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Phase Transitions of Simple Systems

With 81 Figures and 32 Tables

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Preface

Thermodynamic concepts of aggregate states and their phase transitions developed during the 19th Century and are now the basis of our contemporary understanding of these phenomena. Thermodynamics gives an universal, macroscopic description of the equilibrium properties of phase transitions independent of the detailed nature of the substances. However understanding the nature of phase transitions at the microscopic level requires a different approach, one that takes into account the specifics of the interparticle interactions. In this book, we lay the groundwork that connects the microscopic phenomena underlying phase changes with the macroscopic picture, but in a somewhat restricted way. We deal only with systems in which electronic excitations are not important, only with atomic systems, and only with homogeneous systems. We also restrict our analysis to systems in which only pairwise interactions need be included, and, in many parts of the treatment, to systems in which one need consider only the interactions between nearest neighbor atoms. In establishing these restrictions, we can be guided by the solid and liquid states of inert gases and the phase transitions between them, although the subsequent analysis is relevant and applicable for a series of other physical systems.

To study the behavior of a system of many interacting identical particles, we work extensively with its potential energy surface (PES), a surface in a many-dimensional space whose independent variables are the monomer coordinates or some transformation thereof. A central property of any multidimensional PES is its large number of local minima. We can think of the evolution of a system described by this surface as the trajectory taken by the system as it passes from the neighborhood of one local minimum to another. At moderate and low temperatures, the system remains in each of these neighborhoods for a time long compared with the period of atomic oscillations. This allows us to distinguish two forms of the system's excitation: thermal or vibrational excitation corresponds to the energy of oscillations of individual atoms; configurational excitation is that associated with location and change of location among the neighborhoods of the local minima of the PES. From this

perspective, a phase transition corresponds to a change of the configurational excitations of the system.

The approach treats both bulk systems and small systems, and their differences and similarities. One can gain insights into the properties of bulk phase transitions by seeing how they evolve from the equilibria of phase-like forms of systems of only tens of atoms, for example. Some of the information comes from analysis of simple model systems; some comes from simulations, by molecular dynamics for example; some, especially for bulk systems, comes from experimental data.

One particularly illustrative phenomenon is the apparent paradox that, while bulk systems show sharp phase transitions and satisfy the Gibbs phase rule, with two phases in equilibrium at only one pressure if the temperature is fixed, atomic clusters can coexist in two or more phases over a range of temperatures and pressures. The analysis presented here shows how the behavior of bulk systems evolves from the behavior of very small systems, as the number of particles comprising the system grows larger. In the course of the analysis, one encounters surprises that resolve themselves when one comes to understand some of the tacit assumptions underlying traditional development of thermodynamics and kinetics for bulk systems. We learn, by examining microscopic behavior as well as traditional properties such as caloric curves, how the fundamentals of thermodynamics remain valid even when some of those tacit assumptions are not.

Much of the development is based on the model of a simple dense material consisting of particles and voids. We introduce the void as an elementary configurational excitation. In a lattice, a void is very much like a vacancy, but here, “void” implies that the neighbors of the vacancy can relax to a stable form. In an amorphous material, the void need not have a specified shape and may even change its size. The void concept, together with the distinction between configurational and vibrational degrees of freedom, opens the way to analytic and combinatorial approaches to elucidating the phase behavior of small and large systems alike. The liquid and solid, for example, differ in the density of their voids. In small systems, they can coexist over a range of conditions because the solid is stabilized by its low energy with few voids, and the liquid is stabilized by its high entropy with many voids.

This book, devoted as it is to various aspects of the nature of the phase transitions in simple systems, addresses some aspects of the kinetics of phase changes as well as their thermodynamics and equilibrium properties. We hope that this approach will enable colleagues to go further, to extend these ideas to more complex systems, and to apply them in the expanding field of nanoscale materials.

Chicago,
Moscow,
August 2007

R. Stephen Berry
Boris M. Smirnov

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Introduction

To consider phase states and phase transitions, we must look first to thermodynamic concepts. According to classical thermodynamics, the phase or aggregate state of an ensemble of interacting atoms or molecules is a uniform spatial distribution of atoms or molecules that is restricted by boundaries. A transition between two phases of a macroscopic system has a stepwise character and results from variation of thermodynamic parameters, typically (but not necessarily) the temperature. Most commonly, the variable controlling the phase and phase change is an intensive variable. A thermodynamic description of phase transitions has advantages and disadvantages. The advantage of this description is its universal character; it is suitable for many kinds of systems with different interactions between atoms or molecules. But for this reason, a thermodynamic description of aggregate states and phase transitions is formal and does not allow one to exhibit the nature of phenomena under consideration at a microscopic level.

Computer simulation of clusters and bulk ensembles of interacting atoms opens the possibility for us to understand the nature of the phase transitions at that molecular level. But the microscopic character of this phenomenon depends on the form of interatomic interaction. In analyzing this phenomenon from the microscopic standpoint, we will consider ensembles of atoms interacting via a pairwise force; this corresponds to the simplest model and, apart from ionic materials such as alkali halide, represents the predominant interaction. This allows us to understand at a level deeper than the phenomenological that thermodynamics gives us, the nature of an aggregate state of an ensemble of interacting atoms. This approach provides a microscopic description to connect the true phase transition between equilibrium states with related phenomena, in particular, with the glass transition.

A real example of a system with pairwise interaction between atoms is a condensed inert gas. Indeed, because the atoms of inert gases have completed electron shells, the exchange interaction between such atoms and hence the short-range interatomic forces are repulsive in this case. Hence at equilibrium interatomic distances in condensed inert gases, the interaction potential of

two atoms is small in comparison with typical electronic energies. As a result, interactions between two atoms do not influence the interactions of these atoms with other atoms in condensed inert gases. In other words, two-body interactions dominate the behavior of such systems; we can neglect three-body and higher interactions and retain a reasonably accurate picture of the behavior of such systems.

Next, because the exchange interaction between two atoms is dominated by electron coordinates near the axis connecting the atoms, the pairwise character of interaction is conserved at high pressures, and is primarily a repulsive interaction. Therefore inert gases are objects that satisfy models based on a pairwise interaction. Consequently, in the following discussion, we make use of the properties of condensed inert gases in detail. We restrict our discussion only to the “heavy” inert gases Ne, Ar, Kr and Xe, whose atoms may be considered as classical particles under the conditions of phase changes. Ignoring quantum effects simplifies the analysis of an ensemble of identical particles yet retains the essential characteristics of such systems. The study of a bulk ensemble of classical atoms together with known properties of inert gases gives rich insights about these atomic systems and their phase transitions. Moreover we bring the properties of bulk systems into a common context with their very small counterparts, the nanoscale particles and clusters composed of the same inert gas atoms.

To study the phase changes of an ensemble of classical particles, one can separate excitations of such systems into two groups. The first group relates to thermal motion of particles, specifically their oscillations in the total system; the second group consists of configurational excitations, which include diffusion and translational motions because the high density of the systems require configurational excitation for translational motion to be possible. Phase transitions are closely related to configurational excitation of a particle ensemble, and therefore configurational excitation is the principal object of study of this book. At zero temperature the first, vibrational excitations disappear; hence it is convenient to study the configurational excitation of an ensemble of classical particles at zero (vibrational) temperature, to be free from thermal motion of particles. An effective way to characterize the behavior of such a system is to cast that behavior in terms of motions on its potential energy surface (PES) in a many-dimensional space of particle coordinates. The important property of the PES, that is the basis of understanding of the nature of configurational excitation, is that the PES has many local minima which are separated by barriers. Just this fact allows us to separate the thermal and configurational degrees of freedom. Indeed, assuming a typical barrier height is large compared to thermal energy, we find that an ensemble has many oscillations near a given local minimum of the PES before the transition to the neighboring minimum. The first kind of excitations are motions within the region of a single local minimum on the many-dimensional surface; the second kind correspond to motions from one local minimum to another.

Classical thermodynamics, being intrinsically phenomenological, does not allow us to understand phases and phase transitions at the microscopic level. Fortunately, it is possible to study a simple ensemble of classical particles with pairwise interaction to reach a level of understanding at that level. Indeed, we define a phase as a group states of configurational excitations with similar excitation energies if these excitations are realized with roughly similar probabilities. For the dense particle ensembles under consideration, in the present context we have only two phase states, the solid or ordered state and the liquid or disordered state. Of course, one can go to a more detailed description to recognize different solid structures as different phases, and, for small systems at least, distinguish liquid character or liquid-like phases in terms of the behavior of different shells. We shall study these problems in detail later.

By analyzing some phenomena exhibited by an ensemble of classical atoms from the standpoint of the local minima of the PES, we obtain a depend understanding of these phenomena. In reality, one can simplify the concept of the PES by introducing voids as elementary configurational excitations. If we assume individual voids to be identical, the void concept simplifies the understanding and description of the properties of the phase states.

It is convenient to start the void concept from formation of vacancies in a crystal structure of classical particles. Suppose the system contains n particles and v voids. Indeed, assume the number of classical particles of an ensemble $n + v$ is so large that surface particles of this particles give a negligible contribution to its parameters. In the ground configurational state these particle form a close-packed crystal structure, face-centered cubic or hexagonal, that follows from the pairwise interaction between the particles. Each internal particle of this structure has 12 nearest neighbors. In order to prepare a configurationally excited cluster consisting of n particles and v internal vacancies, v internal particles are removed to the outside. If newly-formed vacancies do not border one another (i. e. a number of vacancies $v < n/12$), this system is stable and its state corresponds to a local minimum of the PES. At large excitation ($v > n/12$) such a state is unstable; the system formed by removing atoms and creating site vacancies relaxes by shrinking under its own attractive van der Waals forces. As a result, vacancies are converted into voids. These are free spaces between particles that vary their shape and size in time. We consider and use average parameters of voids. Of course, during relaxation, vacancies can join into bubbles – large empty constituents inside a system of particles. However usually (and in any case, for condensed inert gases) vacancies convert into voids and not into large bubbles. Moreover, the number voids is equal approximately to the number of initial vacancies. This method of generation of voids inside a particle ensemble is convenient for the void analysis.

Describing the phase state of a system of identical classical particles within the framework of the void concept simplifies our understanding of various phenomena connected with configurational excitation and phase transitions. In

particular, displacement of elementary configurational excitations in terms of voids describes some key properties and phenomena in these systems. A void can transfer to a neighboring site; this is precisely the transition between two neighboring local minima of the PES. Because neighboring local minima of the PES are separated by barriers, this transition has an activation character, so it proceeds only slowly at low temperature. A sum of transitions between local minima of PES, each considered as the motion of independent voids, determine diffusion of voids inside the particle ensemble. Naturally the diffusion coefficient of voids decreases sharply with decreasing temperature. Hence at low temperatures, one can prepare an unstable configurational state of this system with voids frozen inside it. The transition into a stable configuration state consists of diffusion of voids to the boundaries, and since this time is long, these states are characterized by long lifetimes at low temperatures. These states are total analogous with glassy states, so we have a possibility to analyze the glassy states for simple systems.

Because the phase states of a system of classical particles differ by the presence or absence the voids inside the system, a phase transition is characterized by displacement of those voids. Hence, growth of nuclei of a new phase inside the system, the nucleation process, can be considered as a result of diffusion of voids in a space separated into two regions by the phase boundary. Considering the growth of nuclei of a new phase as a result of diffusion of voids allows us to analyze some aspects of this phenomenon in a simple manner.

Thus, this book is devoted the analysis of ensembles of classical particles with pairwise interaction between particles and configurational excitations of these ensembles which include the phase transitions and adjacent phenomena. Because we consider simple systems, ensembles of classical particles with pairwise interaction and not at low particle densities, this allows us to describe these phenomena in a simple manner that conserves the strictness of the analysis.

Thermodynamics of Ensembles
of Classical Particles

Excitations in Simple Atomic Ensembles

1.1 Thermodynamics and Dynamics of Particle Ensembles

We consider systems of large numbers of identical particles. From the thermodynamic standpoint, this system can form an aggregate state or a phase. According to the definition [1–5], a phase is a uniform distribution of particles in a region restricted by a boundary. Thermodynamics determines stable, equilibrated aggregate states that correspond to the minima of an appropriate thermodynamic potential in accordance with external conditions [2, 4, 6–8]. In particular, if an ensemble of identical particles is in equilibrium at a certain temperature and pressure, a corresponding equilibrium volume per particle follows from the minimum of the Gibbs thermodynamic potential (or the Gibbs free energy). This means that if an initial volume per particle differs from the equilibrium one, the system will compress or expand until this equilibrium volume is attained.

An ensemble of simple particles, of atoms for example, can be in the solid or liquid state; these aggregate states are characterized by different thermodynamic parameters. At almost any given temperature, one of these aggregate states is stable and the other one is metastable. The stable state is characterized by a lower Gibbs thermodynamic potential. However, at the melting point, the Gibbs thermodynamic potentials for these states are identical. If the distribution of particles differs from that in a stable aggregate state, the ensemble relaxes to a stable aggregate state. This means that parameters of the space and velocity particle distribution tend to those of aggregate states. The final state may be stable or metastable, depending on which locally stable atomic distribution is “closer”, i. e. more kinetically accessible to the initial distribution.

In addition to the stable aggregate states or phases, the distribution of particles of many systems can form a glassy state. From the thermodynamic standpoint, a glassy state does not ordinarily correspond to the global minimum of a thermodynamic potential (i. e. it is not a stable aggregate state, according to our usage here), but the relaxation time for a glassy state is

very long compared to the relaxation time of vibrations. Because relaxation typically involves some activation step, the relaxation time increases dramatically with a temperature decrease, so glassy states are typically realized at low temperatures.

The thermodynamic description of aggregate and glassy states is universal and is valid for any ensemble of many identical particles. Therefore we use it below as a basis and will characterize these states by thermodynamic parameters. But for a deep understanding of the nature of these states when we include in consideration interaction between particles, the connection between the form of interaction between particles and aggregate or glassy states of a particle ensemble may depend on the nature of the interparticle interactions. Moreover, we must leave the realm of thermodynamics when we describe the process of relaxation of an ensemble of particles from a thermodynamically unstable state [9]. Indeed, first, relaxation of such states typically has a non-exponential character [10, 11] although at small deviation from equilibrium, this deviation varies in time in an exponential way. Second, the relaxation time τ_{rel} typically has an Arrhenius temperature dependence,

$$\tau_{\text{rel}} \sim \exp\left(\frac{E_a}{T}\right), \quad (1.1)$$

if the relaxation process proceeds from one local equilibrium state to another and occurs by transition over a barrier. Here E_a is the activation energy to cross the barrier, T is the temperature which, here and below, is expressed in energy units. Relaxation of glassy states may be non-Arrhenius [12–15]. Third, relaxation of glassy states may be non-linear [9], that is, the relaxation time need not be proportional to the degree of excitation. These all exhibit the complexity of this problem.

For this reason a large number of models exist to describe various aspects of phase and glassy transitions. Each model for change of a particle configuration can be connected with certain real objects and hence has a phenomenological character. Therefore although we have a strict thermodynamic description of equilibrium states for ensembles of identical particles, this description loses its universality when we move to discussing the evolution of non-equilibrium ensembles.

Dynamics of particle ensembles may be analyzed by methods of computer simulation for specified interactions between particles and external constraints. In each case, we deal with a specific landscape of the potential energy surface (PES) in a many-dimensional space of particle coordinates; evolution of the particle ensemble corresponds to motion of a point in this space along the PES. In this manner, one can describe dynamics of the particle ensemble. This approach is productive at low temperatures (or low kinetic energies of particles) when the character of the PES landscape is important for the evolution of the system. In the course of evolution, the configuration of the particles varies; simulation allows us to study transitions between different particle configurations.

The objects of our consideration are ensembles of classical atoms with simple interactions between them. In analyzing these ensembles, we will be guided by clusters and bulk systems of inert gases excluding helium, so the atoms can be treated as classical, and we apply the above general principles to these objects. We also treat model systems of particles that interact through Lennard-Jones potentials which have been analyzed widely by numerical methods of computer simulation. Because of its simplicity, various aspects of the phase and glassy transitions for these objects may be analyzed in simpler and more transparent assumptions than for very realistic representations of the rare gas atoms. This allows us to exhibit the essences of the nature of phenomena under consideration.

1.2 Interaction of Inert Gas Atoms

Because ensembles of inert gas atoms are the objects we are using as our guides, we consider interaction of inert gas atoms in detail. In all the cases under consideration, the interaction potential of two inert gas atoms is small compared to a typical value of any electronic excitation energy of the system, in particular, the ionization potentials of these atoms. Figure 1.1 gives the separation dependence of the interaction potential for two inert gas atoms, and Table 1.1 contains the parameters of the minimum of the interaction potential for two identical atoms of inert gases that are examined in this analysis [16–19]. The Table presents various data governing the interactions and collisions of inert gas atoms which are determined by their interaction potential. We note again that the depth of a typical attractive interatomic potential well D_e is small compared to the ionization potentials for inert gas atoms, and the equilibrium distance between two atoms in a diatomic molecule R_e exceeds considerably any typical atomic size a_o . Although the potential well depth D_e differs from the dissociation energy D_o of the corresponding diatomic molecule due to zero-point vibrations of the atoms, for a system of many interacting atoms the contribution of zero-point vibrations to the dissociation energy is small and we shall ignore this.

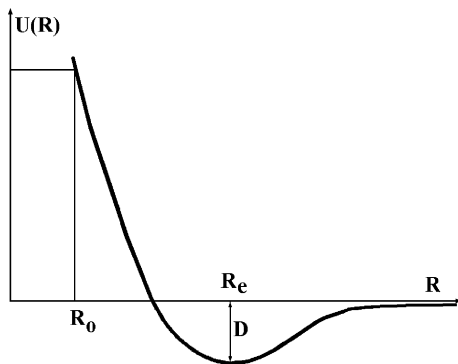


Fig. 1.1. A typical interaction potential between two atoms as a function of the distance between atoms, and the parameters of Table 1.1

Table 1.1. Parameters of the pair interaction potential for inert gas atoms. R_e , D_e are the parameters of the interaction potential minimum, $\gamma = \sqrt{2m_e I}/\hbar$, C is the parameter of the asymptotic expression (1.2) for the exchange interaction potential; parameters k , R_o [20] correspond to variables in the formula (1.3), where $U(R_o) = 0.3$ eV, and the parameter k' are given by formula (1.4).

	Ne	Ar	Kr	Xe
R_e , Å	3.09	3.76	4.01	4.36
D_e , meV	3.64	12.3	17.3	24.4
D_e , K	42	143	200	278
γa_o	1.26	1.08	1.03	0.944
C	15	51	54	14
R_o , Å	2.07	2.85	2.99	3.18
k	7.6	8.1	7.7	5.9
$2R_o\gamma$	9.9	11.6	11.6	11.3
k'	7.1	9.4	9.2	8.6

At relatively large distances between atoms where the interaction potential is relatively small, the interaction can be represented as a sum of long-range and short-range interactions. A long-range interaction is a result of interaction of induced atomic dipoles (Fig. 1.2) and is determined by redistribution of electrons in the region around their parent atoms. One can consider this interaction as an electrostatic interaction of two polarizable charge distributions that leads to a small change in their mean spatial distributions.

The short-range, repulsive part of the interaction is due to the combination of the exchange interaction of the electrons and the Coulomb repulsion of the nuclei. The exchange interaction is determined by overlapping of the wave functions of valence electrons of the neighboring atoms. The exchange interaction effectively drives electrons away from the internuclear axis, unshielding the positive cores from one another and hence producing a repulsive force. As the internuclear distance is made smaller, that force grows, not at the rate given by Coulomb's law but by the rate at which the unshielding occurs. As a consequence, at moderate to large distances between interacting atoms, their exchange interaction $\Delta(R)$ is characterized by a dependence [21–24] $\Delta(R) \sim \exp(-2\gamma R)$, where $\hbar^2\gamma^2/(2m_e)$ is the atomic ionization potential, \hbar is the Planck constant, and m_e is the electron mass. A more precise expres-

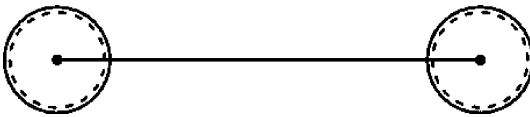


Fig. 1.2. The regions occupied by valence electrons in atoms (*solid circles*) and those responsible for the long-range interaction between atoms (*dotted circles*)

sion for the exchange interaction potential at those distances is [25, 26]

$$\Delta(R) = CR^{\frac{7}{2\gamma}-1} \exp(-2\gamma R), \quad \gamma R \gg 1. \quad (1.2)$$

Table 1.1 lists the parameters of this formula. Since the exchange interaction between two atoms is determined by the overlap of the wave functions of their valence electrons, it is generated predominantly in the region close to the internuclear axis, as shown in Fig. 1.3. The ratio of the volume of this region to the entire volume of valence electrons is $\sim (\gamma R)^2$.

The exchange interaction determines the interatomic repulsion over a range of distances R in which the repulsive interaction potential $U(R)$ is still small compared with the ionization potential I of the atoms, but is large compared with the dissociation energy of the weakly-bound diatomic molecule D_e of rare gas atoms,

$$D_e \ll U(R) \ll I.$$

We can infer that the repulsive interaction potential of two inert gas atoms is ~ 1 eV in the distance range of interest here from measurements of the differential cross section of scattering on small angles for incident atoms of K eV-energies. Because this interaction potential varies sharply with the distance R between atoms, it is convenient to approximate it by the relation

$$U(R) = U(R_o) \left(\frac{R_o}{R} \right)^k = \frac{A}{R^k}, \quad k \gg 1, \quad (1.3)$$

and Table 1.1 contains parameters of this formula which are taken from the review [20]. Together with this, Table 1.1 contains the parameter

$$k' = 2\gamma R_o - \left(\frac{7}{2\gamma} - 1 \right) \quad (1.4)$$

that characterizes the exchange repulsion interaction potential at a separation R_o . As the data of Table 1.1 show, the asymptotic behavior of the repulsive interaction potential (1.2) corresponds also to a sharp increase of repulsion when atoms approach this range of interaction energies.

If several inert gas atoms partake in interaction, their potential energy is a sum of pair interaction potentials of the atoms, within the approximations we use here. Indeed, in the case of a long-range interaction, any

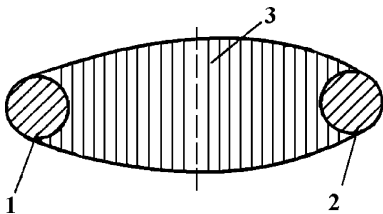


Fig. 1.3. The region occupied by valence electrons in atoms (1,2) and that responsible for the exchange interaction between those atoms (3)

induced dipole moment is relatively small, enough to justify our dropping three-body and higher multibody interaction terms. The exchange interaction potential that leads to repulsion and follows from the overlapping of wave functions of valence electrons is created mostly in a spatial region close to the axis that joins the atoms. Because of the small and very localized volume of the region of the overlapping wave functions (its ratio to the total valence electron volume is $\sim (R_o\gamma)^{-2}$), one can ignore three-body exchange interactions. Hence, the potential energy U of an ensemble of inert gas atoms can be represented as a sum of the pair interaction potentials for these atoms

$$U = \sum_{i,k} U(|\mathbf{R}_i - \mathbf{R}_k|) , \quad (1.5)$$

where \mathbf{R}_i , \mathbf{R}_k are coordinates of the atoms of this ensemble. Moreover, since at longer ranges the pair interaction potential of inert gas atoms drops significantly with increasing interatomic distance, one can, for many purposes, restrict the discussion to interactions between neighboring atoms. Thus, in considering an ensemble of inert gas atoms, we deal with interaction between neighboring atoms only and this interaction has a pairwise form. (An exception that can serve as an example is determining the relative stabilities of the two close-packed lattice structures, the face-centered cubic or fcc and the hexagonal close-packed or hcp structures. To determine the relative energies of these correctly, one must include second- and third-nearest neighbor atoms.)

One more characteristic of the interaction of many inert gas atoms is large values of their electronic excitation energies; these exceed by orders of magnitude the typical energies of interatomic interaction. Hence transitions between electronic levels of a system of interacting inert gas atoms are not relevant to describing the course of evolution of the system; we need consider only the system in its ground electronic state. Thus the development of this system corresponds to its motion in a many-dimensional space of atomic coordinates along the potential energy surface of the ground electronic state. From another perspective, this system is a strong dielectric, a consideration that simplifies its analysis.

A strong and convenient method for analyzing ensembles with simple atomic interactions is based on the scaling or similarity law. The concept of the scaling law is based on composing a quantity of each dimensionality from three dimensional parameters [27–29]. Dimensionality or scaling analysis is used widely in hydrodynamics and gas dynamics [28, 30, 31]. In the case of inert gas systems, the three natural, basic parameters are the atomic mass m , the equilibrium distance between atoms $r_o = R_e$ and the well depth for the pair interaction potential of atoms $\varepsilon_o = D$. These parameters are given in Table 1.2 together with typical values of some quantities constructed from these parameters for inert gases [32]. One then uses the basic parameters to define new variables, scaled by these parameters, to derive relations that apply “universally” for an entire family of substances.

Table 1.2. Reduced parameters of an ensemble of interacting inert gas atoms ($1\text{a.u.m.} = 1.6606 \cdot 10^{-24}\text{g}$)

	Ne	Ar	Kr	Xe
$r_o, \text{\AA}$	3.09	3.76	4.01	4.36
$\varepsilon_o, \text{meV}$	3.64	12.3	17.3	24.4
$m, \text{a.u.m.}$	20.18	39.95	83.80	131.3
$p_o = D/R_e^3, \text{MPa}$	20.2	37.1	43.0	47.1
$V_o = R_e^3, \text{cm}^3/\text{mol}$	17.8	32.0	38.8	49.9
$\rho_o = m\sqrt{2}/R_e^3, \text{g/cm}^3$	1.606	1.764	3.051	3.718

1.3 Similarity Law for Simple Atomic Ensembles

Note that the scaling analysis based on the parameters of Table 1.2 assumes that an analyzing parameter or process is determined mostly by attractive interaction of atoms in the range of their maximum attraction. The scaling analysis is effective for processes and phenomena that are determined by collective interaction of atoms when each atom interacts simultaneously with several surrounding atoms. In such cases, the parameter under consideration follows from many simultaneous interactions that would often create a difficulty when one must sum these interactions in an unscaled representation. In the scaling analysis, we effectively circumvent this summation by using the result of an experiment or computer simulation. Scaling makes it possible to use the result from one system to determine this parameter for other related ensembles. Because of the identical inherent character of their interactions, the parameters for two different systems are connected by the scaling law.

1.4 Evolution of Particle Ensembles

We now consider the evolution of an ensemble of classical particles, using systems of a finite number of inert gas atoms – clusters of inert gases – as our guide. The pair interaction between atoms dominates, and the basic interaction for a test atom is that with neighboring atoms (in contrast to electrolytes with their Coulomb interactions). The limiting case of this system is a cluster with a short-range interaction of a test atom with surrounding ones in which only nearest neighbors interact. In this case, the form of the interaction potential between nearest neighbors can have almost any form consistent with our assumptions.

The evolution of this ensemble of classical atoms is considered as motion of a point along the potential energy surface in a phase space of atomic coordinates. The potential energy surface for a cluster contains many minima separated by saddles; the number of these local minima increases sharply

with cluster size [33–38]. The number of geometrically distinct locally stable structures increases approximately exponentially, with the number n of particles, and the number of permutational isomers of each increases approximately as $n!$ [36, 38, 35]. Hence, one can describe the cluster’s evolution as a result of transitions between local minima of the extremely complex potential energy surface. These motions correspond to saddle-crossing dynamics [38–42]. Within the framework of this description, a rare gas cluster remains near a given minimum of the potential energy surface for a relatively long time interval, since its average total kinetic energy is lower than typical saddle heights. By that, we can infer that the vibrational modes within the vicinity of the local minimum can come to thermal equilibrium [43].

The saddle character of the potential energy surface was first revealed in computer calculations of the cluster energy [33, 34]. In order to find the global minimum of a cluster’s internal energy and the optimal configuration of its atoms, one can start from any atomic configuration, calculate the cluster’s energy for this configuration, and then move to a new atomic configurations with lower energy. In this manner one can hope to reach the global minimum of the cluster’s effective potential energy and the optimal atomic configuration at zero temperature. But this method is virtually impossible to realize because a typical cluster’s PES has so many local minima. For example, the Lennard-Jones cluster of 13 atoms (a cluster with the Lennard-Jones interaction potential between atoms) was characterized by 988 local minima on its potential energy surface [33, 34]; a later, more detailed analysis [39] found 1478 local minima and 17,357 saddle points of the potential energy surface for this Lennard-Jones cluster of 13 atoms; still more recently, that number has reached 1509 [38]. The number of geometrically distinct local minima of the cluster PES increases roughly exponentially with increasing the number of cluster atoms [35, 36, 42].

Understanding the behavior of such a cluster is a natural subject for simulation by molecular dynamics or Monte Carlo methods. Evolution of this system consists of passage of classical particles from the vicinity of an initial local minima of the PES to any of its neighboring minima [37, 38, 42, 40, 44]. Studying the corresponding saddle-crossing dynamics [41] is a convenient method for analyzing cluster evolution. Figure 1.4 demonstrates the character of transitions between neighboring minima of the potential energy surface. In Fig. 1.4 schematic projections of a potential energy surface on planes are given in a space of atomic coordinates. Only one coordinate is used for each transition, the coordinate that corresponds to the lowest energy path connecting the two local minima of the potential energy surface for that given transition. These (curvilinear) coordinates are of course different for each transition. Energy levels for each well indicate an average atomic energy along a coordinate of the transition. Because this average energy is often significantly less than the barrier height, such transitions occur infrequently, only when the kinetic energy of atoms in the transition degree of freedom exceeds its average energy

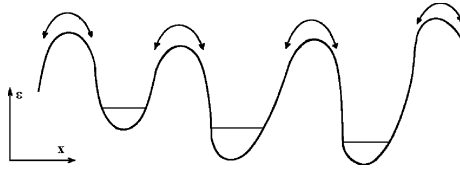


Fig. 1.4. Evolution of an ensemble of atoms in the ground electron state as propagation of a point in the multidimensional space of atomic coordinates, resulting from a transition between neighboring local minima of the potential energy surface. The x -coordinate lies along the axis joining the positions of two neighboring local minima of the potential energy surface; hence this direction is different for each pair of neighboring local minima

adequately. Of course having energy enough to cross a saddle is a necessary but not sufficient condition for a system to find its way across that saddle. If the saddle is very narrow and in some obscure corner of the surface, passage over it may occur extremely infrequently. Hence a cluster typically has many oscillations inside a given well until it passes to another local minimum of the potential energy surface. Then identifying a given local (but not global) minimum of the potential energy surface as a configurational excitation of a cluster, one can separate it from thermal motion associated with atomic oscillations.

We divide the cluster excitation into two parts, thermal and configurational, assuming those to be independent. We characterize a configurational state of this system by the local minimum of the potential energy surface around which the system vibrates. Assuming the dwell time of a system near one minimum of the potential surface is long compared with the period of atomic vibrations in that local minimum, one can separate the energy into two parts [43]. The first is the thermal energy of particle vibrational (and rotational) motion, and the second, configurational part is that of the local minimum of the potential surface in whose region the system resides. At zero temperature, the only energy of the system is the configurational energy of the system at its global minimum on the PES. Next, since the dwell time is high, thermodynamic equilibrium for thermal motion of atoms is established during cluster location in a given configuration state. This means that the thermal motion of the atoms can be characterized by a temperature. If a cluster is isolated, this temperature is dependent of the configurational state. Note that this temperature refers only to thermal motion of atoms, while the character of excitation of configurational states in general need not be connected with this temperature. This implies that one may well find a non-equilibrium distribution of configurational excitations in a thermodynamic analysis of atomic ensembles. This is of course particularly so if the system is undergoing any kind of relaxation.

Figure 1.5 shows the possibility of dividing degrees of freedom for cluster atoms into the configurational and vibrational, with a simple example of 13 atoms and a short-range interaction between atoms, i. e. the total potential

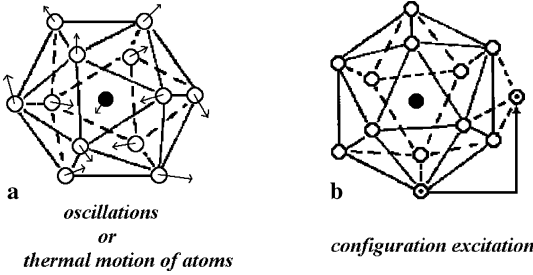


Fig. 1.5. Two types of cluster excitations: cluster oscillations due to thermal motion of atoms (a) and configurational excitation (b)

energy of the cluster is determined by interaction between nearest neighbors predominantly. In the lowest configurational state, the atoms of this cluster form an icosahedron with one central and 12 surface atoms, and all the surface atoms are equivalent. In addition, distances between neighboring surface atoms are equal also, so that joining of the centers of neighboring surface atoms gives a surface consisting of 20 equilateral triangles. Then if we exclude three degrees of freedom for motion of the cluster as a whole (its center-of-mass motion) and another three degrees of freedom associated with the rotation of the cluster about its center, we find 33 remaining vibrational degrees of freedom. These appear for each configurational cluster state. These vibrations or thermal motion of atoms are shown in Fig. 1.5a for the ground configurational state, the regular icosahedron.

As we see, the central atom of the icosahedral cluster forms 12 bonds with surface atoms. Each surface atom has 5 bonds with neighboring surface atoms and one bond with the central one. Hence, there are 30 bonds between surface atoms and the total number of bonds of this cluster is 42 for the ground configurational state. The lowest configurationally excited state corresponds to transition of one surface atom to a face of the cluster surface as shown in Fig. 1.5b. In this configurational state, the promoted atom has only 3 bonds with surface atoms, so the total number of bonds for this state is 39; this configurational excitation yields a loss of three bonds. Note that this state is separated by a barrier from the ground state in a space of atom coordinates. Indeed, exciting the cluster from the ground configuration into this excited one by promoting a surface atom, we can conserve at most only two of the bonds between this atom and its neighbors during the course of the transition, while in the final state this atom has three bonds. Hence the transition between these two configurations proceeds through any of the saddle points located on the top of a barrier or saddle that separates these configurational states.

One more peculiarity relates to this symmetric system. If we enumerate atoms, we have one ground configurational state when each atom occupies a certain position, and this configuration corresponds to a certain point in the many-dimensional space of the potential energy surface. In this case we obtain 180 equivalent points in this space that correspond to this lowest excited configurational state. Indeed, this excited state can be obtained by promoting any of the 12 surface atoms of the cluster, and this promoted atom can