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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  $p_n$  ( $n = 1, \dots, N$ ). Therefore, all various states of the system under consideration can be represented by points in the *phase space*  $\mathbf{P}$  with  $2N$  coordinates  $\{q_n, p_n; n = 1, \dots, N\}$ . A state of the system changes with time and, consequently, the point in space  $\mathbf{P}$  representing this state, also known as the *phase point*, moves along a curve known as a *phase trajectory*.

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

$$d\omega(q; p) = \rho(q; p)dqdp; \rho(q; p) = \rho(q_1, \dots, q_N; p_1, \dots, p_N), dqdp = \prod_{n=1}^N dq_n dp_n, \quad (1.1)$$

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

$$\int_{\mathbf{P}} d\omega(q, p) = \int_{\mathbf{P}} \rho(q, p) dq dp = 1, \quad (1.2)$$

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):

$$\frac{d\rho(q; p)}{dt} = \sum_{n=1}^N \left( \frac{\partial \rho(q; p)}{\partial q_n} \frac{dq_n}{dt} + \frac{\partial \rho(q; p)}{\partial p_n} \frac{dp_n}{dt} \right) = 0 \quad (1.3)$$

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  $f(q; p)$ :

$$\langle f \rangle = \int_{\mathbf{P}} f(q; p) d\omega(q; p) = \int_{\mathbf{P}} f(q, p) \rho(q; p) dq dp, \quad (1.4)$$

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

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

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

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:

$$\langle f \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} f(t) dt. \quad (1.6)$$

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:

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

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  $\mathbf{P}(q; p)$ , and three components of the angular momentum vector  $\mathbf{M}(q; p)$ . The only additive combination of these quantities is a linear combination of the form:

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

where coefficients  $\alpha_j$ ,  $\alpha_{j,E}$ ,  $\alpha_{j,\mathbf{P}}$  and  $\alpha_{j,\mathbf{M}}$  are some constants of the  $j$  subsystem. Conditions required for the determination of these constants include normalization for  $\alpha_j$  and seven constant values of the additive mechanical invariants for  $\alpha_{j,E}$ ,  $\alpha_{j,\mathbf{P}}$  and  $\alpha_{j,\mathbf{M}}$ . 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:

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

where  $E_0$ ,  $\mathbf{P}_0$  and  $\mathbf{M}_0$  are some given values of  $E(q; p)$ ,  $\mathbf{P}(q; p)$  and  $\mathbf{M}(q; p)$ . 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  $E(q; p)$ ,  $\mathbf{P}(q; p)$  or  $\mathbf{M}(q; p)$  is not equal to the given values  $E_0$ ,  $\mathbf{P}_0$  or  $\mathbf{M}_0$ . 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:

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

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

$$\rho(q; p) = Z_{\text{mc}}^{-1}(V; N) \delta[E_0 - E(q; p)], \quad Z_{\text{mc}}(V; N) = \rho(N) \iint \delta[E_0 - E(q; p)] dq dp, \quad (1.11)$$

where  $Z_{\text{mc}}(V; N)$  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:

$$\rho(q; p) = Z_c^{-1}(\beta; V; N) e^{-\beta E(q; p)}, \quad Z_c(\beta; V; N) = \rho(N) \iint e^{-\beta E(q; p)} dq dp, \quad (1.12)$$

where  $\beta$  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:

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

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

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

where  $\mu$  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  $Z_{\text{mc}}(V; N)$ ,  $Z_c(\beta; V; N)$  and  $Z_{\text{gc}}(\beta; V; \mu)$  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  $\Delta q \Delta p$  in the determination of any quantum state is restricted from below (see Landau and Lifshitz (1980) for details):

$$\Delta q \Delta p \sim h^s \text{ (Heisenberg uncertainty principle)}, \quad (1.15)$$

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  $h^s$  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:

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

### 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:

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

### 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:

$$Z_c(\beta; V; N) = \frac{1}{h^{sN} N!} \int \int e^{-\beta E(q; p)} dq dp. \quad (1.18)$$

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  $d\omega(q; p)$  introduced by relations (1.1) and (1.2) can be presented as the product of two factors:

$$d\omega(q; p) = \text{const} \cdot e^{-U(q)} e^{-K(p)} dq dp, \quad (1.19)$$

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  $d\omega(q)$  and  $d\omega(p)$  of the various values of the molecular coordinates and momenta can be written in the form:

$$d\omega(q) = \text{const}_U \cdot e^{-U(q)} dq, \quad d\omega(p) = \text{const}_K \cdot e^{-K(p)} dp, \quad (1.20)$$

where  $\text{const} = \text{const}_U \text{const}_K$ . Since the sum of probabilities of all possible values of the momenta and coordinates must be unity, each of the probabilities  $d\omega(q)$  and  $d\omega(p)$  has to be normalized separately by integrating over the coordinates

and momenta, respectively. Therefore, normalization allows the determination of constants  $\text{const}_U$  and  $\text{const}_K$ .

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  $d\omega(p)$  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  $d\omega(p) = d\omega(p_x, p_y, p_z)$  acquires the form:

$$d\omega(p_x, p_y, p_z) = \text{const}_K \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_B T}\right) dp_x dp_y dp_z. \quad (1.21)$$

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

$$\begin{aligned} d\omega(v_x, v_y, v_z) &= \rho(v_x, v_y, v_z) dv_x, dv_y, dv_z, \rho(v_x, v_y, v_z) \\ &= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(p_x^2 + p_y^2 + p_z^2)}{2k_B T}\right). \end{aligned} \quad (1.22)$$

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:

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

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

$$Z_{\text{gc}}(\beta; V; z) = \sum_{N=0}^{\infty} \frac{z^N}{h^{sN} N!} \int \int e^{-\beta E(q; p; N)} dq dp. \quad (1.24)$$



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  $H_c(\beta; V; N)$ :

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

There exists the following important relationship:

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

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:

$$H_c(\beta; V; N) = -k_B T \ln[Z_c(\beta; V; N)]. \quad (1.27)$$

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

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

where  $\mu$  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:

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