MOLECULAR MODELING APPLICATIONS IN CRYSTALLIZATION

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Introduction to Molecular Modeling

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1.1. Introduction

In recent years modeling methods based on computer simulation have become a useful tool in solving many scientific and engineering problems. Moreover, with the introduction of powerful workstations the impact of applications of computer simulation is expected to increase enormously in the next few years. To some extent, computer-based modeling methods have filled the long existing gap between experimental and theoretical divisions of natural sciences such as physics, chemistry, and biology. Such a dramatic role for computer simulation methods is due to the *statistically exact character* of information that they provide about the *exactly defined model* systems under study. The term "statistically exact information" means "information known within the range defined by standard deviation of some statistical distribution law." This deviation can usually be reduced to an extent required by the problem under study. The term "exactly defined model" means that all parameters required to specify the model *Hamiltonian* are known exactly.

Let us specify the role of computer-based simulation with respect to information obtained by analytical derivation and experiment:

1. The analytically exact information is available only for a few theoretical models that allow exact analytical solutions. The most celebrated example of such a model in statistical physics is the two-dimensional Ising model for the nearest-neighbor interacting spins in the absence of external fields. Its analytically exact solution was obtained by Onsager (1944). However, in the majority of other cases, where exact analytical solutions are not known, it is customary to use different approximations. And it is often the case that these approximations are uncontrollable. The same Ising model in the three-dimensional case does not have an exact solution. Needless to say, even less is known about the models with more realistic

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intermolecular potentials. Therefore, computer simulation is often used to verify different approximations involved in analytical solutions.

2. The experimentally exact information is also never available because it is impossible to completely define the Hamiltonian of an experimental system. In some important experimental problems, such as nucleation, the Hamiltonian is very often unknown because one or more mechanisms can be triggering the observed result. Nucleation can be triggered either by the intrinsic system properties (metastability) or by unknown impurities present in experimental systems. Therefore, modeling models based on computer simulation are required in order to understand the relative role of metastability and impurities on the nucleation phenomenon.

This brief discussion illustrates that very often there is not enough information to link theory and experiment. Thus, analytical approximations involved in the description of an experimentally observed phenomenon are not necessarily related to the real driving forces of this phenomenon. Computer-based modeling methods provide a unique opportunity to build a “coherence bridge” between the analytical approximations involved in the solution of major problems and the experimental information available.

This chapter serves a much simpler goal than review of the modern modeling methods based on computer simulation. We will try to present some basic concepts of statistical mechanics (Section 1.2), thermodynamics (Section 1.3), intermolecular interactions (Section 1.4) and the Monte Carlo method (Section 1.5) which underlie all major modeling methods based on computer simulation (Section 1.6).

1.2. Basics of Statistical Mechanics

1.2.1. *Statistical Distributions*

Let a given macroscopic system have $2N$ degrees of freedom, that is each of N particles (molecules) constituting the system of volume V, will be described by its coordinate q_n and moment $p_n (n = 1, \ldots, N)$. Therefore, all various states of the system under consideration can be represented by points in the *phase space* P with $2N$ coordinates $\{q_n, p_n; n = 1, \ldots, N\}$. A state of the system changes with time and, consequently, the point in space P representing this state, also known as the *phase point*, moves along a curve known as a *phase trajectory*.

Let us also introduce the probability $\omega(q; p) = \omega(q_1, \ldots, q_N; p_1, \ldots, p_N)$ that the system state is represented by a point belonging to the infinitesimal $2N$-dimensional interval $\{[q_n; q_n + \mathrm{d}q_n] \oplus [p_n; p_n + \mathrm{d}p_n]; n = 1, \ldots, N\}$:

$$\mathrm{d}\omega(q; p) = \rho(q; p)\mathrm{d}q\mathrm{d}p; \; \rho(q; p) = \rho(q_1, \ldots, q_N; p_1, \ldots p_N), \; \mathrm{d}q\mathrm{d}p = \prod_{n=1}^{N} \mathrm{d}q_n \mathrm{d}p_n, \tag{1.1}$$

where $\rho(q;p)$ is the probability density in space P also known as the *statistical distribution function*. This function must obviously satisfy the *normalization condition*:

$$\int_P \mathrm{d}\omega(q,p) = \int_P \rho(q,p)\mathrm{d}q\mathrm{d}p = 1, \tag{1.2}$$

which simply expresses the fact that the sum of probabilities of all states must be unity.

It is clear that at any time instant, t, phase points, representing states of a closed system, are distributed in phase space according to the same statistical distribution function $\rho(q;p)$. Therefore, the movement of these points in phase space can be formally described by applying the *continuity equation* expressing the fact of constancy of the total number of phase points (system states):

$$\frac{\mathrm{d}\rho(q;p)}{\mathrm{d}t} = \sum_{n=1}^{N}\left(\frac{\partial\rho(q;p)}{\partial q_n}\frac{\mathrm{d}q_n}{\mathrm{d}t} + \frac{\partial\rho(q;p)}{\partial p_n}\frac{\mathrm{d}p_n}{\mathrm{d}t}\right) = 0 \tag{1.3}$$

This equation, known as the *Lioville equation,* states that the distribution function is constant along the phase trajectories.

If the statistical distribution is known, one can calculate the probabilities of various values of any physical quantities depending on the system states. One also can calculate the mean of any such quantity $f(q;p)$:

$$\langle f \rangle = \int_P f(q;p)\mathrm{d}\omega(q;p) = \int_P f(q,p)\rho(q;p)\mathrm{d}q\mathrm{d}p, \tag{1.4}$$

where the sign $\langle \ldots \rangle$ designates the average over an ensemble of phase points.

It is understandable that in a sufficiently long time, τ, the phase trajectory passes many times through each infinitesimal volume $\Delta q\Delta q$ of the phase space. Let $\Delta t(q;p)$ be the part of the total time τ during which the system states belong to the phase space volume $\Delta q\Delta q$. Then, when the total time τ goes to infinity, the ratio $\Delta t(q;p)/\tau$ tends to the limit:

$$\Delta w(q;p) = \lim_{\tau\to\infty}\frac{\Delta t(q;p)}{\tau}. \tag{1.5}$$

It is important to note that, by virtue of relations (1.4) and (1.5), the averaging with respect to the distribution function, also known as *statistical averaging* allows one to drop the necessity of following the variation of physical quantity $f(q;p)$ with time in order to determine its mean value:

$$\langle f \rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} f(t)\mathrm{d}t. \tag{1.6}$$

Relationship (1.6) is known as the *ergodic theorem* and was first formulated by Boltzmann (see textbook by Landau and Lifshitz (1988) for details).

1.2.2. *Ensembles*

The statistical distribution function $\rho(q; p)$ can be expressed entirely in terms of some combinations of the variables q and p, which remain constant when a system moves as a closed system. These combinations are known as *mechanical invariants* or *integrals of motion*, which remain constant during the motion of a system state in phase space. The distribution function, being constructed from mechanical invariants, is, therefore, itself a mechanical invariant.

It is possible to restrict significantly the number of mechanical invariants on which the function $\rho(q; p)$ can depend. In order to demonstrate this, we have to take into account the fact that the distribution function $\rho_{1+2}(q; p)$ for a non-overlapping combination of two subsystems is equal to the product of distribution functions $\rho_1(q; p)$ and $\rho_2(q; p)$ describing each subsystem:

$$\rho_{1+2}(q; p) = \rho_1(q; p)\rho_2(q; p)$$

Hence, we obtain:

$$\log[\rho_{1-2}(q; p)] = \log[\rho_1(q; p)] + \log[\rho_2(q; p)], \tag{1.7}$$

that is, the logarithm of the distribution function is an additive quantity. We reach the conclusion, therefore, that the logarithm of the distribution function must not be merely a mechanical invariant, but an additive mechanical invariant. As we know from mechanics, there exist only seven independent additive mechanical invariants: the energy $E(q; p)$, three components of the momentum vector $\boldsymbol{P}(q; p)$, and three components of the angular momentum vector $\boldsymbol{M}(q; p)$. The only additive combination of these quantities is a linear combination of the form:

$$\log[\rho_j(q; p)] = \alpha_j + \alpha_{j,E}E_j(q; p) + \boldsymbol{\alpha}_{j,\boldsymbol{P}} \cdot \boldsymbol{P}_j(q; p) + \boldsymbol{\alpha}_{j,\boldsymbol{M}} \cdot \boldsymbol{M}_j(q; p), \quad j = 1, 2, \tag{1.8}$$

where coefficients α_j, $\alpha_{j,E}$, $\boldsymbol{\alpha}_{j,\boldsymbol{P}}$ and $\boldsymbol{\alpha}_{j,\boldsymbol{M}}$ are some constants of the j subsystem. Conditions required for the determination of these constants include normalization for α_j and seven constant values of the additive mechanical invariants for $\alpha_{j,E}$, $\boldsymbol{\alpha}_{j,\boldsymbol{P}}$ and $\boldsymbol{\alpha}_{j,\boldsymbol{M}}$. Therefore, the values of additive mechanical invariants (energy, momentum, and angular momentum) completely define the statistical properties of a closed system, that is, the statistical distribution function $\rho_j(q; p)$ and the mean values of any physical quantity related to them.

The correct way of determining the distribution function for a closed system is:

$$\rho(q; p) = \text{const}\ \delta[E_0 - E(q; p)]\ \delta[\boldsymbol{P}_0 - \boldsymbol{P}(q; p)]\ \delta[\boldsymbol{M}_0 - \boldsymbol{M}(q; p)], \tag{1.9}$$

where E_0, $\boldsymbol{P}_0$ and $\boldsymbol{M}_0$ are some given values of $E(q;p)$, $\boldsymbol{P}(q;p)$ and $\boldsymbol{M}(q;p)$. The presence of the *Dirac delta function* ensures that the distribution function $\rho(q;p)$ is zero at all points in phase space where one or more of seven quantities $E(q;p)$, $\boldsymbol{P}(q;p)$ or $\boldsymbol{M}(q;p)$ is not equal to the given values E_0, $\boldsymbol{P}_0$ or $\boldsymbol{M}_0$. The statistical distribution $\rho(q;p)$ defined by expression (1.9) is known as *microcanonical distribution* describing the *microcanonical ensemble* of system states. The momentum and angular momentum of the closed system depend on its motion as a whole (uniform translation and uniform rotation). Therefore, one may conclude that a statistical state executing a given motion depends only on its energy. In consequence, energy is of great importance in statistical physics. Thus, the j-subsystem distribution function acquires the following simple form:

$$\ln[\rho_j(q;p)] = \alpha_j + \alpha_{j,E} E_j(q;p), \quad j = 1, 2. \tag{1.10}$$

Therefore, the microcanonical distribution function can be simplified as follows:

$$\rho(q;p) = Z_{\mathrm{mc}}^{-1}(V;N)\,\delta[E_0 - E(q;p)],\ Z_{\mathrm{mc}}(V;N) = \rho(N)\int\!\!\int \delta[E_0 - E(q;p)]\mathrm{d}q\mathrm{d}p, \tag{1.11}$$

where $Z_{\mathrm{mc}}(V;N)$ is some normalization constant and $\rho(N)$ is the *degeneracy factor* giving the relative number of indistinguishable configurations in phase space (see Section 2.2.3). The closed systems considered above are not of substantial interest in physics. It is much more important to study systems that interact with their environment, by energy or/and matter exchange. Therefore, let us first consider systems that can exchange energy with their environment. In this case, equation (1.11) is no longer satisfied and an expression for the distribution function $\rho(q;p)$ can be derived directly from relationships given by equations (1.7) and (1.10), which yield:

$$\rho(q;p) = Z_{\mathrm{c}}^{-1}(\beta;V;N)e^{-\beta E(q;p)},\ Z_{\mathrm{c}}(\beta;V;N) = \rho(N)\int\!\!\int e^{-\beta E(q;p)}\mathrm{d}q\mathrm{d}p, \tag{1.12}$$

where β is a constant, whose physical meaning will be described later. The result given by expression (1.12) is one of the most important in statistical physics. It gives the statistical distribution of any macroscopic subsystem that is a comparatively small part of a large closed system. The distribution (1.12), known as the *Gibbs distribution* or *canonical distribution,* describes the *canonical ensemble* of system states (phase points).

So far, we have always tacitly assumed that the number of particles in a system is some given constant and have deliberately passed over the fact that in reality particles may be exchanged between a system and its environment. In other words, the number of particles N in the system will fluctuate about its mean value $\langle N\rangle$. The distribution function now depends not only on the energy of the state but also on the number of particles N in the system. Equation (1.10), therefore, acquires the form:

$$\ln[\rho_j(q;p;N)] = \alpha_j + \alpha_{j,E}E_j(q;p) + \alpha_{j,N}N, \quad j = 1, 2. \tag{1.13}$$

An expression for the distribution function $\rho(q;p;N)$ can be derived directly from relationship (1.13) yielding:

$$\begin{aligned}\rho(q;p;N) &= Z_{\mathrm{gc}}^{-1}(\beta;V)e^{\beta[\mu N - E(q;p;N)]}, Z_{\mathrm{gc}}(\beta;V;\mu)\\ &= \sum_{N=0}^{\infty}\rho(N)\int\int e^{\beta[\mu N - E(q;p;N)]}\mathrm{d}q\mathrm{d}p,\end{aligned} \tag{1.14}$$

where μ is a constant that will be defined later. The distribution $\rho(q;p;N)$, known as the *grand canonical distribution,* describes the *grand canonical ensemble* of system states.

1.2.3. *Partition Functions*

The normalization constants $Z_{\mathrm{mc}}(V;N)$, $Z_{\mathrm{c}}(\beta;V;N)$ and $Z_{\mathrm{gc}}(\beta;V;\mu)$ introduced by relationships (1.11), (1.12), and (1.13) respectively are known as *partition functions*. The partition function can be obtained by summing up the Boltzmann factors, $\exp[-\beta E(q;p)]$, over all states. For systems possessing continuous spectra, the summation over states is substituted by integration over phase space. As will be demonstrated later, the partition function serves as the connection between macroscopic quantities and microscopic states.

The states of a classical system are continuously distributed in phase space and, therefore, cannot be counted. In order to determine the *classical analog* of a quantum state, let us take into account that the uncertainty $\Delta q\Delta q$ in the determination of any quantum state is restricted from below (see Landau and Lifshitz (1980) for details):

$$\Delta q\Delta p \sim h^{sN}(\textit{Heisenberg uncertainty principle}), \tag{1.15}$$

where h is the Planck constant ($h = 6.6256 \cdot 10^{-27}$ erg · sec) and s is a degree of freedom of each molecule constituting the system ($s = 3$ for a one-atom molecule, $s = 5$ for a rigid two-atom molecule, etc.). In other words, any phase point located in a cell of volume h^{sN} cannot be distinguished from any other point located in the same cell. Moreover, there is another source of uncertainty. In quantum mechanics it is impossible to distinguish phase-space configurations such as (A) state S_1 belongs to cell C_1 and state S_2 belongs to cell C_2 and (B) state S_1 belongs to cell C_2 and state S_2 belongs to cell C_1. Therefore, the system containing N particles can possess $N!$ indistinguishable configurations ($N!$ different permutations over N cells) of the same states in phase space. The expression for the degeneracy factor $\rho(N)$, first introduced in expression (1.11), has the form:

$$\rho(N) = \frac{1}{h^{sN}N!}. \tag{1.16}$$

1.2.3.1. *The Microcanonical Ensemble*

In this case the system under consideration is closed (there is neither energy nor matter exchange with the environment). Given expressions (1.10) and (1.11), it is straightforward to derive the following expression for the partition function in the case of a microcanonical ensemble:

$$Z_{\mathrm{mc}}(V; N) = \frac{1}{h^{sN}N!}\int\int \delta[E_0 - E(q; p)]\mathrm{d}q\mathrm{d}p. \tag{1.17}$$

1.2.3.2. *The Canonical Ensemble*

In this case, the system under consideration is "semi-closed" (there is energy but no matter exchange with the environment). Given expressions (1.10) and (1.11), it is straightforward to derive the following expression for the partition function in the case of a canonical ensemble:

$$Z_{\mathrm{c}}(\beta; V; N)\frac{1}{h^{sN}N!}\int\int e^{-\beta E(q;p)}\mathrm{d}q\mathrm{d}p. \tag{1.18}$$

In classical statistics, the energy $E(q, p)$ can be written as the sum of the potential $U(q)$ and kinetic $K(p)$ energies. The potential energy is dependent on the interaction between the system molecules and is a function of their coordinates. The kinetic energy is a quadratic function of the momenta of the molecules. Therefore, the probability $\mathrm{d}\omega(q; p)$ introduced by relations (1.1) and (1.2) can be presented as the product of two factors:

$$\mathrm{d}\omega(q; p) = \mathrm{const} \cdot e^{-U(q)}e^{-K(p)}\mathrm{d}q\mathrm{d}p, \tag{1.19}$$

where the first factor depends only on the molecular coordinates and the second only on their momenta. Equation (1.14) allows the conclusion that the probabilities for molecular coordinates and momenta are independent and the probability of one does not influence probability of the various values of the other. Thus, the probabilities $\mathrm{d}\omega(q)$ and $\mathrm{d}\omega(p)$ of the various values of the molecular coordinates and momenta can be written in the form:

$$\mathrm{d}\omega(q) = \mathrm{const}_U \cdot e^{-U(q)}\mathrm{d}q,\ \mathrm{d}\omega(p)\ \mathrm{const}_K \cdot e^{-K(p)}\mathrm{d}p, \tag{1.20}$$

where $\mathrm{const} = \mathrm{const}_U\mathrm{const}_K$. Since the sum of probabilities of all possible values of the momenta and coordinates must be unity, each of the probabilities $\mathrm{d}\omega(q)$ and $\mathrm{d}\omega(p)$ has to be normalized separately by integrating over the coordinates and momenta, respectively. Therefore, normalization allows the determination of constants const_U and const_K.

Let us consider the probability distribution for the molecular momenta. The kinetic energy of the entire system is equal to the sum of the kinetic energies of all molecules in the system. This means that the probability $\mathrm{d}\omega(p)$ can be expressed as the product of factors, with each factor dependent on the momentum of only one molecule. This means that the momentum probabilities of different molecules are independent (the momentum of one molecule does not affect the probabilities of various momenta of any other molecule). The probability distribution for the momentum of each individual molecule can, therefore, be written.

For a molecule of mass m the kinetic energy $K(p)$ is: $K(p) = K(p_x, p_y, p_z) = (p_x^2 + p_y^2 + p_z^2)/(2m)$, where p_x, p_y, and p_z are the Cartesian coordinates of its momentum. Thus, the probability $\mathrm{d}\omega(p) = \mathrm{d}\omega(p_x, p_y, p_z)$ acquires the form:

$$\mathrm{d}\omega(p_x, p_y, p_z) = \mathrm{const}_K \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT}\right)\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z. \tag{1.21}$$

The normalization constant const_K can be easily found to be $\mathrm{const}_K = (2\pi mk_BT)^{-3/2}$. Changing from momenta to velocities, $\boldsymbol{p} = m\boldsymbol{v}$, one can write the corresponding velocity probability $\mathrm{d}\omega(v) = \mathrm{d}\omega(v_x, v_y, v_z)$ as follows:

$$\begin{aligned}\mathrm{d}\omega(v_x, v_y, v_z) &= \rho(v_x, v_y, v_z)\mathrm{d}v_x, \mathrm{d}v_y, \mathrm{d}v_z, \rho(v_x, v_y, v_z)\\ &= \left(\frac{m}{2\pi k_BT}\right)^{3/2}\exp\left(-\frac{m(p_x^2 + p_y^2 + p_z^2)}{2k_BT}\right).\end{aligned} \tag{1.22}$$

The distribution function $\rho(v_x, v_y, v_z)$ is known in the literature as the *Maxwell-Boltzmann distribution.*

1.2.3.3. *The Grand Canonical Ensemble*

In this case the system under consideration is open (there are both the energy and matter exchanges with the environment). Given expressions (1.21) and (1.22), the following expression can be derived for the partition function in the case of a grand canonical ensemble:

$$Z_{\mathrm{gc}}(\beta; V; \mu) = \sum_{N=0}^{\infty}\frac{e^{\beta\mu N}}{h^{sN}N!}\int\int e^{-\beta E(q;p;N)}\mathrm{d}q\mathrm{d}p. \tag{1.23}$$

This relationship for partition function is sometimes rewritten in terms of the *fugacity*, $z = e^{\beta\mu}$:

$$Z_{\mathrm{gc}}(\beta; V; z) = \sum_{N=0}^{\infty}\frac{z^N}{h^{sN}N!}\int\int e^{-\beta e(q;p;N)}\mathrm{d}q\mathrm{d}p. \tag{1.24}$$

In this section we have introduced three different ensembles that describe a system in thermodynamic equilibrium. The microcanonical ensemble describes a closed system, the internal energy $E(q; p)$ of which is fixed: $E(q; p) = E_0$. The canonical ensemble describes a "semi-closed" system, the energy of which is not fixed. However, the *mean internal energy*, $\langle E \rangle$ of the canonical ensemble is fixed. The grand canonical ensemble describes an open system, the energy and number of particles of which are not fixed. However, the mean energy $\langle E \rangle$ and the number of particles $\langle N \rangle$ of a grand canonical ensemble are fixed.

It is important to note that the forms of partition function (1.17), (1.18), and (1.24) obtained for the equilibrium microcanonical, canonical, and grand canonical ensembles correspond to the maximum entropy achievable in a state of thermodynamic equilibrium (see Sections 1.3.1 and 1.3.2).

1.2.4. *Relationship between Statistical Mechanics and Thermodynamics*

Classical thermodynamics is based on many empirical results, which have been studied, systemized, generalized, and formulated in the form of the *Three Laws of Thermodynamics*. These laws allow derivation of many useful relationships between different quantities characterizing various mechanical and thermal processes. However, there is a flaw inherent in thermodynamics. Thermodynamics provides relationships between various quantities, but does not provide methods to determine their absolute values. For example, thermodynamics establishes a functional relationship between the heat capacity C_V at constant volume V and the heat capacity C_P at constant pressure P. If C_P is known, then C_V can be determined theoretically without need for experiments. However, thermodynamics alone provides no method to allow determination of the value of C_P itself. This is the role of statistical mechanics.

Therefore, statistical mechanics allows solution of the following two major problems:

1. derivation of expressions for macroscopic thermodynamic quantities from microscopic mechanics (for example, from the molecular energy levels that can be determined by spectroscopic methods);
2. derivation of microscopic properties (for example, the nature of intermolecular interactions) from the measurable macroscopic quantities.

All quantities used in thermodynamics can be divided into three major groups. The first group contains *external quantities*, parameters such as volume V, number of particles N, external fields (gravitational, electromagnetic), etc., the absolute values of which are fixed either by the external environment or by an experimentalist. The second group contains *mechanical quantities*, such as internal energy E and pressure P. The third group is specific to thermodynamics and contains *thermal quantities*, parameters such as temperature, entropy, etc. These quantities do not have any microscopic meaning and can be defined exclusively on the macroscopic level. For example, one can define the molecular energy, but it is impossible to define the temperature of a single molecule. Therefore, thermal quantities are defined by the entire ensemble.

For the sake of simplicity, let us consider the most widely used case of canonical ensemble and introduce the function $H_c(\beta;\, V;\, N)$:

$$Z_c(\beta;\, V;\, N) = e^{-\beta H_c(\beta;\, V;\, N)}. \tag{1.25}$$

There exists the following important relationship:

$$\begin{aligned}\left[\frac{\partial}{\partial\beta}(\beta H_c(\beta;\, V;\, N))\right]_{V,N} &= -\frac{\partial}{\partial\beta}\ln[Z_c(\beta;\, V;\, N)]\\ &= Z_c^{-1}(\beta;\, V;\, N)\frac{1}{h^{sN}N!}\int\int E(q;\, p)e^{-\beta E(q;p)}\mathrm{d}q\mathrm{d}p = \langle E\rangle,\end{aligned} \tag{1.26}$$

where the brackets $[...]_{V,N}$ designate an expression taken at constant V and N. Relationship (1.26) is easily recognizable in traditional thermodynamics if one accepts the following treatments:

1. $\beta = 1/k_B T$ is the inverse temperature ($k_B = 1.38054 \times 10^{-16}$erg/K is the *Boltzmann constant*).
2. $H_c(\beta;\, V;\, N)$ is the *Helmholtz free energy* of the canonical ensemble (see Section 1.3.8).

Thus, within the framework of statistical mechanics the Helmholtz free energy of canonical ensemble $H_c(\beta;\, V;\, N)$ can be defined as follows:

$$H_c(\beta;\, V;\, N) = -k_B T\ln[Z_c(\beta;\, V;\, N)]. \tag{1.27}$$

The same considerations carried out for the grand canonical ensemble allow derivation of another important relationship:

$$\mu = \left[\frac{\partial H_{gc}(\beta;\, V;\, \mu)}{\partial N}\right]_{T,V}, \tag{1.28}$$

where μ is the *chemical potential* for one molecule. Therefore, basic relationships (1.26) and (1.28) provide the linkage between statistical mechanics and thermodynamics.

1.2.5. *Fluctuations*

Let us consider the most widely utilized case of the canonical ensemble. The normalization condition for this ensemble can be rewritten as:

$$\frac{1}{h^{sN}N!}\int\int e^{\beta[H_c(\beta;\, V;\, N)-E(q;p)]}\mathrm{d}q\mathrm{d}p = 1. \tag{1.29}$$

Differentiation of this relationship twice with respect to β gives:

$$\frac{1}{h^{sN}N!}\int\int e^{\beta[H_c(\beta;V;N)-E(q;p)]}\left[\left(\frac{\partial}{\partial\beta}(\beta H_c(\beta;\ V;\ N))-E(q;p)\right)^2 + \frac{\partial^2}{\partial\beta^2}[\beta H_c(\beta;\ V;\ N)]\right]\mathrm{d}q\mathrm{d}p=0. \tag{1.30}$$

Now, taking into account relationship (1.26) for $\langle E\rangle$, we obtain:

$$\langle(E-\langle E\rangle)^2\rangle\equiv\langle E^2\rangle-\langle E\rangle^2=-\frac{\partial^2}{\partial\beta^2}[\beta H_c(\beta;\ V;N)]=-\frac{\partial\langle E\rangle}{\partial\beta}, \tag{1.31}$$

where

$$\langle E^2\rangle=\frac{1}{h^{sN}N!}\int\int E^2(q;p)e^{[H_c(\beta;V;N)-E(q;p)]}\mathrm{d}q\mathrm{d}p.$$

It is important to note that differentiation with respect to β in expressions (1.30) and (1.31) is carried out at constant volume V. Therefore, expression (1.31) can be rewritten as follows:

$$\langle(E-\langle E\rangle)^2\rangle\equiv\langle E^2\rangle-\langle E\rangle^2=k_BT^2C_V,\ \text{where}\ C_V=\left[\frac{\partial\langle E\rangle}{\partial T}\right]_V. \tag{1.32}$$

Relationship (1.32) is fundamental since it relates fluctuations of the microscopic energy to a macroscopic measurable quantity, such as the heat capacity at constant volume. C_V and E are additive quantities (see Section 1.2.2 for the definition of additivity), that is, they are proportional to N. Therefore, the relative contribution of fluctuations can be quantitatively estimated from the ratio:

$$\frac{1}{\langle E\rangle}\langle(E-\langle E\rangle)^2\rangle^{1/2}\sim\frac{N^{1/2}}{N}=N^{-1/2}. \tag{1.33}$$

This ratio demonstrates that, even though the energy fluctuations are quite sizable in absolute value ($\sim N^{1/2}$), their contribution is negligible compared to the mean internal energy $\langle E\rangle\sim N$ itself.

To conclude this section let us note that the problem of fluctuations is not always trivial because of their small relative value. There is a non-zero probability of the existence of huge local fluctuations confined within small volumes. Such huge fluctuations are extremely important in consideration of many physical phenomena such as light scattering, nucleation, phase transition, plasma oscillations, etc.

1.3. Equilibrium Thermodynamics

Thermodynamic variables can be defined as variables describing macroscopic states of matter. They include those that have both thermodynamic and purely mechanical significance, such as energy and volume. There are also variables of another kind, such as entropy and temperature, that originate from statistical laws and have no meaning when applied to nonmacroscopic systems. Thermodynamic variables are subjected to fluctuations. However, these fluctuations are negligible because thermodynamic variables are varying only with the macroscopic state of matter (see Section 1.2.5).

1.3.1. *Entropy*

Let us consider a closed system of energy E in *statistical equilibrium*, that is in a state obtained in the result of all possible relaxation processes which could occur in the system. Its N_s subsystems of energies $E_j (j = 1, \dots, N_s)$ can be described in terms of the statistical distributions $\rho(E_j)$ considered as some functions of energy. Therefore, the probability $\Delta w(E_j)$ for the j subsystem to have energy in the interval $[E_j, E_j + \Delta E_j]$ can be given by the following expression:

$$\Delta w(E_j) = \rho(E_j)\Delta\Gamma(E_j),\ \Delta\Gamma(E_j) = \frac{\mathrm{d}\Gamma(E_j)}{\mathrm{d}E_j}\Delta E_j, \quad j = 1, \dots, N_s, \tag{1.34}$$

where $\Gamma(E_j)$ is a number of the j-subsystem states with energies less than or equal to E_j and $\Delta\Gamma(E_j)$ is a number of the j-subsystem states corresponding to the energy interval ΔE_j. The interval ΔE_j is equal in order of magnitude to the mean energy fluctuation of the j subsystem. The quantity $\Delta\Gamma(E_j)$ represents the "degree of broadening" of a macroscopic state of energy E with respect to microscopic states and by virtue of this is usually called the *statistical weight* of the macroscopic state of the j subsystem. The normalization condition for the probability $\Delta w(E_j)$ is:

$$\int \mathrm{d}w(E_j) = \int \rho(E_j)\mathrm{d}\Gamma(E_j) = 1. \tag{1.35}$$

The concept of statistical equilibrium implies that the function $\rho(E_j)$ has a very sharp maximum at $E_j = \langle E_j \rangle$, being appreciably different from zero only in the immediate neighborhood of this point. Therefore, condition (1.35) can be rewritten in the following simple form:

$$\rho(\langle E_j \rangle)\Delta\Gamma(\langle E_j \rangle) = 1, \ \text{where } \Delta\Gamma(\langle E_j \rangle) = \frac{\mathrm{d}\Gamma(\langle E_j \rangle)}{\mathrm{d}E_j}\Delta E_j. \tag{1.36}$$

The definition (equation (1.10)) of the distribution function for the j subsystem, $\rho(\langle E_j \rangle)$, acquires the form:

$$\log[\rho(\langle E_j \rangle)] = \alpha_j + \alpha_{j,E}\langle E_j \rangle. \tag{1.37}$$

It is important to emphasize that $\log[\rho(\langle E_j \rangle)]$ is a linear function of $\langle E_j \rangle$.

The logarithm of statistical weight $\Delta\Gamma(E_j)$:

$$S_j = \log[\Delta\Gamma(E_j)], \tag{1.38}$$

is known as the j-subsystem *entropy*. The entropy, like the statistical weight itself, is dimensionless. Because the number of states $\Delta\Gamma(E_j)$ is not less than unity, the entropy cannot be negative. Substituting equations (1.36) and (1.37) into equation (1.38) results in an expression for the entropy:

$$S_j = -\log[\rho(\langle E_j \rangle)] = -\langle \log[\rho(E_j)] \rangle = -\rho(E_j)\log[\rho(E_j)]. \tag{1.39}$$

Let us now return to the closed system as a whole. The statistical weight of the system, $\Delta\Gamma(E)$, defined as the product of its subsystem weights, yields the following expression for the entropy of a closed system:

$$S = \sum_{j=1}^{N_s} S_j = -\sum_{j=1}^{N_s} \rho(E_j)\log[\rho(E_j)], \tag{1.40}$$

showing that the entropy is an additive quantity.

The microcanonical ensemble describing a closed system has the form (see equation (1.11)):

$$\Delta w(E) = Z_{\text{mc}}^{-1}\delta(E_0 - E)\prod_{j=1}^{N_s}\Delta\Gamma(E_j), \quad \text{where } E = \sum_{j=1}^{N_s} E_j. \tag{1.41}$$

If equation (1.38) is taken into account, this expression can be rewritten as follows:

$$\Delta w(E) = Z_{\text{mc}}^{-1}\delta(E_0 - E)e^S\prod_{j=1}^{N_s}\Delta E_j, \quad \text{where } S = \sum_{j=1}^{N_s} S_j(E_j). \tag{1.42}$$

Expression (1.42) emphasizes that the quantity $\Delta w(E)$ is the probability that the subsystems of a closed system have energies in given intervals $\{[E_j, E_j + \Delta E_j]; j = 1, \ldots, N_s\}$. The factor $\delta(E_0 - E)$ ensures that the total system energy E has the given value E_0.

Attention should be drawn to the significance of time in the definition of entropy. The entropy is a quantity that describes the average properties of the system over some non-zero interval of time (Δt). In order to determine the entropy for the given (Δt) we have to imagine the system divided into subsystems so small that their relaxation times are small in comparison with (Δt). Since these subsystems have to be macroscopic, when the intervals (Δt) are too short, the concept of entropy becomes meaningless so that it is not possible to speak of an "instantaneous" value of entropy.

1.3.2. *The Law of Entropy Increase*

If at some initial states a closed system is not in statistical equilibrium, its macroscopic state will vary in time until eventually the system reaches equilibrium. It follows from equation (1.42), which expresses the probability of energy distribution between the system subsystems, that this probability is an increasing function of time. This increase in probability is significant because it is exponential with respect to entropy. On the basis of this result, it may be concluded that any process occurring in a nonequilibrium system develops in such a way that the system continuously passes from states of lower entropy to those of higher entropy until finally the entropy reaches its maximum possible value, which corresponds to complete statistical equilibrium. Therefore, if a closed system is in a nonequilibrium state at some time, the most probable path for the system to take as it moves towards equilibrium is the path that results in an increase in entropy. The concept of the "most probable" evolution path means that the probability of transition to states of higher entropy is much higher than the probability of any other path. If decreases in entropy due to negligible fluctuations are ignored, one can formulate the *law of entropy increase* as:

> if at some time instant the entropy of a closed system does not have its maximum value, then at subsequent instants the entropy will not decrease; it will increase or at least remain constant.

It follows from the law of entropy increase that all processes occurring within macroscopic systems can be divided into *irreversible* and *reversible processes*. The irreversible processes are those that are accompanied by an increase in entropy of the closed system as a whole. The reversible processes are those in which the entropy of the closed system as a whole remains constant.

The law of entropy increase or the *second law of thermodynamics* was discovered by R. Clausius in 1865. Its statistical explanation was first given by L. Boltzmann in the 1870s. Other interesting details and consequences of the second law of thermodynamics can be found in Haase (1969).

1.3.3. *Adiabatic Processes*

There is a special class of interactions between a system and its environment that consists only in a change in the external conditions. By external conditions we mean various external fields. In practice, the external conditions are most often determined by the fact that the system must have a prescribed volume V. The presence of finite volume can be regarded as a particular type of external field, because the walls limiting the volume are equivalent to an infinite potential barrier that prevents the molecules of the system from escaping. If the system is subjected only to such interactions which result in changes in external conditions, it is said to be *thermally isolated.* It should be emphasized that, although a thermally isolated system does not interact directly with other systems, its energy may vary with time, that is, the thermally isolated system is "semi-closed" and its description can be given in terms of the canonical ensemble (see Sections 1.2.2 and 1.2.3).

Let us suppose that the system is thermally isolated and is subjected to a process due to variations in external conditions that vary sufficiently slowly. Such a process is known as an *adiabatic process.* The main characteristic of such a process is that the system entropy remains unchanged, that is, the adiabatic process is reversible.

1.3.4. *Temperature*

Let us consider two subsystems in *thermodynamic equilibrium* (statistical equilibrium), forming a closed system. For a given energy E, the entropy S of this system has its maximum value. The energy $E = E_1 + E_2$, where E_1 and E_2 are the energies of the first and second subsystems, respectively, and the entropy S of the system $S = S_1(E_1) + S_2(E_2)$. The entropy of each subsystem is a function of its energy. The condition for the maximum entropy at thermodynamic equilibrium is given by the equation:

$$\frac{\mathrm{d}S}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} + \frac{\mathrm{d}S_2}{\mathrm{d}E_2}\frac{\mathrm{d}E_2}{\mathrm{d}E_1} = \frac{\mathrm{d}S_1}{\mathrm{d}E_1} - \frac{\mathrm{d}S_2}{\mathrm{d}E_2} = 0(E_2 = E - E_1, \quad E = \text{const}). \tag{1.43}$$

Thus, if the system is in a state of thermodynamic equilibrium, the derivative of entropy with respect to energy is the same for every one of its subsystems, and constant throughout the system. Thermodynamic variable, which is the reciprocal of the derivative of system entropy S with respect to its energy E, is known as the system temperature T:

$$\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{1}{T}. \tag{1.44}$$

The temperatures of subsystems in thermodynamic equilibrium are equal: $T_1 = T_2$. Like entropy, the temperature is a purely statistical quantity having meaning only for macroscopic systems.

1.3.5. *Pressure*

The macroscopic state of a system at rest in thermodynamic equilibrium is entirely determined by only two variables, for example by the energy E and volume V. All other thermodynamic variables can be expressed as functions of these two. To demonstrate this let us derive an expression for pressure in an adiabatic process (constant entropy process). For this purpose, let us first calculate the force $\boldsymbol{F}$ exerted by the system on the surface bounding its volume. The force acting on the surface element d$\boldsymbol{A}$ is:

$$\boldsymbol{F} = \left[\frac{\partial E(\boldsymbol{r})}{\partial \boldsymbol{r}}\right]_S = -\left[\frac{\partial E}{\partial V}\right]_S \frac{\partial V}{\partial \boldsymbol{r}} = -\left[\frac{\partial E}{\partial V}\right]_S \mathrm{d}\boldsymbol{A}, \tag{1.45}$$

where $\partial V = \partial \boldsymbol{r} \cdot \mathrm{d}\boldsymbol{A}$, $E(\boldsymbol{r})$ is the system energy as a function of the radius vector $\boldsymbol{r}$ of the surface element d$\boldsymbol{A}$ and the symbol $[\ldots]_S$ designates an expression taken at constant entropy. The requirement of constant entropy emphasizes that the process resulting in the force $\boldsymbol{F}$ applied to the surface area d$\boldsymbol{A}$ is adiabatic. Hence, the force applied to the surface element is normal to this element and proportional to its area. Its magnitude per unit area is:

$$P = -\left(\frac{\partial E}{\partial V}\right)_S. \tag{1.46}$$

This quantity is known as pressure.

1.3.6. *Internal Energy*

Internal energy E of a thermodynamic system can be defined as the total system energy with the kinetic and potential energies of the system as a whole subtracted. This energy can be experimentally measured in two different ways:

1.3.6.1. *Measuring the Work W Done on the Given System by External Forces*

Negative work ($W < 0$) means that the system itself does work equal to $|W|$ on some external object (for example in expanding). In this case the system is assumed to be thermally isolated. Therefore, any change of its energy is due to the work done on it. If it is assumed that the system is in a state of mechanical equilibrium, i.e. at each time instant the pressure P is constant throughout the system, the work done on the system per unit time is:

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -P\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{1.47}$$

In compression $\mathrm{d}V/\mathrm{d}t < 0$, so that $\mathrm{d}W/\mathrm{d}t > 0$. Result (1.47) is applicable to both reversible and irreversible conditions.

1.3.6.2. *Measuring the Energy Q which the System Gains or Loses by Direct Transfer*

This energy change occurs in addition to the work done and it assumes that the system is not thermally isolated. The energy quantity Q is known as *heat* gained or lost by the system.

Therefore, the change in the internal energy of the thermodynamic system per unit time may be presented in the form:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}Q}{\mathrm{d}t} - P\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{1.48}$$

Let us assume that at every time instant during the process the system may be regarded as being in a state of thermal equilibrium at given internal energy and volume. This does not necessarily mean that the process is reversible because the system may not be in equilibrium with its environment. Taking into account equations (1.44) and (1.46) for the partial differentials of function $E = E(S, V)$, we can see that $\mathrm{d}Q = T\mathrm{d}S$. Therefore, the relationship (1.48) can be rewritten as follows:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = T\frac{\mathrm{d}S}{\mathrm{d}t} - P\frac{\mathrm{d}V}{\mathrm{d}t}, \quad \text{or } \mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V. \tag{1.49}$$

It is important to note that the work $\mathrm{d}W$ and heat $\mathrm{d}Q$ gained by the system during an infinitesimal change of the system state are not total differentials. Only their sum $\mathrm{d}E = \mathrm{d}W + \mathrm{d}Q$, that is, the change of internal energy $\mathrm{d}E$ is the total differential. It therefore makes sense to introduce the concept of internal energy E at a given state and it is meaningless to speak about the heat Q which system possesses in a given state. The internal energy of the system at equilibrium cannot be divided into mechanical and thermal parts. However, such a division is possible when the system goes from one state into another.

The relationship (1.49) expresses the *first law of thermodynamics*. As can be seen from equation (1.49), this law is just a statement of internal energy conservation, which specifies two ways for the energy to change: as work done on, or by, the system and as heat flowing into, or out of, the system.

1.3.7. *Enthalpy*

If the volume of a system remains constant during a process, then $\mathrm{d}E = \mathrm{d}Q$ (see equation (1.49)). The quantity of heat gained by the system is equal to the change of its internal energy. If the process occurs at constant pressure, the quantity of heat gained or lost during the process can be written as the following differential:

$$\mathrm{d}Q = \mathrm{d}R = \mathrm{d}(E + PV) = T\mathrm{d}S + V\mathrm{d}P, \tag{1.50}$$

since $\mathrm{d}(VP) = V\mathrm{d}P + P\mathrm{d}V$. The quantity $R = E + VP$ is known as the *enthalpy* or *heat function* of the system. The change of the enthalpy in a process occurring at constant pressure is, therefore, equal to the quantity of heat gained or lost by the system. It follows from expression (1.50) that:

$$T = \left(\frac{\partial R}{\partial S}\right)_P, = \left(\frac{\partial R}{\partial P}\right)_S. \tag{1.51}$$

If the system is thermally isolated (which does not imply that the system is a closed one), then $\mathrm{d}Q = 0$. This means that $R = \text{const}$, that is, the enthalpy is conserved in processes occurring at constant pressure and involving a thermally isolated system.

1.3.8. *The Helmholtz Free Energy*

The work done on a thermodynamic system in an infinitesimal isothermal reversible change of the system state can be given as follows:

$$\mathrm{d}W = \mathrm{d}H = \mathrm{d}(E - TS) = -S\mathrm{d}T - P\mathrm{d}V, \tag{1.52}$$

since $\mathrm{d}(TS) = T\mathrm{d}S + S\mathrm{d}T$. The quantity $H = E - TS$ is another function of the system state, known as the *Helmholtz free energy* of the thermodynamic system that possesses the total differential. Therefore, the work done on the system in a reversible isothermal process is equal to the change in its Helmholtz free energy. It follows from expression (1.52) that:

$$S = -\left(\frac{\partial H}{\partial T}\right)_V, \quad P = -\left(\frac{\partial H}{\partial V}\right)_T. \tag{1.53}$$

Utilizing the relationship $E = F + TS$ one can express the internal energy in terms of the Helmholtz free energy as follows:

$$E = H - T\left(\frac{\partial H}{\partial T}\right)_V = -T^2\left[\frac{\partial}{\partial T}\left(\frac{H}{T}\right)\right]_V. \tag{1.54}$$

1.3.9. *The Gibbs Free Energy*

One additional total differential $\mathrm{d}F$, with respect to pressure P, and temperature T, still remains for consideration. Its derivation is straightforward:

$$\mathrm{d}F = \mathrm{d}(E - TS + PV) = \mathrm{d}(R - TS) = \mathrm{d}(H + PV) = -S\mathrm{d}T + V\mathrm{d}P. \tag{1.55}$$

The quantity F introduced by this relationship is known as the *Gibbs free energy* of the thermodynamic system. It follows from expression (1.55) that:

$$S = -\left(\frac{\partial F}{\partial T}\right)_P, \quad V = \left(\frac{\partial F}{\partial P}\right)_T. \tag{1.56}$$

The enthalpy R is expressed in terms of the Gibbs free energy F in the same way as the internal energy E is expressed in terms of the Helmholtz free energy H (see equation (1.54)):

$$R = F - T\left(\frac{\partial F}{\partial T}\right)_P = -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_P. \tag{1.57}$$

1.3.10. *"Open" Thermodynamic Systems*

Equations (1.49), (1.50), (1.52), and (1.55) demonstrate that if one knows any of the thermodynamic quantities, internal energy E, enthalpy R, the Helmholtz free energy H, or the Gibbs free energy F, as a function of the corresponding two thermodynamic variables, then by taking the partial derivatives of that quantity one can determine all the remaining thermodynamic quantities.

Thermodynamic quantities R, H, and F also have the property of additivity as previously shown for energy E and entropy S. This property follows directly from their definitions (see equations (1.50), (1.52), and (1.55)) if one assumes that pressure and temperature are constants throughout a system in an equilibrium state. The additivity of a quantity signifies that when the amount of matter (such as the number N of particles) is changed by a given factor, the quantity is changed by the same factor. In other words, one can state that the additive thermodynamic quantities are some linear functions with respect to the additive variables.

Let us express the internal energy E of the system as a function of entropy S, volume V, and number of particles N. Since S and V are themselves additive, this function has to have the following form:

$$E(S, V, N) = Nf_E\left(\frac{S}{N}, \frac{V}{N}\right). \tag{1.58}$$

The quantity E is presented as the most general linear function in S, V, and N. The same considerations allow one to conclude that the enthalpy R, which is a function of entropy S, pressure P, and number of particles N, has the following form:

$$R(S, P, N) = Nf_R\left(\frac{S}{N}, P\right). \tag{1.59}$$

The Helmholtz and Gibbs free energies, which are the functions of T, V, N and P, T, N, respectively, allow the following forms:

$$H(T, V, N) = Nf_{\mathrm{H}}\left(T, \frac{V}{N}\right), (P, T, N) = Nf_{\mathrm{G}}(P, T). \tag{1.60}$$

In the foregoing discussions we have assumed that the number of particles N is a parameter with a given constant value. Let us now consider N as an independent variable of an "open" thermodynamic system. Then the expressions for the total differentials of the thermodynamic quantities have to contain terms proportional to $\mathrm{d}N$:

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N, \tag{1.61}$$