. 7 on the pros and cons of the widely accepted interpretation of the solution viscosity of flexible ionic polymers, in other words, of the rod-model of these polymers. Specifically, we reconsider the merits of the "rod-model" of flexible ionic polymers, which is prevalent in the polyelectrolyte literature. The recent results of computer simulations are discussed in Chap. 8, in which the purely repulsive DLVO potential and the new potential containing long-range attraction obtained in Chap. 6 are compared under the same conditions in the Monte-Carlo simulation, demonstrating that the observed discrepancy from the DLVO theory is accounted for by the attraction. In the last chapter, some colloidal phenomena, which have been accounted for by the DLVO potential, are shown to be explainable also by using the new potential. The logical problem in the previous arguments in favor of the DLVO potential or the repulsion-only assumption is thereby clarified.

The present monograph is characterized by an unconventional point of view of charged colloidal dispersions based on three tenets. First, it is claimed that an electrostatic long-range weak attraction is operative, in addition to the widely recognized short-range strong repulsion, between similarly charged macrions. According to the Coulomb law, cations repel other cations. This raises the question: Is the above claim then incompatible with the Coulomb law? *Definitely not.* If we can prepare a solution of cations only, they repel naturally each other. In real solutions or dispersions, however, cationic species have to coexist with their oppositely charged species to maintain electric neutrality as a whole. Therefore, if we pay attention to similarly charged macroions only, repulsion is observed to be in action, but in reality, we cannot ignore their oppositely charged counterions, which attract the macroions. There is a possibility that, when this attraction overwhelms the repulsion between the macroions, two macroions are pulled together. This very point is clearly explained by Feynman [Feynman RP, Leighton RB, Sands M (1965) The Feynman lecture on physics. Addison-Wesley, Reading, MA, vol 1, p.2 3] as follows:

> *"Suppose that we have two unlikes that attract each other, a plus and a minus, and that they stick very close together. Suppose that we have another charge some distance away. Would it feel any attraction? It would feel practically none ... On the other hand, if we get very*

> *close with the extra charge, attraction arises, because the repulsion of likes and attraction of unlikes will tend to bring unlikes closer together and push likes farther apart. Then the repulsion will be less than the attraction."*

The second central hypothesis is that we accept the mean-field approach to describe macroionic systems on the basis of the Poisson-Boltzmann equation, as done also for the Debye-Hückel theory and the DLVO theory. Our calculations depart from the DLVO theory in indicating the existence of a long-range attraction between similarly charged macroions, based on the physical picture described above. We do not discuss other rationalizations of this attraction that have been recently reported. Though detailed discussion is given in Chap. 2, it was demonstrated in the framework of the mean field approach [Fowler RH, Guggenheim EA (1939) Statistical thermodynamics. Cambridge University Press, London, Chap. 9; McQaurrie DA (1976) Statistical mechanics. Harper Collins Publishers, New York, Chap. 15] that Helmholtz and Gibbs free energies were *not generally equal* for ionic solutions and that this difference was due to interionic interaction. In solutions of simple ions, which are not highly charged, the interaction may be not so intense. For highly charged colloidal particles, the two free energies have to be carefully distinguished. In the DLVO theory, however, the two free energies are assumed to be equal. As will be discussed in Chap. 6, the mean field approach leads to the conclusion that the intermacroion interaction is *repulsive in the level of the Helmholtz free energy*, as is commonly recognized. When we proceed to the Gibbs free energy level, the mean field approach shows the presence of an attraction between macroions. The basic theme of this monograph is to discuss whether the assumption of equal free energies is correct or not for macroionic systems.

Finally, our discussion is consciously limited to structure formation in macroionic systems. In our view, systematic discussion of fundamental physicochemical properties of macroionic solutions or dispersions cannot be undertaken, because the corresponding experimental data are still scanty.

The work to be described in the present monograph is due to outstanding effort and capability of our coworkers, to whom our most sincere thanks are dedicated. It is our privilege to thank the following scientists, who played central roles in their respective fields, gave us pertinent comments, and read and corrected the manuscripts: Professor Kensaku Ito (Toyama University), Dr. Toshiki Konishi (Central Laboratory, Rengo Co., Ltd.), Professor Hideki Matsuoka (Kyoto University), Dr. Tadatomi Shinohara (Kyoto Sangyo University), Dr. B.V.R. Tata (Indira Gandhi Centre for Atomic Research), Professor Junpei Yamanaka (Nagoya City University), Dr. Hiroshi Yoshida (Hitachi Laboratory), and Professor Tsuyoshi Yoshiyama (Kyoto Sangyo University). Helpful comments on Chap. 8 were received from Professor Mitsunori Fukuda (Hyogo University of Education).

The following scientists were very generous in reading and correcting the manuscript: Dr. Jack Douglass, Professor Robert M. Fitch, Professor Kenneth S. Schmitz, and Dr. M. Smalley.

Last but not least, our sincere thanks go to Professor Helmut Ringsdorf, University of Mainz, and Professor Raj Rajagopalan, University of Florida, for their kind assistance in publication and to Dr. Marion Hertel, Springer Verlag, for her patience.

Kyoto Japan
January 2005

Norio Ise
Ikuo S. Sogami

Contents

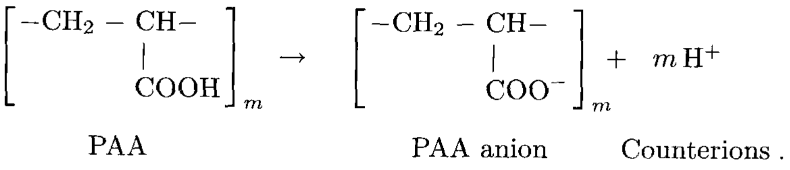
1

Introduction

1.1 Macroionic Systems and the Scope of the Book

In the present monograph, we will discuss ionic polymer solutions and colloidal dispersions. When these substances are dissolved into a solvent, they produce ionic species having large molecular weights and their counterions. We know a variety of naturally occurring ionic polymers and chemically synthesized compounds. Examples of the former are nucleic acids and some proteins, which play an important role in biological systems. Examples of synthetic ionic polymers are polyacrylic acid (PAA), polystyrenesulfonic acid (PSS) and polyallylamine (PAAm).

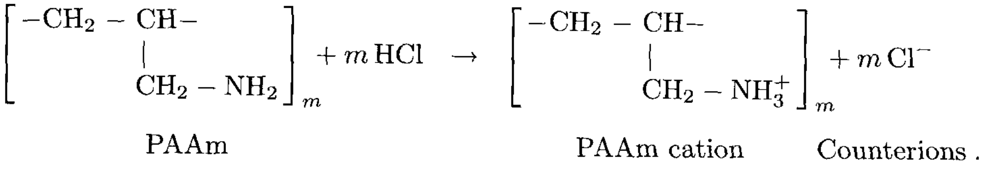
PAA is a high polymer, in which m acrylic acid molecules $\mathrm{CH_2{=}CH(COOH)}$ are linearly polymerized by *covalent bonds*. The number m is called the degree of polymerization and is usually of the order of 10^3. When PAA is dissolved in a dissociating solvent like water, anionic macroions and counterions are produced. In the following scheme, the counterions are protons but they may be metal cations such as $\mathrm{Na^+}$:



$$\left[\begin{array}{l} -\mathrm{CH_2}-\mathrm{CH}- \\ \qquad\qquad | \\ \qquad\quad \mathrm{COOH} \end{array}\right]_m \rightarrow \left[\begin{array}{l} -\mathrm{CH_2}-\mathrm{CH}- \\ \qquad\qquad | \\ \qquad\quad \mathrm{COO^-} \end{array}\right]_m + \; m\,\mathrm{H^+}$$

PAA PAA anion Counterions .

PAAm is a cationic polymer and dissociates into PAAm cations and anionic counterions as shown below:



$$\left[\begin{array}{l} -\mathrm{CH_2}-\mathrm{CH}- \\ \qquad\qquad | \\ \qquad\quad \mathrm{CH_2}-\mathrm{NH_2} \end{array}\right]_m + m\,\mathrm{HCl} \rightarrow \left[\begin{array}{l} -\mathrm{CH_2}-\mathrm{CH}- \\ \qquad\qquad | \\ \qquad\quad \mathrm{CH_2}-\mathrm{NH_3^+} \end{array}\right]_m + m\,\mathrm{Cl^-}$$

PAAm PAAm cation Counterions .

In the case of NaCl, it dissociates into Na^+ and Cl^-, which both have low molecular weights. On the other hand, PAA anions and PAAm cations have high molecular weights. If m is 10^3, one polymer ion (macroion) has an analytical charge number Z_a of 10^3, which is exceedingly larger than 1 for Na^+. Since the interionic interaction is proportional to the square of the charge number, the physical properties of macroionic solutions are largely different from those of simple salt solutions. Furthermore, the macroionic solutions behave in ways considerably different from non-ionic polymer solutions. This basic point was correctly realized by Trommsdorf and Staudinger [1]. They noticed in 1931 that the viscosity of aqueous solutions of metal salts of PAA was much higher than that of non-ionic polymers, attributed it to a kind of structure formation by electrostatic interaction and made the following statement:

> *Like in NaCl solutions ⋯, PAA ions are surrounded by Na^+ in solutions of sodium salt of polyacrylic acid, and Na^+ interacts with PAA anions. As the consequence, the relative position of PAA anions is fixed. This is a kind of structure formation. This structure is distorted in flow, so that the solution viscosity is increased.*

These molecules are flexible in solution because of the free rotation around C-C bonds in the main chain. They cannot assume a definite conformation or shape. Even if they are stretched out into rods, the end-to-end distance is about 100 nm, so that their shapes and the distribution in solution cannot be directly observed.

In order to confirm the properties indirectly inferred, we avail ourselves of colloidal particles, which are so large that they can be "seen" by microscope. We study the dynamics and distribution of particles in their dispersions. The colloid field was called "*Die Welt der Vernachlässigten Dimensionen* " [2] and was one of the fields which could not be studied smoothly. Recent technical developments, however, have made it possible to control the particle diameter, its distribution, and the charge number. As a result, it is now possible to study the behavior of well-defined particles in dispersions in real time. The microscopic information thus obtained is expected to provide support to the indirectly derived conclusion on the behavior of "invisible"}, flexible ionic polymers in solution.

In this monograph our discussion will be limited to a recent topic, namely structure formation in dilute solutions or dispersions. We imply by the structure formation that solute ions or colloidal particles form a more or less three-dimensionally regular distribution, though not in the solid state. Such a structure was anticipated in an early stage of the investigation of ionic systems. For example, in the case of simple electrolyte solutions, Ghosh assumed lattice-like ionic arrangements to calculate the osmotic coefficient (the activity coefficient of the solvent) [3]. With such an assumption, the interionic distance is inversely proportional to the cube-root of the concentration. On the other hand, physico-chemical properties at low concentrations are experimentally found to show square-root relationships. This concentration dependence could be accounted for by the Debye-Hückel (DH) theory of strong electrolytes [4]. When the concentration is raised, however, the cube-root dependence is found experimentally [5]. For ionic polymer solutions, a cube-root law is also experimentally observed [6]. In early theoretical treatments of ionic polymer solutions, some sorts of lattice-like distribution of rodlike macroions were explicitly or implicitly assumed [7–11].

Regardless of whether the geometrical model of infinitely long rods is realistic or not, we need to mention that, like in the case of Ghosh, *space-filling* ordered arrangements were assumed in these theories. In other words, the entire solution was assumed to be uniformly covered by the regular arrangement. This is what we call the one-state structure in the present monograph. Such a structure can be easily accepted by invoking repulsive interaction between similarly charged macroions which are confined by closed container walls.

What we wish to emphasize in the present monograph is not such a uniform distribution of macroions, however. Instead, we pay attention to *localized, ordered structures* of ionic polymers or particles, or *self-sustaining structures* without the help of walls. As a result of the existence of such structures, the systems are microscopically inhomogeneous. Although the existence of this inhomogeneity is surprising in condensed systems, it has been inferred for flexible ionic polymer solutions by scattering experiments (Chap. 3) and "visualized" for colloidal dispersions (Chap. 4). These experimental observations are difficult to explain when we admit the existence of repulsion only or if we assume no interaction between macroions [11]. The observations led the present authors to accept an attraction between macroions albeit similarly charged. In the present monograph, we wish to describe and understand the microscopic inhomogeneity in macroionic systems from experimental and theoretical points of view, while we try not to be redundant with some recent publications [12–15].

1.2 Principles for Structure Analysis on Macroionic Systems

The structure of a macroionic system means the average configuration of macroionic solutes in the dispersion. Analysis of such structures is made by using diffraction and scattering methods with visible light, X-rays and neutrons. The macroionic solutes forming an ordered configuration give rise to coherent contributions to diffraction and scattering amplitudes. By contrast, contributions from the solvent molecules associated always with random phases due to thermal motion are cancelled out on average.

Electromagnetic waves of visible light and X-rays being incident into solutions are scattered by charged constituents of atoms and molecules, viz, electrons and atomic nuclei. As shown below, the scattering effect of electromagnetic waves by charged particles is proportional to the inverse-square of the mass of the particle (See (1.10) and (1.13)). Accordingly the scattering effects from atomic nuclei are negligibly small. The scattering effect of a proton (the lightest atomic nucleus) is smaller than that of an electron by a factor 4.0×10^6, since the ratio of masses of the proton and electron is about 2.0×10^3. Therefore, the structure analysis of macroionic solution by electromagnetic waves observes electron distributions in macromolecules in the solution.

To investigate colloidal dispersions, in which the size of the particles is approximately of the order of visible light, the optical microscope is useful in addition to laser diffraction analysis. In particular, the method of optical microscopy can be used to observe both random motion and ordering formation of colloidal particles.

If the macroions do not include atoms with magnetic moments, neutrons can penetrate a cloud of electrons and interact directly with atomic nuclei through the strong nuclear force. Accordingly, by observing scattering cross sections of neutrons, it is possible to obtain information concerning the distribution of atomic nuclei of solutes. To make structural analysis of macroionic systems by neutron scattering and diffraction, we must use a facility where cold neutrons and an apparatus with a long camera length are available.

In this section, we explain basic concepts and theories that are necessary to understand scattering and diffraction of electromagnetic waves using a simple model. States of electrons bound in macromolecules and their interactions with electromagnetic waves must be described, respectively, by quantum mechanics and quantum field theory [16–18] in principle. However, it is well known that a simple oscillator model for bound electrons, i.e., the *Thomson model*, is effective for the structure analysis of matter. In this section we use the Thomson model with modification to explain the scattering of electromagnetic waves by bound electrons.

In the Thomson model, the electron is assumed to be bound around an equilibrium position and make a simple harmonic oscillation with a proper frequency. The electron which is accelerated by external electromagnetic waves executes a forced oscillation and emits electromagnetic waves. The motion of the electron is described by Newton's equations of motion. We formulate the scattering theory of electromagnetic waves by bound electrons in the classical Thomson model by using minimum information on the quantum distributions of electrons inside atoms and molecules.

1.2.1 Electromagnetic Waves Emitted by Accelerated Electrons

Suppose that one electron around the equilibrium point E in a solute molecule is accelerated by electromagnetic waves. We observe expanding electromagnetic waves emitted by the electron at the point P on a spherical surface which has its origin at E and a sufficiently large radius R.

Note that the electromagnetic wave emitted at the time $\tau = t - R/c$ from the point E is observed at the time t at the point P where c is the speed of light. The observed electric and magnetic fields, $\boldsymbol{E}$ and $\boldsymbol{B}$, are calculated to be

$$\boldsymbol{E} = -\frac{e}{c^2}\frac{1}{R}\boldsymbol{n} \times [\boldsymbol{n} \times \boldsymbol{a}(\tau)] \tag{1.1}$$

and

$$\boldsymbol{B} = \boldsymbol{n} \times \boldsymbol{E} \tag{1.2}$$

where $\boldsymbol{a}(\tau)$ is the acceleration of the electron at τ and $\boldsymbol{n}$ is the unit vector for the direction from E to P. Derivation of these equations is explained in standard textbooks on electromagnetism [19]. The *Poynting vector* which represents the energy flux carried by the electromagnetic field per unit time is given by

$$\boldsymbol{S} = \frac{c}{4\pi}\boldsymbol{E} \times \boldsymbol{B} = \frac{c}{4\pi}\boldsymbol{E}^2\boldsymbol{n} = \frac{e^2}{4\pi c^3}\frac{1}{R^2} \mid \boldsymbol{n} \times \boldsymbol{a}(\tau) \mid^2 \boldsymbol{n}. \tag{1.3}$$

Then, the electromagnetic energy $\mathrm{d}P$ passing through the solid angle $\mathrm{d}\Omega$ in unit time is given by the *Larmor formula* [19]

$$\mathrm{d}P = (\boldsymbol{n} \cdot \boldsymbol{S})R^2\mathrm{d}\Omega = \frac{e^2}{4\pi c^3} \mid \boldsymbol{n} \times \boldsymbol{a}(\tau) \mid^2 \mathrm{d}\Omega\,. \tag{1.4}$$

1.2.2 The Modified Thomson Model

Let us assume that an electron with mass m executes a harmonic oscillation with proper frequency ω_0 around an equilibrium position. The forced oscillation of the electron by an external electric field is described by Newton's equation of motion.

Suppose that a monochromatic electromagnetic wave being incident into a macroionic dispersion has a wavelength λ inside the dispersion, a frequency ν and a unit vector $\boldsymbol{n}_0$ representing the direction of propagation. Choosing an origin O inside the dispersion, we express the equilibrium position E by a vector $\boldsymbol{r}$ and a displacement from E by $\boldsymbol{\eta}$. In the complex number representation, the incident electric field at the time t at E is expressed by

$$\boldsymbol{E}_0(\boldsymbol{r}, t) = \boldsymbol{E}_0\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r}-\mathrm{i}\omega t} = \boldsymbol{\epsilon}_0 E_0\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r}-\mathrm{i}\omega t} \tag{1.5}$$

where $\boldsymbol{k}_0 = (2\pi/\lambda)\boldsymbol{n}_0$ is the wave vector and $\omega = 2\pi\nu$ is the angular frequency. Here the electric field is decomposed as $\boldsymbol{E}_0 = E_0\boldsymbol{\epsilon}_0$ with E_0 the strength of the electric field and $\boldsymbol{\epsilon}_0$ the polarization vector. As is well known, observed quantities must be calculated by taking real parts in the complex number representation.

The electron around the equilibrium position E is driven by the external electric field $\boldsymbol{E}_0(\boldsymbol{r}, t)$ in (1.5) to make a forced oscillation described by the equation

$$m\frac{\mathrm{d}^2\boldsymbol{\eta}}{\mathrm{d}t^2} = -m\omega_0^2\boldsymbol{\eta} - m\gamma\frac{\mathrm{d}\boldsymbol{\eta}}{\mathrm{d}t} - eE_0\boldsymbol{\epsilon}_0\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r}-\mathrm{i}\omega t}\,. \tag{1.6}$$

Here, the velocity of the electron is assumed to be so small compared with the speed of light that effects of the magnetic component of the Lorentz force are negligible. On the right-hand side of this equation, the first and second terms represent, respectively, the elastic force with spring constant $m\omega_0^2$ and the damping factor associated with emission of radiation. The third term expresses the external force by the incident wave, and its phase factor $e^{i\boldsymbol{k}_0\cdot\boldsymbol{r}}$ plays a crucial role in analyzing interference and diffraction of the scattered electromagnetic field.

It is crucial to recognize that the space part $\boldsymbol{k}_0 \cdot \boldsymbol{r}$ of the phase factor in (1.6) is independent of the time variable. Namely, the displacement vector $\boldsymbol{r}$ of the equilibrium point E is assumed not to depend on t. Otherwise (1.6) becomes a highly nonlinear differential equation with respect to t, which is hard to solve. As a matter of fact, the existence of the static equilibrium position E is a basic prerequisite for the Thomson model of the atom in which electrons are assumed to execute oscillatory motion around such equilibrium positions inside a sphere with positive charges. However, this basic postulate was disproved by the *Earnshaw theorem* insisting that "*A charged particle cannot have an equilibrium point in a static electric field*" [20].

The Earnshaw theorem is readily proved by the following argument. Suppose that a charged particle takes an equilibrium position in a static electric field. Then, such a position must be on the top (at the bottom) of the electric potential, and accordingly the second derivative of the electric potential takes positive (negative) values in an infinitesimal region surrounding the position. This implies that the divergence of the electric field strength which is the gradient of the electric potential is non-vanishing at the position. Consequently, owing to the Gauss theorem in (2.2) in Sect. 2.2, the equilibrium position for the particle must already be occupied by another charge. This is a contradiction.

Rutherford who had discovered atomic nuclei proposed a dynamical model of the atom, in place of the Thomson model, where electrons revolve around the nucleus. This model is free from criticism by the Earnshaw theorem. However, the new dynamical model was also doomed to suffer difficulty. As described in Sect. 1.2.1, the acceleration causes the charged particle to emit electromagnetic radiation. Accordingly the revolving electrons inside the atom have to fall into the nucleus in 10^{-11} second by losing their energy by radiation. This difficulty of the Rutherford model could be resolved only by the theory of quantum mechanics in which the stationary states of electrons are described by the new concept of quantum probabilistic distribution.

The advent of quantum mechanics has partially and effectively revived the once-denied Thomson model of the oscillating electron for electromagnetic radiation. In the *modified Thomson model*, the acceleration mechanism of the electron around the equilibrium position E is described by the Newtonian equation (1.6) provided that quantum mechanics is allowed to describe the position E by a probabilistic distribution inside an atom. Namely, we calculate first the electromagnetic waves emitted by the accelerated electron by solving