

Constant Temperature Molecular Dynamics Methods

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How the canonical distribution is realized in simulations based on deterministic dynamical equations is explained in this review. Basic formulations and their recent extensions of two constant temperature molecular dynamics methods; the constraint and the extended system methods, are discussed. In both methods, the canonical distribution is derived analytically as a stationary solution of a generalized Liouville's equation which expresses the conservation of probability in a phase space. In the constraint method, the total kinetic energy of a system is kept to a constant by imposing a constraint. The extended system method replaces a macroscopic heat bath by an additional degree of freedom. The addition of only one degree of freedom is enough to derive the canonical distribution. Originally, the control of the kinetic energy is aimed, but recent developments reveal that the canonical distribution is attained by controlling only a ratio of any pair of quantities to a ratio of their canonical ensemble averages. The method is now applicable even to a system which does not have a kinetic energy term. A classical spin system is a typical example.

§ 1. Introduction

1.1. *The purpose of this review*

The molecular dynamics method is one of typical statistical mechanical computer simulation techniques employed in study of a many particle system. When a large number of particles gather together and move around, the behavior of this macroscopic system is usually too complicated for analytical treatments in statistical mechanics. A drastic simplification in modeling and several approximations are necessary in most cases in process of solving a problem. The computer simulation technique started as a new approach which avoids approximations and obtains rigorous results in a complex system. A remarkable development in computer performance increases the importance of the simulation significantly. At present, the simulation is not confined only in statistical physics, but it is widely applied to problems in solid state physics, physical chemistry and material sciences, and becomes a major research approach in these fields. Recent developments in simulations are reflected in publication of many books on this subject.^{1)~5)}

The purpose of this article is to review how the molecular dynamics method is modified to realize simulations at constant temperature. We concentrate on two methods based on deterministic time-reversal dynamical equations; the constraint and the extended system methods.

A constant temperature condition in a system of interest is attained via a thermal

contact with an external system (a heat bath) in a realistic situation. We have little knowledge about thermal interactions and suppose generally that they are complicated. The behavior of a system should not depend on the detail of the heat bath in a thermodynamical point of view. Therefore, random behaviors caused by thermal agitations are supposed as a characteristic feature of a system at isothermal condition, and they are usually treated with stochastic approaches.

In this sense, it was a surprise that deterministic dynamics equations could produce the canonical distribution and that it could be proved analytically. The basic idea of the methods, the mechanism to realize the canonical distribution, and the recent developments in the constraint and the extended system methods will be presented from a theoretical viewpoint.

The difficulties encountered in the molecular dynamics simulations, a background appearing simulations in ensembles different from the traditional microcanonical ensemble, and the development of constant pressure and constant temperature methods are outlined in the remaining part of this section.

It is necessary to review the differences between the microcanonical and the canonical ensembles for a detailed analysis of simulation methods. They will be discussed in § 2.

A constraint method is discussed in § 3. The total kinetic energy is kept to a constant by imposition of a constraint in this method. The original formulation of the extended system method proposed by Nosé and the developments along its line are discussed in § 4. Section 5 is devoted to the developments of the extended system method based on the equations reformulated by Hoover. The dynamical properties in the isothermal methods are discussed in § 6.

1.2. *Limitations in simulations in the microcanonical ensemble*

The movement of every particle in a large physical system is studied in molecular dynamics simulations. The classical equations of motion of particles (Newton's equation) are integrated numerically to reproduce the particle trajectories. The macroscopic properties of the system are obtained from the average over the configurations thus obtained. In molecular dynamics simulations, we usually consider the movement of a fixed number of particles in a unit cell whose size and shape are fixed. In a classical mechanical system free from an external force, the total energy is conserved. Therefore, the macroscopic properties we can obtain in molecular dynamics simulations are those at a constant (E , V , N) condition, E : the total energy, V : the volume, and N : the number of the particles. This condition corresponds to the microcanonical ensemble in statistical mechanics. In the microcanonical ensemble, only the phase space points which fulfill the condition $H(\mathbf{p}, \mathbf{q}) = E$ is allowed in a phase space $\Gamma = (\mathbf{p}, \mathbf{q})$.

The particles move obeying the principle of classical mechanics, therefore, we can know dynamical properties as well as equilibrium properties. This is a merit of the molecular dynamics method over another simulation method, Monte Carlo method. However, the limitation that a simulation is carried out in the microcanonical ensemble (at constant energy and volume) is sometimes inconvenient.

- 1) Ordinary laboratory experiments are usually carried out at constant temper-

ature and pressure. The difference of these conditions makes direct comparison with experiments difficult. Simulations in the same condition with experiments are more appropriate and advisable.

2) It is difficult to carry out simulations exactly at specific temperature and pressure in the molecular dynamics method. The temperature T is related to the average of the kinetic energy of a system with the equipartition theorem,

$$\left\langle \sum_i \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} NkT. \quad (1.1)$$

The pressure P is calculated from the virial theorem,

$$P = \left\langle \frac{1}{3V} \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - \sum_{i,j} \mathbf{q}_{ij} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_{ij}} \right) \right\rangle, \quad (1.2)$$

where \mathbf{q}_i is the coordinate of particle i , and $\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$. $\Phi(\mathbf{q})$ is a potential energy. Generally, we try to control the temperature and pressure to accord with our intended values at a preliminary simulation process by scaling the velocity and the size of the unit cell. However, only after simulations are carried out, we can know that simulations are done at what temperature and pressure. Therefore, we cannot carry out simulations exactly at temperature and pressure we aimed.

3) The statistical mechanical expression for some thermodynamical quantities depends on the statistical mechanical ensembles. An ensemble is specified by the external condition describing an equilibrium state. Thermodynamical quantities are derived from a thermodynamical potential (the entropy S at constant (E, V, N) condition, and the free energy at constant temperature (T, V, N) condition) by differentiating with control quantities. For quantities relating to the first derivative, the statistical mechanical expression is identical in every ensemble, but the expression for quantities relating to higher derivative and fluctuations depends on the ensemble. The statistical mechanical expression in the microcanonical ensemble is often inconvenient and less known. An investigation was carried out to relate the fluctuation of the kinetic energy with the heat capacity in the microcanonical ensemble.⁶⁾

1.3. The molecular dynamics methods at constant pressure

Constant temperature and constant pressure molecular dynamics methods are developed to resolve inconveniences in the microcanonical ensemble. In some of early attempts, the values of pressure and temperature are monitored during the simulation and the adjustment of the total kinetic energy and the size of the unit cell is carried out.

It is important to take into consideration the external system surrounding a physical system to realize a constant pressure and temperature condition. This corresponds to a statistical mechanical concept of the canonical and pressure ensembles. A constant temperature condition is attained by thermally contacted with an external system. To control the pressure, the change of the volume, or the transfer of the work should be allowed.

A refined version of the constant pressure simulation method was presented by Andersen.⁷⁾ The idea of the extended system method was introduced for the first time

in this work. To break a constraint imposed by the use of the classical dynamics, an external system is attached into a simulated system. The exchange of work and heat between a physical system and an external system enables the extension of the molecular dynamics method to a constant temperature and pressure condition. Andersen considered the volume of the unit cell as a variable, and introduced an external system consisting of kinetic energy and potential energy terms for the volume. The equations of motion for the volume is defined so that the deviation of the internal pressure calculated by Eq. (1·2) from its average works as a negative feedback and keeps the pressure around a constant. The simulation is carried out in a constant enthalpy-constant pressure ensemble. The properties in this new ensemble were studied by Ray et al.^{8)~10)}

The size and shape of a unit cell and also the symmetry change at a phase transition between solid phases. The constant pressure method was immediately extended to cope with this problem by Parrinello and Rahman.^{11),12)} The change of not only the size but also the shape of a simulation unit cell is allowed. This extension changes the style of research approach to the structural phase transitions. Before that, we usually assumed possible stable structures, compared the stability between them, and determined the most stable structure. In Parrinello-Rahman approach, a particle system chooses a stable structure by itself and the whole system changes into a new structure. The method is further extended to a system under anisotropic external stress^{12),13)} and to a molecular system,¹⁴⁾ and is applied to the phase changes in various types of crystal.^{15),16)}

A constraint method in which Eq. (1·2) is kept to a constant value was proposed.¹⁷⁾ However, the constraint approach has a difficulty in setting the initial pressure to an objective value.

1.4. *The constant temperature methods*

The methods for temperature control are full of variety. They are classified into several types: 1) the constraint method, 2) the extended system method, and 3) the stochastic method. A key factor in distinguishing between these methods is the way in which the thermal contact between a physical system and a heat bath is taken into consideration.

1.4.1. *The constraint method*

The total kinetic energy is kept to a constant value by imposition of a constraint. The average of the kinetic energy is related with the temperature by Eq. (1·1). The kinetic energy fluctuates around its average value, but the relative amplitude of the fluctuation becomes very small in a large system. Therefore, the suppression of the thermal fluctuation of the kinetic energy does not affect seriously on static and dynamical quantities. A constant temperature condition is attained by keeping the kinetic energy to a constant value.

The earliest proposal of the simulation at constant temperature is the velocity scaling algorithm by Woodcock.¹⁸⁾ The temperature control has been carried out commonly by a velocity scaling in a preliminary simulation process. After the temperature is adjusted near an objective temperature, simulations without the

scaling are performed to calculate the statistical mechanical averages. Woodcock also applied this scaling in the main part of the simulation. The scaling breaks the energy conservation in a system, and the trajectory in a phase space becomes discontinuous at the instant of the scaling. For a long time since its proposal, it was not clear whether this approach can really produce the canonical distribution or not.

A new constraint method is formulated from the study in a nonequilibrium state. The transport properties are calculated as a response to an external perturbation added to a system in nonequilibrium molecular dynamics approach.^{19),20)} For example, a flow with a linear velocity gradient profile (Couette flow) is employed for calculation of the viscosity. The temperature of the system increases inevitably by imposition of nonequilibrium boundary conditions. A constraint of a constant kinetic energy is imposed on the equations of motion to keep the temperature to a constant value.^{21),22)} The principle of least constraint by Gauss states that a constraint force added to restrict the particle motion on a constraint hypersurface should be normal to the surface in a realistic constraint dynamics. From this principle, the equations of motion

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad (1.3)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\Phi}{\partial\mathbf{q}_i} - \zeta\mathbf{p}_i \quad (1.4)$$

are derived.²³⁾ The method is now called as the Gaussian thermostat method. A coefficient ζ of the constraint force term is a Lagrangian undetermined multiplier and is determined as

$$\zeta = -\left(\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial\Phi}{\partial\mathbf{q}_i}\right) / \left(\sum_i \frac{\mathbf{p}_i^2}{m_i}\right) \quad (1.5)$$

to satisfy the constant kinetic energy constraint.

A remarkable feature of this method is that the functional form of the equilibrium distribution can be studied analytically. It has the canonical distribution form in the coordinate part of the phase space.

Via the analysis of this method, the velocity scaling algorithm proposed by Woodcock is now understood as an approximate algorithm which agrees with the Gaussian thermostat method in order of Δt . Δt is a unit time step in simulation.

1.4.2. The extended system method

An additional degree of freedom corresponding to a heat bath is introduced in the extended system method. The total energy of the physical system is allowed to fluctuate by a thermal contact with a heat bath. In the original formulation by Nosé based on a Hamiltonian,^{24),25)} two frames of variables; real variables corresponding to realistic motion of particles and virtual variables, are introduced. The relations between these two kinds of variables are consistently derived from an assumption of the scaling of the time $dt' = dt/s$, t' is a real time, t is a virtual time, and the scaling factor s corresponds to a heat bath variable. An assumption is made to derive the equations of motion that a Hamiltonian formulation is applicable in terms of the

virtual variables. Choosing a potential energy for s appropriately, it is proved that the canonical distribution is realized in a physical system.

This approach attracts considerable attention. The method is combined with constant pressure method and many applications are reported.^{26)~29)} The application is not limited to molecular simulations. Applications to lattice gauge theories,^{30),31)} reactive dynamics,³²⁾ vibrational relaxations,^{33),34)} and an extension to a quantum mechanical problem³⁵⁾ are also reported. A resemblance of the behavior of the variable s with a temperature shifting factor is employed to calculate the free energy and other quantities in a wide range of temperature from simulations at only several temperatures.^{36),37)} An extension in line of the Hamiltonian formulation is carried out by Jellinek,³⁸⁾ and Jellinek and Berry.³⁹⁾

The equations in terms of virtual variables have a complicated and unfamiliar form. The equations can be transformed into those in real variables.²⁵⁾ A further simplification is done by Hoover.⁴⁰⁾ Then, the equations of motion for particles have the same form as Eqs. (1.3) and (1.4). The friction coefficient is a variable in the extended system method. An equation for ζ is,

$$\frac{d\zeta}{dt} = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - gkT \right) / Q, \quad (1.6)$$

where g is the number of degree of freedom, T is the temperature, and Q is a parameter which determines the speed of temperature control. The time derivative of ζ is determined by the difference between the kinetic energy and its average. These simple equations (1.3), (1.4) and (1.6) which are now known as the Nosé-Hoover thermostat,⁴¹⁾ form a closed system of equations. The time development of a system is completely described by them. These equations do not have a canonical form, and do not conserve the volume in $(\mathbf{p}, \mathbf{q}, \zeta)$ phase space. It changes in proportion to the Boltzmann factor, $\exp[-H(\mathbf{p}, \mathbf{q})/kT]$, $H(\mathbf{p}, \mathbf{q})$ is the total energy of a physical system. This is the mechanism that the extended system method produces the canonical distribution.

The original formulation in virtual variables and the Nosé-Hoover form are completely equivalent when only one heat bath is connected to a system. However, the Nosé-Hoover form is perhaps more general and can be easily extended to various situations.

An important progress in line of the Nosé-Hoover formulation is presented by Bulgac and Kusnezov.⁴²⁾ The essence of the extended system method is now clarified. It is only necessary to control a ratio of a pair of quantities to realize the canonical distribution. The requirement for the pair is that the ratio of the canonical ensemble averages of those two quantities is kT or a function of temperature only. It can also apply to a system which does not have a kinetic energy term.

The Nosé-Hoover thermostat equations are tested in relation with the ergodic problems. The whole argument is based on the ergodic property in the extended system. A harmonic oscillator connected to a heat bath is a model often employed.^{40),43)~45)} General and fundamental behaviors in a thermostated system are mainly studied by Hoover and Holian.^{46)~49)}

A constant temperature method proposed by Berendsen et al.⁵⁰⁾ has a similar

structure to the constraint and the extended system methods. With a minor modification, the same equations of motion Eqs. (1.3) and (1.4) are derived. An additional equation for the coefficient ζ is

$$\zeta = C\delta K = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - gkT \right) / Q, \quad (1.7)$$

in this case.⁴⁾ The relation between the deviation of the kinetic energy δK and ζ is differential $\zeta = d(\delta K)/dt$ in the constraint method, is linear $\zeta = \delta K$ in Berendsen et al., and integral $\zeta = \int dt \delta K$ in the extended system method. In the constraint and the extended system methods, the equations have a time-reversal symmetry, and a theoretical analysis guarantees the canonical distribution in equilibrium. The method by Berendsen et al. is not yet analyzed but it is clear that the method does not allow a solution of the canonical distribution form.⁴¹⁾

1.4.3. The stochastic method

The effect of a thermal contact with a heat bath on a particle is considered to be very complicated, but the equilibrium properties should not depend upon the detail of the type of a heat bath and thermal interactions. In a macroscopic scale, the thermal motion of a particle seems to be driven by a random force. A stochastic treatment of a particle is justified in this situation. The Monte Carlo and Brownian dynamics methods are typical stochastic simulation techniques. The main idea for the stochastic constant temperature molecular dynamics method is to apply these techniques to a microscopic system.

Schneider and Stoll⁵¹⁾ considered equations similar to the Langevin's equation for Brownian dynamics,

$$m_i \frac{d^2 \mathbf{q}_i}{dt^2} = - \frac{\partial \Phi}{\partial \mathbf{q}_i} - \gamma \frac{d\mathbf{q}_i}{dt} + \mathbf{R}_i(t), \quad (1.8)$$

a friction force and a random force $\mathbf{R}_i(t)$ are added to the equation. The amplitude of the random force is related to the temperature T and the friction coefficient γ by the second fluctuation dissipation theorem,

$$\langle \mathbf{R}_i(t_1) \mathbf{R}_j(t_2) \rangle = \delta_{ij} 2kT \gamma \delta(t_1 - t_2). \quad (1.9)$$

The temperature is kept at a constant value by the balance between the thermal agitation due to the random force and the slowing down due to the friction.

More direct temperature control mechanism was proposed by Andersen.⁷⁾ A particle collides occasionally with hypothetical particles, loses its memory in collision, and the velocity of the particle is reset to a new velocity randomly selected from a Maxwell distribution at temperature T . A similar method was also proposed by Bonomi.⁵²⁾

The canonical distribution is realized in both stochastic approaches. A phase space trajectory becomes discontinuous when a randomness appears. We must choose carefully the frequency of the random force and random collision acting on a particle. When the collision rate is very high, a particle lost its memory of the movement in a short time and the velocity autocorrelation function damps very

quickly at a long time region.⁵³⁾ The collision rate should be chosen considerably low.

The stochastic method has a merit over the deterministic methods such as the extended system method and the constraint method. In several situations, a deterministic dynamical system exhibits a nonergodic behavior, and it takes quite a long time to reach an equilibrium state. We can avoid this inconvenience by using the stochastic method.

§ 2. The difference between the microcanonical and canonical ensembles

We compare the differences between a constant energy condition at which ordinary molecular dynamics simulations are carried out and a constant temperature condition that we aim to realize. Statistical mechanics relates the macroscopic properties of a many particle system in equilibrium with the microscopic averages over various particle configurations.

2.1. The microcanonical ensemble

A constant energy condition corresponds to the microcanonical ensemble. The external control parameters for this ensemble are the total energy E , the volume V , and the number of particles N . If we fix these parameters to specific values, we can get the same equilibrium condition. In an isolated system described by a Hamiltonian $H(\mathbf{p}, \mathbf{q})$

$$H(\mathbf{p}, \mathbf{q}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{q}), \quad (2.1)$$

the dynamical equations for particles in a canonical form,

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i = -\frac{\partial\Phi}{\partial\mathbf{q}_i} \quad (2.2)$$

or in Newton's equation

$$m_i \frac{d^2\mathbf{q}_i}{dt^2} = \mathbf{F}_i = -\frac{\partial\Phi(\mathbf{q})}{\partial\mathbf{q}_i} \quad (2.3)$$

conserve the total energy (the Hamiltonian) $H(\mathbf{p}, \mathbf{q})$. \mathbf{q}_i , \mathbf{p}_i , \mathbf{F}_i and m_i are the coordinate, momentum, force and mass of particle i . Hereafter, we often use shortened notations $\mathbf{q} = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N)$ and $\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$. $\Phi(\mathbf{q})$ is a potential energy of a system. We consider an atomic system here, but the extension to a molecular system is straightforward.

Phase space points (\mathbf{p}, \mathbf{q}) on a constant energy hypersurface satisfying $H(\mathbf{p}, \mathbf{q}) = E$ are only allowed to appear in the average. It is postulated that every allowed phase point contributes to the average in the microcanonical ensemble in equal weight. This is the fundamental assumption of statistical mechanics known as the principle of equal a priori probability. This principle is closely related to the ergodic hypothesis that a trajectory of a phase space vector (\mathbf{p}, \mathbf{q}) will pass through almost all point in the allowed portion of phase space. We are interested mainly in the

properties of a macroscopic system and we usually assume that the ergodic property is satisfied in simulation. However, in some situations we must be careful whether the ergodic property is really satisfied or not.

An equilibrium distribution function $f(\mathbf{p}, \mathbf{q})$ expresses the probability that a phase space point (\mathbf{p}, \mathbf{q}) appears in statistical mechanical averages. In the microcanonical ensemble, it will be

$$f_{\text{mc}}(\mathbf{p}, \mathbf{q}) = C \delta(H(\mathbf{p}, \mathbf{q}) - E). \quad (2.4)$$

The δ function form reflects the constraint $H(\mathbf{p}, \mathbf{q}) = E$. The ensemble average of a quantity $A(\mathbf{p}, \mathbf{q})$ is defined as

$$\langle A \rangle = \frac{\int A(\mathbf{p}, \mathbf{q}) f(\mathbf{p}, \mathbf{q}) d\mathbf{p}d\mathbf{q}}{\int f(\mathbf{p}, \mathbf{q}) d\mathbf{p}d\mathbf{q}}. \quad (2.5)$$

The macroscopic properties of a system can be derived from the thermodynamical relations. The starting point for this calculation is the famous Boltzmann relation,

$$S = k \ln W, \quad (2.6)$$

where S is the entropy, k is the Boltzmann constant, and W is the number of microscopic states. The entropy in the microcanonical ensemble is a thermodynamical potential from which we can derive all the thermodynamical quantities by differentiating with control parameters E , V and N .

In the microcanonical ensemble, two choices for this basic equation are possible,

$$W_1 = \int f_{\text{mc}}(\mathbf{p}, \mathbf{q}) d\mathbf{p}d\mathbf{q} \quad (2.7)$$

and

$$\begin{aligned} W_2 &= \int^E dE' \int f_{\text{mc}}(\mathbf{p}, \mathbf{q}) d\mathbf{p}d\mathbf{q} \\ &= C \int \theta(E - H(\mathbf{p}, \mathbf{q})) d\mathbf{p}d\mathbf{q}. \end{aligned} \quad (2.8)$$

$\theta(x)$ is the Heaviside function, $\theta(x) = 1$, for $x > 0$, and $\theta(x) = 0$, for $x < 0$, and $\delta(x) = d\theta(x)/dx$. These two definitions are in agreement to order $1/N$. We will take Eq. (2.8) as our primary definition. The expression is generally simple in this choice than in Eq. (2.7).

The mathematical formulation of the microcanonical ensemble was considered not to be convenient for deriving statistical mechanical formulae. The difference and the relation of the fluctuations between the canonical and the microcanonical ensembles were discussed by Lebowitz et al.⁶⁾ Their motivation for this study was that they recognized the difference between the Monte Carlo and the molecular dynamics simulation results. They got a famous relation Eq. (2.16) for the fluctuation of the kinetic energy in the microcanonical ensemble, which has been employed in calculation of the heat capacity in molecular dynamics simulations.

A simple and elegant method for deriving the statistical mechanical expressions in the microcanonical ensemble is reported by Pearson et al.⁵⁴⁾ They employ a characteristic property of a classical particle system in which the kinetic energy is given by a quadratic form of momenta. The integration in $3N$ dimensional momentum space is easily carried out. The entropy and the average of a quantity $A(\mathbf{q})$ are given as

$$\begin{aligned} S &= k \ln W_2 = k \ln \left[C \int \theta(E - H(\mathbf{p}, \mathbf{q})) d\mathbf{p}d\mathbf{q} \right] \\ &= k \ln \left[C' \int \frac{2}{3N} (E - \Phi(\mathbf{q}))^{(3/2)N} d\mathbf{q} \right], \end{aligned} \quad (2.9)$$

$$\langle A(\mathbf{q}) \rangle_{\text{mc}} = \frac{\int A(\mathbf{q}) (E - \Phi(\mathbf{q}))^{(3/2)N-1} d\mathbf{q}}{\int (E - \Phi(\mathbf{q}))^{(3/2)N-1} d\mathbf{q}}, \quad (2.10)$$

where C is a constant and $\langle \rangle_{\text{mc}}$ indicates the ensemble average in the microcanonical ensemble. The inverse of the temperature is defined by the thermodynamical relation,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_v = k \frac{\int \frac{3N}{2} (E - \Phi(\mathbf{q}))^{(3/2)N-1} d\mathbf{q}}{\int (E - \Phi(\mathbf{q}))^{(3/2)N} d\mathbf{q}} = \frac{3Nk}{2\langle K \rangle}. \quad (2.11)$$

We use the kinetic energy K , as a shortened notation for $E - \Phi(\mathbf{q})$, $K(\mathbf{q}) = K(\mathbf{p}(\mathbf{q})) = E - \Phi(\mathbf{q})$. Thus, the temperature is related to the average of the kinetic energy by the equipartition theorem,

$$T = \frac{2}{3Nk} \langle K \rangle_{\text{mc}} = \frac{2}{3Nk} \frac{\int (E - \Phi(\mathbf{q})) (E - \Phi(\mathbf{q}))^{(3/2)N-1} d\mathbf{q}}{\int (E - \Phi(\mathbf{q}))^{(3/2)N-1} d\mathbf{q}}. \quad (2.12)$$

The heat capacity is

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T} \right)_v = 1 / \left(\frac{\partial T}{\partial E} \right)_v \\ &= k / \left[1 - \left(1 - \frac{2}{3N} \right) \langle K \rangle_{\text{mc}} \left\langle \frac{1}{K} \right\rangle_{\text{mc}} \right]. \end{aligned} \quad (2.13)$$

The average of the inverse of the kinetic energy is approximated in the thermodynamical limit by

$$\left\langle \frac{1}{K} \right\rangle_{\text{mc}} = \frac{1}{\langle K \rangle} \left(1 + \frac{\langle (\delta K)^2 \rangle}{\langle K \rangle} \right), \quad (2.14)$$

where the average and the fluctuation of K are $K = \langle K \rangle + \delta K$, and $\langle (\delta K)^2 \rangle = \langle K^2 \rangle - \langle K \rangle^2$, and Eq. (2.13) becomes

$$C_v = k \left[\frac{2}{3N} - \frac{\langle (\delta K)^2 \rangle}{\langle K \rangle^2} \right]. \tag{2.15}$$

This approximate formula is first obtained by Lebowitz et al.⁶⁾ Inverting this relation, the fluctuation of the kinetic energy in the microcanonical ensemble is given in terms of the heat capacity

$$\langle (\delta K)^2 \rangle_{\text{mc}} = \langle (\delta \Phi)^2 \rangle_{\text{mc}} = \frac{2}{3N} \langle K \rangle^2 \left[1 - \frac{2}{3N} (C_v/k) \right]. \tag{2.16}$$

2.2. The canonical ensemble

The properties of a system at constant temperature are treated in the canonical ensemble. The temperature T is chosen as a control parameter instead of the total energy E . A schematical image of this ensemble is shown in Fig. 1. A physical system is surrounded by a large external system. The exchange of particles is not allowed, but the energy transfer is allowed between these two systems. The external system is very large in comparison with a physical system, and is called as a heat reservoir or a heat bath. The temperature change in this external system due to the heat transfer with a physical system is supposed to be negligibly small and the temperature is essentially a constant. The temperature of our physical system in thermodynamical sense is this temperature T of the external system. If we define an internal temperature by the average of the total kinetic energy as in Eq. (2.12), the temperature is maintained at a constant value by thermal contact with the heat bath.

Because of the thermal contact between the physical system and the heat bath, the total energy of the system fluctuates and its distribution becomes the canonical distribution,

$$f_c(\mathbf{p}, \mathbf{q}) = C \exp[-H(\mathbf{p}, \mathbf{q})/kT]. \tag{2.17}$$

The relation between the distribution functions Eqs. (2.4) and (2.17) is given by the Laplace transformation with the energy E , and the resulted distribution is a function of the inverse temperature $1/kT$.

$$f_c(\mathbf{p}, \mathbf{q}; T) = \int dE \exp[-E/kT] f_{\text{mc}}(\mathbf{p}, \mathbf{q}; E). \tag{2.18}$$

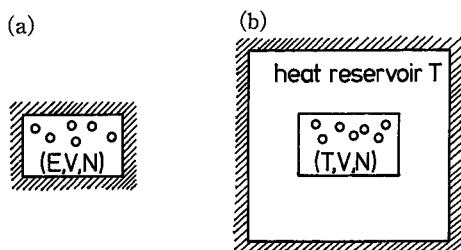


Fig. 1. Schematic images for a system (a) in the microcanonical and (b) in the canonical ensembles. The shaded area is a heat insulating wall.

The thermodynamical potential in the canonical ensemble is the free energy $F(T, V, N)$,

$$\begin{aligned} F(T, V, N) &= -kT \ln \left[\int f_c(\mathbf{p}, \mathbf{q}) dpdq \right] \\ &= -kT \ln \left[C \int \exp[-H(\mathbf{p}, \mathbf{q})/kT] dpdq \right]. \end{aligned} \tag{2.19}$$

The heat capacity is expressed as a fluctuation of the total energy in the canonical ensemble,

$$C_v = [\langle H^2 \rangle_c - \langle H \rangle_c^2] / kT^2. \quad (2\cdot20)$$

The average and the fluctuation of the kinetic energy are easily obtained as

$$\langle K \rangle_c = \frac{3N}{2} kT, \quad (2\cdot21)$$

$$\langle (\delta K)^2 \rangle_c = \frac{2}{3N} \langle K \rangle^2 = \frac{3N}{2} (kT)^2. \quad (2\cdot22)$$

The expressions for the quantities which are the first order derivative of the thermodynamical potential (e.g., the total energy E , or the pressure P), agree in any ensemble, but the expressions for the quantities relating to second or higher order derivatives or to fluctuations are different in each ensemble. The heat capacity is a typical example. We must use Eq. (2·13) or (2·15) in ordinary molecular dynamics simulations, but in Monte Carlo simulations at constant temperature, Eq. (2·20) is an appropriate expression.

The fluctuation of the kinetic energy at constant temperature Eq. (2·22) is larger than that at constant energy Eq. (2·16),

$$\langle (\delta K)^2 \rangle_c = \frac{2}{3N} \langle K \rangle^2 > \langle (\delta K)^2 \rangle_{mc} = \frac{2}{3N} \langle K \rangle^2 / \left[1 - \frac{2}{3N} \frac{C_v}{k} \right]. \quad (2\cdot23)$$

This inequality relation will be employed to determine whether the canonical distribution is realized in simulations at constant temperature.

§ 3. The constraint method

3.1. The Gaussian constraint method

The average of the kinetic energy is usually used as a measure of the temperature in molecular dynamics simulations. The kinetic energy should fluctuate both in the microcanonical and the canonical ensembles as shown in Eqs. (2·16) and (2·22), but the relative amplitude of the fluctuations becomes very small in a large system. Therefore, a constant temperature condition is attained by suppressing thermal fluctuations of the kinetic energy and keeping it to a constant value.

A constant kinetic energy condition can be attained by imposing a constraint

$$R(\mathbf{p}, \mathbf{q}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} - \frac{g}{2} kT = 0, \quad (3\cdot1)$$

to the equations of motion.^{21),22)} g is the number of degrees of freedom, but we do not specify its value at this stage. This constraint depends on the velocities. This type of problem is classified as the non-holonomic case in classical dynamics. The molecular dynamics method with non-holonomic constraint is discussed by Haile and Gupta.⁵⁵⁾ There is some ambiguity how the constraint is imposed to a mechanical system.

A method proposed by Evans et al.²³⁾ is based on the principle of least constraint by Gauss which states that the actual constrained motion should occur along a trajectory obtained by normal projection of a force onto a constraint hypersurface. A constraint force which is necessary to restrict the trajectory on a constraint hypersurface is the least in this choice.

A non-holonomic constraint is generally expressed as

$$R(\mathbf{q}, \dot{\mathbf{q}}, t) = 0. \quad (3.2)$$

Differentiation of Eq. (3.2) with respect to time gives a relation which the acceleration $\ddot{\mathbf{q}}$ should satisfy,

$$\mathbf{n}(\mathbf{q}, \dot{\mathbf{q}}, t) \cdot \ddot{\mathbf{q}} + w(\mathbf{q}, \dot{\mathbf{q}}, t) = 0, \quad (3.3)$$

where $\mathbf{n}(\mathbf{q}, \dot{\mathbf{q}}, t) = \partial R / \partial \dot{\mathbf{q}}$ and $w(\mathbf{q}, \dot{\mathbf{q}}, t) = \dot{\mathbf{q}} \cdot \partial R / \partial \mathbf{q} + \partial R / \partial t$. An unconstrained motion described by

$$m\ddot{\mathbf{q}}_u = \mathbf{F}_u \quad (3.4)$$

gives a trajectory which leaves the constraint hypersurface defined by Eq. (3.2). A constraint force \mathbf{F}_c is added to the equation of motion to prevent the deviation from the constraint hypersurface,

$$m\ddot{\mathbf{q}}_c = \mathbf{F}_u + \mathbf{F}_c. \quad (3.5)$$

The constraint force \mathbf{F}_c is minimum when \mathbf{F}_c is chosen perpendicular to the constraint surface or parallel to the gradient $\mathbf{n}(\mathbf{q}, \dot{\mathbf{q}}, t)$. (See Fig. 2.)

A constraint force from the constant temperature constraint is proportional to the velocity, $\mathbf{n}_i(\mathbf{q}, \dot{\mathbf{q}}, t) = \partial R / \partial \dot{\mathbf{q}}_i = m_i \dot{\mathbf{q}}_i = \mathbf{p}_i$. The equations of motion are modified as

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad (3.6)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial \Phi}{\partial \mathbf{q}_i} - \zeta \mathbf{p}_i. \quad (3.7)$$

A coefficient ζ of the constraint force term is a Lagrangian undetermined multiplier, and is determined to satisfy the time derivative of the constraint equation (3.1),

$$\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \dot{\mathbf{p}}_i = \sum_i \frac{\mathbf{p}_i}{m_i} \cdot \left(-\frac{\partial \Phi}{\partial \mathbf{q}_i} - \zeta \mathbf{p}_i \right) = 0. \quad (3.8)$$

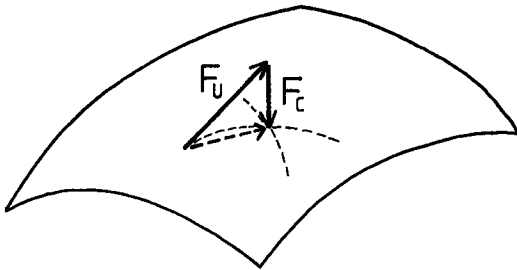


Fig. 2. Normal projection of a force onto a constraint hypersurface.

Therefore, we obtain

$$\zeta = -\left(\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \right) / \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} \right) \quad (3.9)$$

$$= -\sum_i \left(\frac{d\mathbf{q}_i}{dt} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \right) / gkT$$

$$= -\frac{d\Phi}{dt} / gkT.$$

When the value of the total kinetic energy is set equal to $(g/2)kT$ at an initial step, Eqs. (3·6) and (3·7) keep its value.

3.2. The equilibrium distribution function in the Gaussian constraint method

Carrying out simulations with this constraint equations, we can obtain the canonical distribution in the coordinate part of a phase space $\Gamma = (\mathbf{p}, \mathbf{q})$. This can be proved analytically.⁵⁶⁾ The distribution function $f(\mathbf{p}, \mathbf{q})$ expresses a probability that a phase space point (\mathbf{p}, \mathbf{q}) will appear. A generalized Liouville equation expresses the conservation of the probability in the phase space Γ ,

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \Gamma} \cdot (\dot{\Gamma} f) = 0. \quad (3 \cdot 10)$$

The first and second terms express a change inside a volume element and a change passing through the surface of a volume element. We define a total time derivative of f along a phase space trajectory by

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma}, \quad (3 \cdot 11)$$

then, Eq. (3·17) is reexpressed as

$$\frac{df}{dt} = - \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} \right) f. \quad (3 \cdot 12)$$

In ordinary mechanics, the right-hand side of the above equation is zero, and the famous Liouville's theorem $df/dt = 0$ holds. It means that the equilibrium distribution function does not change by the time evolution.

The $(\partial/\partial \Gamma) \cdot \dot{\Gamma}$ term does not vanish in our case and is calculated as

$$\begin{aligned} \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} &= \sum_i \left(\frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) \\ &= - \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot (\zeta \mathbf{p}_i) = - \sum_i \left(3\zeta + \mathbf{p}_i \cdot \frac{\partial \zeta}{\partial \mathbf{p}_i} \right) \\ &= -3N\zeta - \sum_i \mathbf{p}_i \cdot \frac{\partial \zeta}{\partial \mathbf{p}_i} = -(3N-1)\zeta. \end{aligned} \quad (3 \cdot 13)$$

The last part in the above equation becomes

$$\begin{aligned} \sum_i \mathbf{p}_i \cdot \frac{\partial \zeta}{\partial \mathbf{p}_i} &= - \sum_i \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \left[\left(\sum_j \frac{\mathbf{p}_j}{m_j} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_j} \right) / \left(\sum_j \frac{\mathbf{p}_j^2}{m_j} \right) \right] \\ &= - \left(\sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \right) / \left(\sum_j \frac{\mathbf{p}_j^2}{m_j} \right) + 2 \left(\sum_j \frac{\mathbf{p}_j}{m_j} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_j} \right) \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} \right) / \left(\sum_j \frac{\mathbf{p}_j^2}{m_j} \right)^2 \\ &= \zeta - 2\zeta = -\zeta. \end{aligned} \quad (3 \cdot 14)$$

If we take into consideration of the momentum conservation explicitly, Eq. (3·13) results in $-(3N-4)\zeta$. The time derivative of the potential energy is equal to

$$\frac{d\Phi}{dt} = \sum_i \dot{\mathbf{q}}_i \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} = \sum_i \frac{\mathbf{p}_i}{m_i} \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} = -\zeta \sum_i \frac{\mathbf{p}_i^2}{m_i} = -\zeta g kT. \quad (3 \cdot 15)$$

Therefore, if we choose $g=3N-1$ or $3N-4$, Eq. (3·12) is expressed as

$$\frac{df}{dt} = -\frac{1}{kT} \frac{d\Phi}{dt} f. \quad (3 \cdot 16)$$

The solution of this equation is

$$f(\mathbf{p}, \mathbf{q}) = \delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m_i} - \frac{g}{2} kT\right) \exp[-\Phi(\mathbf{q})/kT]. \quad (3 \cdot 17)$$

The distribution in the coordinate part has the canonical form, whereas that in the momentum space is a δ function form because of imposition of a constraint.

The probability in a volume element along a phase space trajectory is not conserved in the Gaussian constraint method. A conserved quantity is $\exp[\Phi(\mathbf{q})/kT] \times f(\mathbf{p}, \mathbf{q})$. Therefore, the probability in a phase space along the trajectory changes in proportion to $\exp[-\Phi(\mathbf{q})/kT]$. Equation (3·17) only states that the relative probability of two phase points along a trajectory is expressed in a canonical distribution form. To identify $f(\mathbf{p}, \mathbf{q})$ with the equilibrium distribution function in statistical mechanics, we must assume that a trajectory determined by Eqs. (3·6), (3·7) and (3·9) passes through almost all point in an accessible part of a phase space (ergodicity). This assumption is essential for the proof. We are not certain whether this is true or not in a particular case. However, we usually assume that the ergodic property is satisfied in a many particle system. In this situation, the exact canonical ensemble average is obtained in simulations with the Gaussian constraint method for quantities which are functions of coordinates only.

3.3. The velocity scaling algorithm

A simple algorithm to maintain the total kinetic energy to a constant value was proposed by Woodcock in 1971.¹⁸⁾ This was the first attempt to carry out a simulation in a controlled condition. The velocities of all the particles in a system are multiplied by a common factor to scale the kinetic energy to an intended value. This procedure is carried out in every time step of simulation.

We explain Woodcock's constant temperature method in terms of a leap frog algorithm which is equivalent to Verlet's algorithm. These are a closed system of difference equations in which the coordinate at time $t + \Delta t$, $\mathbf{q}_i(t + \Delta t)$, and the velocity at $t + \Delta t/2$, $\mathbf{v}_i(t + \Delta t/2)$, are obtained from the knowledge of the coordinate at t , $\mathbf{q}_i(t)$, and the velocity at $t - \Delta t/2$, $\mathbf{v}_i(t - \Delta t/2)$. The force $\mathbf{F}_i(t)$ is calculated from coordinates at time t . New velocities and coordinates are obtained as

$$\mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) = \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) + \left(\frac{\mathbf{F}_i(t)}{m_i}\right) \Delta t, \quad (3 \cdot 18)$$

$$\mathbf{q}_i(t + \Delta t) = \mathbf{q}_i(t) + \mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) \Delta t. \quad (3 \cdot 19)$$

These are the difference version of the equations of motion,

$$\frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{F}_i}{m_i}, \quad (3 \cdot 20)$$

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{v}_i. \quad (3 \cdot 21)$$

In Woodcock's method, an estimate of the velocity at $t + \Delta t/2$, $\mathbf{v}_i(t + \Delta t/2)$, is corrected to satisfy a constraint of the constant kinetic energy,

$$\mathbf{v}_i^*(t + \frac{\Delta t}{2}) = s \mathbf{v}_i(t + \frac{\Delta t}{2}). \quad (3 \cdot 22)$$

The scaling factor s is determined from the relation,

$$\sum_i \frac{m_i}{2} \left(\mathbf{v}_i^*(t + \frac{\Delta t}{2}) \right)^2 = s^2 \sum_i \frac{m_i}{2} \left(\mathbf{v}_i(t + \frac{\Delta t}{2}) \right)^2 = \frac{g}{2} kT. \quad (3 \cdot 23)$$

Thus,

$$s = \left[gkT / \left\{ \sum_i m_i \left(\mathbf{v}_i(t + \frac{\Delta t}{2}) \right)^2 \right\} \right]^{1/2}. \quad (3 \cdot 24)$$

The coordinate at $t + \Delta t$ is now obtained as

$$\mathbf{q}_i(t + \Delta t) = \mathbf{q}_i(t) + \mathbf{v}_i^*(t + \frac{\Delta t}{2}) \Delta t. \quad (3 \cdot 25)$$

This velocity scaling procedure is very simple and convenient. However, it was not clear for long years since its proposal whether this approach can really produce the canonical distribution or not. There was also not a consensus how often the scaling procedure should be employed. Some were optimistic and scaled in every time step. Some were skeptical and recommended applying scaling as few times as possible because the trajectory in a phase space becomes discontinuous at the instant of the scaling.

Now, we know Woodcock's method is an approximate algorithm to solve the Gaussian constraint method described in § 3.1, which gives the correct canonical distribution in the coordinate space with accuracy of order Δt if the scaling is carried out in every time step.⁵⁷⁾ Δt is a unit time step used in solving difference equations.

3.4. Relation between the Gaussian constraint method and velocity scaling algorithm

We will analyze by what differential equation the velocity scaling algorithm can be approximated. This analysis was first given by Andersen.⁵⁷⁾ The velocity scaling algorithm consists of two difference equations (in a leap frog form) Eqs. (3·18) and (3·25), a scaling Eq. (3·22), and Eq. (3·24) for the scaling factor s .

An acceleration is expressed by a difference of the velocity,

$$\begin{aligned} \frac{d^2 \mathbf{q}_i}{dt^2} &= \frac{d\mathbf{v}_i}{dt} = \left(\mathbf{v}_i^*(t + \frac{\Delta t}{2}) - \mathbf{v}_i(t - \frac{\Delta t}{2}) \right) / \Delta t \\ &= \left(s \mathbf{v}_i(t + \frac{\Delta t}{2}) - \mathbf{v}_i(t - \frac{\Delta t}{2}) \right) / \Delta t \end{aligned}$$

$$= \frac{\mathbf{F}_i(t)}{m_i} + \frac{s-1}{\Delta t} \mathbf{v}_i\left(t + \frac{\Delta t}{2}\right). \quad (3 \cdot 26)$$

In the final line of the above equation, the force terms are separated into an ordinary force and an additional part which is proportional to $s-1$ and the velocity. The scaling factor s defined in Eq. (3·24) is calculated as

$$\begin{aligned} s &= \left[\sum_i m_i \left\{ \mathbf{v}_i\left(t + \frac{\Delta t}{2}\right) \right\}^2 / gkT \right]^{-1/2} \\ &= \left[\sum_i m_i \left\{ \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) + \frac{\mathbf{F}_i(t)}{m_i} \Delta t \right\}^2 / gkT \right]^{-1/2} \\ &= \left[\left\{ \sum_i m_i \left\{ \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) \right\}^2 + 2 \sum_i \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) \cdot \mathbf{F}_i(t) \Delta t + O((\Delta t)^2) \right\} / gkT \right]^{-1/2}. \end{aligned} \quad (3 \cdot 27)$$

The third term in the brace is only indicated as a quantity of order $(\Delta t)^2$. The kinetic energy at $t - \Delta t/2$ is assumed to be $(g/2)kT$.

$$\begin{aligned} s &= \left[1 + \frac{2}{gkT} \sum_i \mathbf{v}_i\left(t - \frac{\Delta t}{2}\right) \cdot \mathbf{F}_i(t) \Delta t + O((\Delta t)^2) \right]^{-1/2} \\ &= \left[1 + \frac{2}{gkT} \sum_i \mathbf{v}_i(t) \cdot \mathbf{F}_i(t) \Delta t + O((\Delta t)^2) \right]^{-1/2}. \end{aligned} \quad (3 \cdot 28)$$

Exactly speaking, the error in the second line of Eq. (3·28) is of order $(\Delta t)^3$. A cancellation among terms of order $(\Delta t)^2$ occurs. Finally, we get an approximate expression for s ,

$$\begin{aligned} s &= [1 + 2\zeta \Delta t + O((\Delta t)^2)]^{-1/2} \\ &= 1 - \zeta \Delta t + O((\Delta t)^2). \end{aligned} \quad (3 \cdot 29)$$

ζ in the above equation is the same as that in Eq. (3·9). Therefore, we get a differential equation and an expression for an undetermined multiplier,

$$\frac{d^2 \mathbf{q}_i}{dt^2} = \frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{F}_i(t)}{m_i} - \zeta \mathbf{v}_i(t) + O(\Delta t), \quad (3 \cdot 30)$$

$$\zeta = \sum_i \mathbf{v}_i(t) \cdot \mathbf{F}_i(t) / gkT. \quad (3 \cdot 31)$$

The leading term in Eq. (3·30) is equivalent to that in the Gaussian constraint method, Eqs. (3·6), (3·7) and (3·9). If the scaling is carried out in every time step, and if the unit time step Δt is chosen to a reasonably small value, the simulation with the velocity scaling algorithm gives equal results with those in the Gaussian constraint method, and the distribution in the coordinate space is the canonical distribution. The error in this approximation is of order Δt . It should be noted that the accuracy is one order less than that of the ordinary Verlet's algorithm, $O((\Delta t)^2)$.

§ 4. The extended system method I: The formulation based on a Hamiltonian

4.1. The basic idea of the extended system method

We consider an isolated system in a fixed simulation unit cell in ordinary molecular dynamics simulations. The total energy and the volume of a physical system are constant under this situation. To break the conservation law which restricts the behavior of a physical system, and to realize a constant temperature or a constant pressure condition, a physical system is extended to a composite system consisting of a physical system and an external system. The conservation law still holds in an extended system, but the total energy or the volume of a physical system is allowed to fluctuate.

This idea accords well with a schematical image of the canonical or the pressure ensemble in statistical mechanics. We usually imagine a system surrounded by a heat reservoir at constant temperature. The major difference between the extended system method and a real situation is that we consider a very small system for an external system instead of a macroscopic reservoir.

The idea of the extended system method was first presented by Andersen in his work on the constant pressure method.⁷⁾ He also considered the volume V of a simulation unit cell as a variable, and that a constant pressure condition is attained by changing the volume to balance an internal pressure determined by the particle movement and the interatomic interactions with an external pressure. We assume that a unit cell is a cube of edge length L , $L = V^{1/3}$. The coordinate, velocity and momentum are scaled by L as

$$\mathbf{q}'_i = L\mathbf{q}_i, \quad (4.1)$$

$$\mathbf{v}'_i = L\dot{\mathbf{q}}_i = L\mathbf{v}_i, \quad (4.2)$$

$$\mathbf{p}'_i = \mathbf{p}_i/L. \quad (4.3)$$

The variables with a prime are the real variables corresponding to real physical quantities. The variables without a prime are the scaled variables introduced to derive a constant pressure method. The transformation from real to scaled variables is a canonical transformation in constant pressure case.

A Hamiltonian of an extended system consisting of a physical system and a piston which determines the size of the volume is postulated in terms of scaled variables as

$$H^* = \sum_i \frac{V^{-2/3} \mathbf{p}'_i{}^2}{2m_i} + \Phi(V^{1/3} \mathbf{q}) + \frac{p_v^2}{2W} + P_{\text{ex}} V. \quad (4.4)$$

W is a parameter corresponding to a piston mass, p_v is a conjugate momentum of the volume, and P_{ex} is an external pressure. $P_{\text{ex}} V$ is a potential energy for the volume change. The work necessary to it is $P_{\text{ex}} \Delta V$.

Applying the Hamiltonian formalism to Eq. (4.4), the equation of motion for the volume is derived as

$$\begin{aligned}
 W \frac{d^2 V}{dt^2} &= -\frac{\partial H^*}{\partial V} = \frac{1}{3V} \left(\sum_i V^{-2/3} \frac{\mathbf{p}_i^2}{m_i} - V^{1/3} \mathbf{q}_i \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \right) - P_{\text{ex}} \\
 &= \left[\frac{1}{3V} \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - \sum_i \mathbf{q}_i \cdot \frac{\partial \Phi}{\partial \mathbf{q}_i} \right) \right] - P_{\text{ex}} = P - P_{\text{ex}} .
 \end{aligned} \tag{4.5}$$

The quantity in a square bracket in Eq. (4.5) is equal to a term appearing in the virial theorem (Eq. (1.2)). The pressure is obtained as an average of this term. If we call this term as an instantaneous pressure, Eq. (4.5) states that the change of the volume is governed by the balance between an internal pressure P and an external pressure P_{ex} . The internal pressure P is determined microscopically from the movement of the particle and the interatomic interactions.

A temperature version of the extended system method was proposed by Nosé.^{24,25)} A schematical image of the canonical ensemble is a system surrounded by and thermally contacted with a large external system (a heat bath). (See Fig. 1(b).) In a constant temperature method by Nosé, a degree of freedom s is introduced instead of a large external system. A physical system exchanges energy with this additional degree of freedom. The total energy of the physical system can fluctuate under this condition.

The thermal interactions between a system and a heat bath are expressed as a scaling of particle's velocity by a variable s . A real velocity \mathbf{v}_i' of particle i is obtained by multiplying a scaling factor s to a virtual velocity \mathbf{v}_i ,

$$\mathbf{v}_i' = s \mathbf{v}_i . \tag{4.6}$$

Two kinds of variables are also introduced for momentum and time. We will express virtual variables without a prime as \mathbf{p}_i , t or \mathbf{v}_i . The primed ones as \mathbf{p}_i' , t' and \mathbf{v}_i' are real variables. The coordinate is the same in both frames, but we also define a virtual coordinate \mathbf{q}_i and a real coordinate \mathbf{q}_i' to complete a formulation. The real variables describe the real motion of a particle. The virtual variables are artificially introduced for control of the temperature. The relation between two frames of variables is given by a noncanonical transformation,

$$\mathbf{q}_i' = \mathbf{q}_i , \tag{4.7}$$

$$\mathbf{p}_i' = \mathbf{p}_i / s , \tag{4.8}$$

$$t' = \int dt / s . \tag{4.9}$$

This transformation can be explained in a unified fashion from a basic assumption of the scaling of the infinitesimal time,

$$dt' = dt / s . \tag{4.10}$$

This relation was extracted from the following speculation. Consider the motion of a particle during one simulation time step. The velocity \mathbf{v} is defined as a ratio of the difference of the coordinate $\Delta \mathbf{q}$ and the time Δt ,

$$\mathbf{v} = \frac{\Delta \mathbf{q}}{\Delta t} . \tag{4.11}$$

The temperature of a system is related to the average of the kinetic energy. A temperature control will be achieved via control of the velocity. Assume that the speed of a particle is larger than an objective value. If we lengthen the time Δt required for the movement of $\Delta \mathbf{q}$, the velocity is reduced. On the other hand, the motion is accelerated by shortening the time period Δt . Therefore, the control of the temperature could be achieved by introduction of a flexible time. The change of the time length is expressed as scaling by the variable s .

With Eq. (4·10), the velocity scaling in Eq. (4·6) is interpreted as

$$\mathbf{v}'_i = \frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}_i}{dt} = s \frac{d\mathbf{q}_i}{dt} = s \mathbf{v}_i. \quad (4 \cdot 12)$$

This type of transformations from virtual to real variables and vice versa is employed later to transform the equations of motion in a virtual variable formulation to those with real variables.

4.2. The equations of motion

A Hamiltonian is postulated to describe an extended system consisting of a physical system and a heat bath,

$$H^* = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \Phi(\mathbf{q}) + \frac{p_s^2}{2Q} + gkT \ln s. \quad (4 \cdot 13)$$

The first two terms are the kinetic energy and the potential energy of a physical system we are interested in. Every where we expect a momentum \mathbf{p}_i to appear, it is replaced by a real momentum $\mathbf{p}'_i = \mathbf{p}_i/s$. The last two terms correspond to an added degree of freedom, where p_s is a conjugate momentum of s , Q is a parameter which behaves as a mass for the motion of s and T is the temperature for the heat bath. The parameter g is essentially equal to the number of degree of freedom of the physical system. Its exact value will be chosen to satisfy the canonical distribution exactly in equilibrium.

An additional degree of freedom s is introduced to break the conservation of the total energy which is inevitably imposed on the molecular dynamics simulations as a result of the use of classical mechanics. The total Hamiltonian Eq. (4·13) is still conserved in the whole extended system, but the total energy of a physical system,

$$H_0(\mathbf{p}', \mathbf{q}') = \sum_i \frac{\mathbf{p}'_i{}^2}{2m_i} + \Phi(\mathbf{q}') \quad (4 \cdot 14)$$

can fluctuate and the distribution of the energy will follow the canonical distribution. A potential energy for s , $gkT \ln s$ is chosen to guarantee the canonical distribution.

We assume that the Hamiltonian formalism can be applied to Eq. (4·13) with the virtual variables. The equations of motion are obtained via canonical equations as²⁴⁾

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H^*}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2}, \quad (4 \cdot 15)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H^*}{\partial \mathbf{q}_i} = -\frac{\partial \Phi}{\partial \mathbf{q}_i}, \quad (4 \cdot 16)$$

$$\frac{ds}{dt} = \frac{\partial H^*}{\partial p_s} = \frac{p_s}{Q}, \quad (4.17)$$

$$\frac{dp_s}{dt} = -\frac{\partial H^*}{\partial s} = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i s^2} - gkT \right) / s. \quad (4.18)$$

These equations exhibit a negative feedback mechanism to control the temperature at a fixed value. The acceleration of s is proportional to the deviation of the total kinetic energy from its average value $gkT/2$. This mechanism keeps the kinetic energy around $gkT/2$. This will be shown later more clearly in the real variable equations.

We transform the equations of motion Eqs. (4.15)~(4.18) to equations with real variables.²⁵⁾ This form is more convenient in application of simulations. The transformations are carried out in stepwise fashion via basic relations Eqs. (4.7)~(4.9) between the virtual and real variables. An additional relation

$$p'_s = p_s / s, \quad (4.19)$$

is also introduced.

$$\frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}_i}{dt} = s \frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i s} = \frac{\mathbf{p}'_i}{m_i}, \quad (4.20)$$

$$\frac{d\mathbf{p}'_i}{dt'} = s \frac{d}{dt} \left(\frac{\mathbf{p}_i}{s} \right) = \frac{d\mathbf{p}_i}{dt} - \frac{1}{s} \frac{ds}{dt} \mathbf{p}_i = -\frac{\partial \Phi}{\partial \mathbf{q}'_i} - \frac{1}{s} \frac{ds}{dt'} \mathbf{p}'_i, \quad (4.21)$$

$$\frac{ds'}{dt'} = s \frac{ds'}{dt} = s \frac{ds}{dt} = s'^2 \frac{p'_s}{Q}, \quad (4.22)$$

$$\frac{dp'_s}{dt'} = s \frac{d}{dt} \left(\frac{p_s}{s} \right) = \frac{dp_s}{dt} - \frac{1}{s} \frac{ds}{dt} p_s = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - gkT \right) / s - \frac{1}{s} \frac{ds}{dt'} p'_s. \quad (4.23)$$

Hoover pointed out that if a new variable $\zeta = (1/s) ds/dt' = s' p'_s / Q$ is chosen, the equations can be simplified as⁴⁰⁾

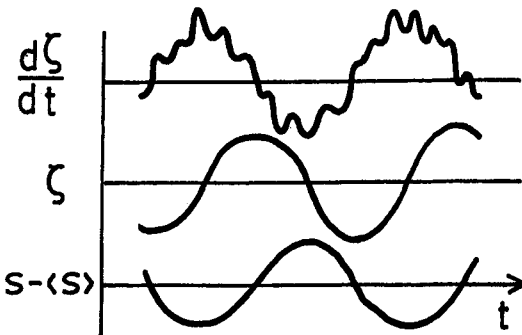


Fig. 3. A schematic time evolution of $(d\zeta/dt)$ or the kinetic energy, ζ , and the heat bath variable s . A negative feedback mechanism works to keep the kinetic energy around its averaged value.

$$\frac{d\mathbf{q}'_i}{dt'} = \frac{\mathbf{p}'_i}{m_i}, \quad (4.24)$$

$$\frac{d\mathbf{p}'_i}{dt'} = -\frac{\partial \Phi}{\partial \mathbf{q}'_i} - \zeta \mathbf{p}'_i, \quad (4.25)$$

$$\frac{d \cdot \ln s'}{dt'} = \zeta, \quad (4.26)$$

$$\frac{d\zeta}{dt'} = \left(\sum_i \frac{\mathbf{p}_i^2}{m_i} - gkT \right) / Q. \quad (4.27)$$

This form is now known as the Nosé-Hoover thermostat.⁴¹⁾ We will discuss about this form in detail in § 5. A negative feedback mechanism is more apparent in the Nosé-Hoover thermostat form (see Fig. 3). Equations (4.24) and (4.25)

have the same form as those describing the motion of a body with a frictional force. However, the friction coefficient ζ is not a constant and can be positive or negative in our case. The time development of ζ is driven by the imbalance between the kinetic energy and its average value $(g/2)kT$. If the kinetic energy is larger than $(g/2)kT$, the time derivative of ζ is positive, $d\zeta/dt > 0$, and then ζ increases and will become positive. The equation with positive ζ is equivalent with that of a system with a friction force. The velocity of the particle decreases and the kinetic energy also decreases. If the kinetic energy becomes lower than $(g/2)kT$, the feedback mechanism works in the opposite direction. ζ decreases, and in the negative ζ region, the system is heated up. In this way, the kinetic energy fluctuates around its average value $(g/2)kT$. The time average of a time derivative of a variable will vanish. This guarantees the average of the kinetic energy coincides with the result of the equipartition theorem $(g/2)kT$.

4.3. The equilibrium distribution function^{24),25)}

The total Hamiltonian H^* Eq. (4.13) is conserved. On the assumption of the ergodic property in the extended system, the time average along the trajectory described by the equations of motion Eqs. (4.15)~(4.18) agrees with the microcanonical ensemble average in the extended system. The equilibrium distribution function is expressed in a δ function form as $\delta(H^* - E)$. E is a value of the Hamiltonian H^* , and is a control parameter in this ensemble. We carry out a projection of the distribution $\delta(H^* - E)$ in a phase space $(\mathbf{p}, \mathbf{q}, p_s, s)$ onto a subspace $(\mathbf{p}, \mathbf{q}, p_s)$ in which the canonical distribution will be attained.

The partition function Z of the extended system is

$$Z = \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{q} \delta \left[H_0(\mathbf{p}/s, \mathbf{q}) + \frac{p_s^2}{2Q} + gkT \ln s - E \right], \quad (4.28)$$

where we ignore a constant factor $1/(N!h^{3N})$.

Before the integration with respect to the variable s , we transform the virtual momentum \mathbf{p}_i and coordinate \mathbf{q}_i to the real variables $\mathbf{p}'_i = \mathbf{p}_i/s$, $\mathbf{q}'_i = \mathbf{q}_i$. The volume element changes as

$$d\mathbf{p}d\mathbf{q} = s^{3N} d\mathbf{p}' d\mathbf{q}'. \quad (4.29)$$

The volume of the phase space is not conserved because this transformation is not canonical. Since there is no upper limit for momentum in nonrelativistic classical mechanics, we can exchange the order of the integration. Hence,

$$Z = \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N} \delta \left[H_0(\mathbf{p}', \mathbf{q}') + \frac{p_s^2}{2Q} + gkT \ln s - E \right]. \quad (4.30)$$

Now the argument of the δ function in the above equation has only one zero as a function of the variable s . We employ an equivalence relation $\delta(f(s)) = \delta(s - s_0)/|f'(s_0)|$; s_0 is the zero of $f(s)$, $f(s_0) = 0$ and $f'(s) = df/ds$,

$$s_0 = \exp \left[- \left\{ H_0(\mathbf{p}', \mathbf{q}') + \frac{p_s^2}{2Q} - E \right\} / gkT \right], \quad (4.31)$$

and $f'(s) = gkT/s$ in this case. The behavior of a logarithmic function which increases monotonically from the negative to the positive infinities is a key factor for this simplification.

The partition function Eq. (4·28) is now transformed to

$$Z = \frac{1}{gkT} \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N+1} \delta\left(s - \exp\left[-\left\{H_0(\mathbf{p}', \mathbf{q}') + \frac{p_s^2}{2Q} - E\right\}/gkT\right]\right). \quad (4 \cdot 32)$$

The integration with respect to s is easily carried out in this form, and we get

$$Z = \frac{1}{gkT} \left\{ \int dp_s \exp\left[\frac{3N+1}{g}\left(E - \frac{p_s^2}{2Q}\right)/kT\right] \right\} \times \int d\mathbf{p}' \int d\mathbf{q}' \exp\left[-\frac{3N+1}{g}H_0(\mathbf{p}', \mathbf{q}')/kT\right]. \quad (4 \cdot 33)$$

The integrations in p_s and $(\mathbf{p}', \mathbf{q}')$ part are separated, and they can be integrated independently. The p_s part gives a constant dependent on the parameters E, T, Q and g .

If we choose $g=3N+1$, the partition function Z of the extended system is equivalent to that of the physical system in the canonical ensemble Z_c except for a constant factor, $Z = C Z_c$, where

$$Z_c = \int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT]. \quad (4 \cdot 34)$$

This means that the equilibrium distribution function is

$$f(\mathbf{p}', \mathbf{q}') = \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT]. \quad (4 \cdot 35)$$

We can also apply the projection from the extended system onto a physical phase space in a similar fashion in calculation of the ensemble average of a quantity $A(\mathbf{p}/s, \mathbf{q})$ in the extended system. It agrees with the canonical ensemble average of $A(\mathbf{p}', \mathbf{q}')$ in a physical system,

$$\begin{aligned} \langle A(\mathbf{p}/s, \mathbf{q}) \rangle_{\text{ES}} &= \frac{\int A(\mathbf{p}/s, \mathbf{q}) f_{\text{ES}}(\mathbf{p}, \mathbf{q}, p_s, s) dpdqdp_s ds}{\int f_{\text{ES}}(\mathbf{p}, \mathbf{q}, p_s, s) dpdqdp_s ds} \\ &= \frac{\int A(\mathbf{p}', \mathbf{q}') f_c(\mathbf{p}', \mathbf{q}') d\mathbf{p}' d\mathbf{q}'}{\int f_c(\mathbf{p}', \mathbf{q}') d\mathbf{p}' d\mathbf{q}'} = \langle A(\mathbf{p}', \mathbf{q}') \rangle_c. \end{aligned} \quad (4 \cdot 36)$$

Suffixes ES and c indicate the extended system and the canonical ensemble, respectively. Thus, we can get the canonical ensemble average from the time average obtained in simulations in the extended system,

$$\lim_{t \rightarrow \infty} \frac{1}{t} \int^t A(\mathbf{p}/s, \mathbf{q}) dt = \langle A(\mathbf{p}/s, \mathbf{q}) \rangle_{\text{ES}} = \langle A(\mathbf{p}', \mathbf{q}') \rangle_c. \quad (4 \cdot 37)$$

The first equality is satisfied if an extended system is ergodic. The second equality

is proved in this subsection.

The time average in Eq. (4·37) is calculated in terms of a virtual time. The length of a time step is flexible and is different in each time step in a virtual variable formulation. The total time period t_0 in a virtual time is related to that in a real time t_1 by

$$t_1 = \int^{t_1} dt' = \int^{t_0} \frac{dt}{s}. \quad (4 \cdot 38)$$

If one carries out simulations with real variable equations, the time average in terms of a real time is different from that in Eq. (4·37) and corresponds to a weighted average in the extended system,²⁵⁾

$$\begin{aligned} \lim_{t_1 \rightarrow \infty} \frac{1}{t_1} \int^{t_1} A(\mathbf{p}', \mathbf{q}') dt' &= \left(\lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int^{t_0} A(\mathbf{p}/s, \mathbf{q}) \frac{dt}{s} \right) / \left(\lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int^{t_0} \frac{dt}{s} \right) \\ &= \left\langle \frac{A(\mathbf{p}/s, \mathbf{q})}{s} \right\rangle_{\text{ES}} / \left\langle \frac{1}{s} \right\rangle_{\text{ES}}. \end{aligned} \quad (4 \cdot 39)$$

Comparing Eqs. (4·32) and (4·36), we see the weighted average in the extended system Eq. (4·39) is identical to $\langle A(\mathbf{p}', \mathbf{q}') \rangle_c$ if we choose g as $g=3N$.

$$\lim_{t_1 \rightarrow \infty} \frac{1}{t_1} \int^{t_1} A(\mathbf{p}', \mathbf{q}') dt' = \langle A(\mathbf{p}', \mathbf{q}') \rangle_c. \quad (4 \cdot 40)$$

The canonical ensemble average is obtained with $g=3N+1$ in virtual variable equations (4·15)~(4·18), and with $g=3N$ in real variable equations (4·24)~(4·27). We consider the differences in these two frames. If an equal g value is chosen in both frames, the trajectories in the phase space Γ are completely identical, but they pass through with different speed. An equal distribution in a virtual phase space is realized from the principle of a priori equal probability because we assumed the Hamiltonian formalism in this frame. Then, the distribution in a real phase space is not an equal distribution. This reflects that the equations of motion in real frame cannot be directly derived from a Hamiltonian.

The relation between the virtual real frames is generally discussed by Jellinek.^{38),39)} His conclusions are (1) the scaling relations of phase space variables like Eqs. (4·7), (4·8), and (4·19) should be distinguished from the scaling of time, Eq. (4·10). (2) When the scaling of the time is not employed, a trajectory in a real space $(\mathbf{p}', \mathbf{q}', p'_s, s)$ is exactly the same that in $(\mathbf{p}/s, \mathbf{q}, p_s/s, s)$ which can be obtained from the trajectory in a virtual space $(\mathbf{p}, \mathbf{q}, p_s, s)$. (3) The microcanonical distribution is guaranteed by the quasi-ergodic property known as the von Neumann-Birkoff theorem at least in subregions of an energy shell in a virtual $(\mathbf{p}, \mathbf{q}, p_s, s)$ space, in which the coordinates and momenta are canonically conjugated. (4) The time scaling results in a weighted distribution in the phase space. (5) There are infinitely many choices for the scaling relations and the potential term for s to realize the canonical distribution.

As a special case of this biased distribution, the time scaling by the power of the variables s, s^m , gives a distribution corresponding to a shifted temperature. The shifted temperature in Eq. (4·39) is

$$T' = T \left(1 + \frac{1}{3N} \right). \quad (4 \cdot 41)$$

The parameter g is reduced to $3N$ to correct this deviation.

4.4. The temperature shift method

The shifting of the temperature in a weighted average with s is pointed out in the previous subsection. This effect is applied to calculation of the thermodynamical quantities at temperatures different from the simulated point by Branka and Parrinello,³⁶⁾ and by Otsuka.³⁷⁾ A weighted average $\langle s^m A(\mathbf{p}/s, \mathbf{q}) \rangle_T$ in the extended system at temperature T is obtained in a fashion similar to calculation of the partition function Z ,²⁴⁾

$$\begin{aligned} \langle s^m A(\mathbf{p}/s, \mathbf{q}) \rangle_T &= \frac{\int dp'_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N+1+m} \delta(s-s_0) A(\mathbf{p}', \mathbf{q}')}{\int dp'_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N+1} \delta(s-s_0)} \\ &= \exp \left[\frac{mE}{(3N+1)kT} \right] \left(\frac{3N+1}{3N+1+m} \right)^{1/2} \\ &\quad \times \frac{\int d\mathbf{p}' \int d\mathbf{q}' A(\mathbf{p}', \mathbf{q}') \exp \left[-\frac{3N+1+m}{3N+1} H_0(\mathbf{p}', \mathbf{q}')/kT \right]}{\int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT]} \end{aligned} \quad (4 \cdot 42)$$

with $g=3N+1$, s_0 is the same as in Eq. (4·31). A fluctuation formula for s is obtained as a special case of Eq. (4·42),

$$\begin{aligned} \left\langle \left(\frac{s - \langle s \rangle}{\langle s \rangle} \right)^2 \right\rangle_T &= \left(\frac{(3N+2)^2}{(3N+1)(3N+3)} \right)^{(3N+1)/2} \times \frac{\left\langle \exp \left[-\frac{2}{3N+1} H_0(\mathbf{p}', \mathbf{q}')/KT \right] \right\rangle_c}{\left\langle \exp \left[-\frac{1}{3N+1} H_0(\mathbf{p}', \mathbf{q}')/KT \right] \right\rangle_c^2} - 1 \end{aligned} \quad (4 \cdot 43)$$

and this formula is approximated in a large system as

$$\left\langle \left(\frac{s - \langle s \rangle}{\langle s \rangle} \right)^2 \right\rangle_T = \frac{1}{(3N)^2} \left(\frac{1}{kT} \right)^2 \{ \langle H_0^2 \rangle_c - \langle H_0 \rangle_c^2 \} = \frac{C_V}{(3N)^2 k}, \quad (4 \cdot 44)$$

where the heat capacity C_V is given in Eq. (2·20).

A shifted temperature T_m is defined by³⁶⁾

$$T_m = \frac{3N+1}{3N+1+m} T. \quad (4 \cdot 45)$$

Then, a ratio of a weighted average of $s^m A$ and s^m at T is equivalent with the canonical ensemble average at T_m , $\langle A(\mathbf{p}', \mathbf{q}') \rangle_{cT_m}$.

$$\frac{\langle s^m A \rangle_T}{\langle s^m \rangle_T} = \frac{\int d\mathbf{p}' \int d\mathbf{q}' A(\mathbf{p}', \mathbf{q}') \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT_m]}{\int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT_m]} \\ = \langle A(\mathbf{p}', \mathbf{q}') \rangle_{cT_m}. \quad (4.46)$$

The power m is a continuous real number, which can take the value of both, positive and negative, signs. From the simulation at T , we can get quantities in the neighborhood of T .³⁷⁾ The reliability for the calculation decreases as the shift increases. The temperature shift in the extended system method resembles the Monte Carlo technique for calculation of the free energy.⁵⁸⁾ From the definition of the free energy $F(T)$,

$$F(T) = -kT \ln Z_c = -kT \ln \left\{ \int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT] \right\}, \quad (4.47)$$

the average of the power of s is expressed as

$$\langle s^m \rangle_T = \frac{T_m^{1/2} \exp[-\{F(T_m) - E\}/kT_m]}{T^{1/2} \exp[-\{F(T) - E\}/kT]}. \quad (4.48)$$

Equation (4.48) is employed to relate the free energy at T with that at T_m .³⁶⁾

The temperature shift method is useful for study of a small system. The method was applied to simulations of a 13 Lennard-Jones atom cluster.^{36),37)} By this method we can obtain quantities in a wide range of temperature from simulations only at several temperatures. However, the temperature shift Eq. (4.45) becomes very small in a large system. The difficulty at the accurate calculation of the weighted averages increases with the power of s . Therefore, this will not be so convenient in a large system as in a small system.

4.5. The extension of the Hamiltonian formulation

A generalization of the extended system method along the line of the Hamiltonian formulation is discussed by Jellinek,³⁸⁾ and Jellinek and Berry.³⁹⁾ They distinguish the scaling of phase space variables and the scaling of time. We first consider the problem of the phase space scaling. Generalized relations between the virtual and real variables are given as

$$q'_{i\lambda} = q_{i\lambda} f_{i\lambda}(s), \quad (4.49)$$

$$p'_{i\lambda} = p_{i\lambda} / h(s), \quad (4.50)$$

$$p'_s = p_s / u(s). \quad (4.51)$$

The suffix λ indicates the x , y or z components. Not only the momenta but coordinates and a conjugate momentum of s are scaled. The Hamiltonian in an extended system is defined as

$$H^*(\mathbf{p}', \mathbf{q}', p'_s, s) = \sum_i \frac{\mathbf{p}'_i{}^2}{2m_i} + \Phi(\mathbf{q}') + \frac{p'_s{}^2}{2Q} + kTv(s). \quad (4.52)$$

The potential energy for s is also generalized to $kTv(s)$. A similar procedure is

employed to derive the canonical distribution in a physical system. A key factor is the Jacobian corresponding to Eq. (4·29) appearing in the transformation from virtual to real variables,

$$d\mathbf{p}d\mathbf{q}d\mathbf{p}_s = u(s) \left(\prod_{i,\lambda} \frac{h_{i\lambda}(s)}{f_{i\lambda}(s)} \right) d\mathbf{p}' d\mathbf{q}' d\mathbf{p}'_s. \quad (4 \cdot 53)$$

After this transformation, the only s dependent part in the argument of a δ function, $\delta(H^* - E)$, is the potential $kTv(s)$. $v(s)$ should be a continuous monotonically increasing function of s with a range $-\infty \leq v(s) \leq +\infty$, to satisfy a requirement mentioned before. Then, a unique solution for $H^*(s) - E = 0$ is

$$s_0 = v^{-1}(-H_1/kT), \quad (4 \cdot 54)$$

where $H_1 = H_0(\mathbf{p}', \mathbf{q}') + p_s'^2/2Q - E$. $v^{-1}(x)$ is an inverse function of $v(x)$. A canonical distribution at temperature T is realized if $v(s)$ is chosen to satisfy

$$\frac{u(s_0)}{v'(s_0)} \left(\prod_{i,\lambda} \frac{h_{i\lambda}(s_0)}{f_{i\lambda}(s_0)} \right) = \exp[-H_1/kT], \quad (4 \cdot 55)$$

$v'(s) = dv/ds$. One of the conclusion obtained from Jellinek's extension is that there are infinitely many choices for the functional form of the potential $v(s)$ to realize the canonical distribution. As pointed out in § 4.3, a scaling of time changes the distribution. A new scaling relation for time is introduced,

$$dt' = dt/w(s). \quad (4 \cdot 56)$$

The canonical distribution in the real time average will also be obtained. The requirement in this case is

$$\frac{u(s_0)}{w(s_0)v'(s_0)} \left(\prod_{i,\lambda} \frac{h_{i\lambda}(s_0)}{f_{i\lambda}(s_0)} \right) = \exp[-H_1/kT]. \quad (4 \cdot 57)$$

By the addition of a factor $w(s)$ the variety of the method seems to increase further. The argument for static thermodynamical quantities is carried out in the same fashion as before. We can obtain the canonical ensemble averages from any of the extensions given in Eqs. (4·49)~(4·51) and (4·56).

A careful examination is required for dynamical quantities. A merit of the molecular dynamics simulation over another simulation method, the Monte Carlo method, is that the dynamical properties are also obtained. As we will discuss later in § 6, the dynamical properties in the extended system method are reliable if the application is limited to those in equilibrium in a large system. However, a requirement should be satisfied. The discussion in § 6 is based on the analysis of the relative amplitude of the additional force term to the force derived from a potential. The ordinary force term must be identical with that in Newton's equation. The modified equations will be reexpressed in a quasi-Newtonian form,

$$m_i \frac{d^2 \mathbf{q}_i}{dt^2} = - \frac{\partial \Phi(\mathbf{q})}{\partial \mathbf{q}_i} A + B. \quad (4 \cdot 58)$$

An additional factor A changes directly the speed of the particle. This factor should

be always kept to the unity,

$$A=1, \quad (4 \cdot 59)$$

to obtain a realistic dynamical behavior. Real variable equations (4·24) and (4·25) satisfy this requirement, but virtual variable equations (4·15) and (4·16) do not. From latter equations,

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H^*}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2}, \quad (4 \cdot 15)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H^*}{\partial \mathbf{q}_i} = -\frac{\partial \Phi}{\partial \mathbf{q}_i}, \quad (4 \cdot 16)$$

a quasi-Newtonian equation is derived as follows:

$$\begin{aligned} m_i \frac{d^2 \mathbf{q}_i}{dt^2} &= \frac{d}{dt} \left(m_i \frac{d\mathbf{q}_i}{dt} \right) = \frac{d}{dt} \left(\frac{\mathbf{p}_i}{s^2} \right) \\ &= \frac{1}{s^2} \frac{d\mathbf{p}_i}{dt} - \frac{2}{s^3} \frac{ds}{dt} \mathbf{p}_i \\ &= -\frac{\partial \Phi}{\partial \mathbf{q}_i} \frac{1}{s^2} - \frac{2}{s^3} \frac{ds}{dt} \mathbf{p}_i. \end{aligned} \quad (4 \cdot 60)$$

$A=1/s^2$ for a virtual variable formulation is not the unity. This shows clearly that the time evolution in a virtual frame does not correspond to a realistic dynamics of particles.

The extended system method is sometimes interpreted via a scaling of a mass,²⁶⁾

$$m'_i = m_i s^2, \quad (4 \cdot 61)$$

which is apparent in Eq. (4·60). m'_i and m_i are a real and a virtual masses. The kinetic energy $K = \sum_i \mathbf{p}_i'^2 / 2m_i'$ is controlled to a constant value by changing a mass. It is well known in classical statistical mechanics that the equilibrium properties do not depend upon the mass of the particle. Therefore, the changing of the mass does not affect on the static properties of a system. This type of reasoning is enough to explain how a constant temperature condition is attained in the extended system method. However, the author recommends the interpretation based on the scaling of the infinitesimal time as explained in § 4.1. The dynamical properties cannot be interpreted consistently by a mass scaling.

A quasi-Newtonian form for the generalization by Jellinek is obtained in the following way. A starting virtual Hamiltonian is obtained from Eq. (4·52) expressing with virtual variables,

$$\begin{aligned} H^*(p_{i\lambda}/h_{i\lambda}(s), q_{i\lambda}f_{i\lambda}(s), p_s/u(s), s) \\ = \sum_{i,\lambda} \frac{p_{i\lambda}^2}{2m_i \{h_{i\lambda}(s)\}^2} + \Phi(q_{i\lambda}f_{i\lambda}(s)) + \frac{p_s^2}{2Q\{u(s)\}^2} + kTv(s). \end{aligned} \quad (4 \cdot 62)$$

The equations of motion for the coordinate and the momentum are obtained via canonical equations,

$$\frac{dq_{i\lambda}}{dt} = \frac{\partial H^*}{\partial p_{i\lambda}} = \frac{p_{i\lambda}}{m_i h_{i\lambda}^2}, \quad (4.63)$$

$$\frac{dp_{i\lambda}}{dt} = -\frac{\partial H^*}{\partial q_{i\lambda}} = -\frac{\partial q'_{i\lambda}}{\partial q_{i\lambda}} \frac{\partial \Phi}{\partial q'_{i\lambda}} = -f_{i\lambda} \frac{\partial \Phi}{\partial q'_{i\lambda}}. \quad (4.64)$$

The equations are transformed to real variable equations by Eqs. (4.49), (4.50) and (4.56) in the fashion similar to § 4.2,

$$\begin{aligned} \frac{dq'_{i\lambda}}{dt'} &= w \frac{d}{dt} (q_{i\lambda} f_{i\lambda}) = w f_{i\lambda} \frac{dq_{i\lambda}}{dt} + w q_{i\lambda} \frac{df_{i\lambda}}{dt} \\ &= w \frac{f_{i\lambda}}{m_i h_{i\lambda}} p'_{i\lambda} + C, \end{aligned} \quad (4.65)$$

$$\begin{aligned} \frac{dp'_{i\lambda}}{dt'} &= w \frac{d}{dt} \left(\frac{p_{i\lambda}}{h_{i\lambda}} \right) = \frac{w}{h_{i\lambda}} \frac{dp_{i\lambda}}{dt} - \frac{w}{h_{i\lambda}^2} p_{i\lambda} \frac{dh_{i\lambda}}{dt} \\ &= -w \frac{f_{i\lambda}}{h_{i\lambda}} \frac{\partial \Phi}{\partial q'_{i\lambda}} + D. \end{aligned} \quad (4.66)$$

C and D are terms irrelevant to extract a Newtonian force term. Finally, a quasi-Newtonian form is obtained as

$$\begin{aligned} \frac{d^2 q'_{i\lambda}}{dt'^2} &= \frac{d}{dt'} \left(m_i \frac{dq'_{i\lambda}}{dt'} \right) = \frac{d}{dt'} \left(w \frac{f_{i\lambda}}{h_{i\lambda}} p'_{i\lambda} + C \right) \\ &= w \frac{f_{i\lambda}}{h_{i\lambda}} \frac{dp'_{i\lambda}}{dt'} + C' \\ &= -\frac{\partial \Phi}{\partial q'_{i\lambda}} \left(w \frac{f_{i\lambda}}{h_{i\lambda}} \right)^2 + C''. \end{aligned} \quad (4.67)$$

The additional factor in this case is

$$A = \left(w \frac{f_{i\lambda}}{h_{i\lambda}} \right)^2. \quad (4.68)$$

The requirement Eq. (4.59) gives a relation between the scaling factors,

$$h_{i\lambda}(s) = w(s) f_{i\lambda}(s). \quad (4.69)$$

A periodic boundary condition is employed in most simulations. The separate scaling in each coordinate as in Eq. (4.49) is not consistent with the periodic boundary condition. In this case, different scalings for x , y and z components are only allowed. Equation (4.69) is further reduced to

$$h_{i\lambda}(s) = w(s) f_{i\lambda}(s). \quad (4.70)$$

The scaling of the unit cell size is employed in the constant pressure method as shown in Eqs. (4.1)~(4.3). The appearance of a similar term $f_{i\lambda}(s)$ suggests a temperature control via pressure. This possibility is also pointed out in the Nosé-Hoover thermostat form.

A canonical transformation of this type,

$$p'_i = p_i/s, \quad q'_i = sq_i \quad (4.71)$$

is employed in the work by Grilli and Tosatti³⁵⁾ which gives a possibility to calculate the canonical ensemble averages in a quantum system. The canonical transformation Eq. (4.71) is necessary to conserve the canonical exchange relation between a coordinate and a momentum.

Other significant extensions in Jellinek's work are the replacement of the time scaling factor s to a general function $w(s)$.

§ 5. The extended system method II: The Nosé-Hoover thermostat formulation

5.1. The Nosé-Hoover thermostat^{24),40),41)}

In § 4, the equations of motion in terms of real variables are derived from the virtual variable equations via the scaling relations Eqs. (4.7), (4.8) and (4.10). The basic equations are

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} \quad (\text{Eq. (4.24)}), \quad (5.1)$$

$$\frac{dp_i}{dt} = -\frac{\partial \Phi}{\partial q_i} - \zeta p_i \quad (\text{Eq. (4.25)}), \quad (5.2)$$

$$\frac{d\zeta}{dt} = \left(\sum_i \frac{p_i^2}{m_i} - gkT \right) / Q \quad (\text{Eq. (4.27)}), \quad (5.3)$$

$$\frac{d \ln s}{dt} = \zeta \quad (\text{Eq. (4.26)}). \quad (5.4)$$

We do not use the primed notations because all the variables appearing in this section are real variables. We can easily and clearly recognize a negative feedback mechanism in this form (see Fig. 4). Equations (5.1) and (5.2) are effectively the equations of motion with a frictional force. However, the friction coefficient ζ is not a constant but a variable. It can have the values in both signs. When ζ is positive, the

movement of the particles is slowed down, but the motion is accelerated in the negative ζ region. The change of ζ is governed by the deviation of the kinetic energy from its average value. Consider a motion in a phase space

$$A = (\zeta, \delta K), \quad (5.5)$$

where the deviation of the Kinetic energy K , $\delta K = K - \langle K \rangle$ is proportional to $d\zeta/dt$, $d\zeta/dt \propto \delta K = K - \langle K \rangle$. The velocity in this space

$$\dot{A} = \left(\frac{d\zeta}{dt}, \frac{d\delta K}{dt} \right), \quad (5.6)$$

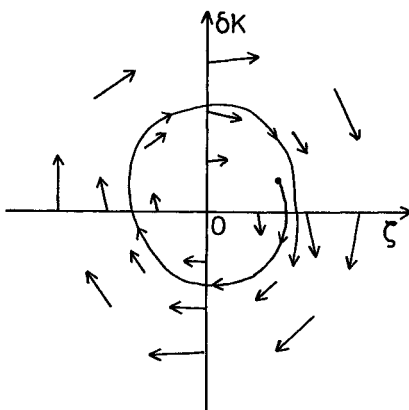


Fig. 4. The movement in a phase space $(\zeta, \delta K)$. Arrows indicate velocity vectors.

is depicted in Fig. 4. From Eq. (5.3), $\delta\zeta/dt > 0$ when $\delta K > 0$, and $d\zeta/dt < 0$ when $\delta K < 0$. From Eq. (5.2), $d\delta K/dt < 0$ when $\zeta > 0$ and $d\delta K/dt > 0$ when $\zeta < 0$. The trajectory in this phase space circles around the origin clockwise. The kinetic energy fluctuates and is kept around a constant.

This reformulation of the extended system method given by Hoover,⁴⁰⁾ is based on the above mentioned equations and is now known as the Nosé-Hoover thermostat.⁴¹⁾ The first three of them Eqs. (5.1)~(5.3) form a closed system of equations. The time evolution of the system within a phase space $(\mathbf{p}, \mathbf{q}, \zeta)$ is uniquely determined from these equations. In this sense, Eq. (5.4) is redundant. However, if we also solve this equation, a quantity

$$H^* = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{q}) + \frac{Q}{2}\zeta^2 + gkT \ln s, \quad (5.7)$$

is conserved. This corresponds to the total Hamiltonian Eq. (4.13) of the extended system in a virtual variable formulation. This conservation law can be used as a measure that the simulation is carried out correctly. The transformations (4.7) and (4.8) are not canonical, Eq. (5.7) is no longer a Hamiltonian, and we cannot derive Eqs. (5.1)~(5.4) from this.

The real variable formulation in § 4 and the Nosé-Hoover thermostat equations are completely equivalent when a physical system is connected to only one heat bath and the interaction between a particle and a heat bath is identical for every particle. However, in the Nosé-Hoover thermostat form, we can extend the method to various situations in which there is no counterpart in the Hamiltonian formulation. A separate control for several groups of degrees of freedom is a typical example (see § 5.3).⁵⁹⁾

5.2. Another proof of the canonical distribution⁴⁰⁾

A proof that the extended system method guarantees the canonical distribution is also demonstrated in the fashion similar to that employed in the constraint method. Consider an extended phase space $\Gamma = (\mathbf{p}, \mathbf{q}, \zeta)$ in this case. A distribution function $f(\mathbf{p}, \mathbf{q}, \zeta)$ is defined in this phase space. The conservation of the probability is expressed by a generalized Liouville equation similar to Eq. (3.10),

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \Gamma} \cdot (\dot{\Gamma} f) = 0. \quad (5.8)$$

We are interested in the change of f along a phase space trajectory. Therefore, we consider a total time derivative of f ,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma}. \quad (5.9)$$

Then, Eq. (5.8) is reexpressed as

$$\frac{df}{dt} = - \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} \right) f. \quad (5.10)$$

In our case, $(\partial/\partial \Gamma) \cdot \dot{\Gamma}$ is not equal to zero, and the Liouville's theorem, $df/dt = 0$, does

not hold in constant temperature simulations.

$$\begin{aligned}\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} &= \sum_i \left(\frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) + \frac{\partial}{\partial \zeta} \dot{\zeta} \\ &= \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot (-\zeta \mathbf{p}_i) = -g\zeta.\end{aligned}\quad (5\cdot11)$$

We define a function

$$H_T = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \Phi(\mathbf{q}) + \frac{Q}{2} \zeta^2. \quad (5\cdot12)$$

Its time derivative is

$$\frac{dH_T}{dt} = \sum_i \left(\dot{\mathbf{p}}_i \cdot \frac{\partial H_T}{\partial \mathbf{p}_i} + \dot{\mathbf{q}}_i \cdot \frac{\partial H_T}{\partial \mathbf{q}_i} \right) + \dot{\zeta} \frac{\partial H_T}{\partial \zeta} = -gkT\zeta. \quad (5\cdot13)$$

Comparing Eqs. (5·11) and (5·13), the generalized Liouville equation (5·10) is reduced to

$$\frac{df}{dt} = -\frac{1}{kT} \frac{dH_T}{dt} f, \quad (5\cdot14)$$

and a solution of this equation is easily obtained

$$f(\mathbf{p}, \mathbf{q}, \zeta) = C \exp[-H_T/kT], \quad (5\cdot15)$$

which has a canonical distribution form.

The probability in a volume element along a phase space trajectory is not conserved in the Nosé-Hoover equation. A conserved quantity is $\exp[H_T/kT] f(\mathbf{p}, \mathbf{q}, \zeta)$. Therefore, the probability along the trajectory in a phase space changes in proportion to $\exp[-H_T/kT]$. If the ergodic property is satisfied in the extended system, a trajectory covers almost all allowed points in a phase space. The distribution f can be identified with the equilibrium distribution function and the canonical distribution in a physical system is realized in this situation.

We comment on the conserved quantities in the Nosé-Hoover thermostat equations. A pseudo-Hamiltonian Eq. (5·7) is conserved,

$$\frac{d}{dt} H^* = \frac{d}{dt} (H_T + gkT \ln s) = -gkT\zeta + gkT \frac{d \ln s}{dt} = 0. \quad (5\cdot16)$$

This shows clearly that an additional equation (5·4) is introduced to compensate the energy dissipation of H_T .

The sum of the force or torque vanishes with central forces. The equations for the total linear momentum $\mathbf{P} = \sum_i \mathbf{p}_i$ and the total angular momentum $\mathbf{L} = \sum_i \mathbf{q}_i \times \mathbf{p}_i$ are obtained as

$$\begin{aligned}\frac{d}{dt} \sum_i \mathbf{p}_i &= \sum_i -\frac{\partial \Phi}{\partial \mathbf{q}_i} - \zeta \sum_i \mathbf{p}_i = -\zeta \sum_i \mathbf{p}_i, \\ \frac{d}{dt} \sum_i \mathbf{q}_i \times \mathbf{p}_i &= \sum_i \mathbf{q}_i \times \frac{d\mathbf{p}_i}{dt}\end{aligned}\quad (5\cdot17)$$

$$= \sum_i \mathbf{q}_i \times \left(-\frac{\partial \Phi}{\partial \mathbf{q}_i} - \zeta \mathbf{p}_i \right) = -\zeta \sum_i \mathbf{q}_i \times \mathbf{p}_i. \quad (5 \cdot 18)$$

These equations are integrated comparing with Eq. (5·13),

$$\mathbf{P} = \sum_i \mathbf{p}_i = \exp \left[-\int^t \zeta dt' \right] \mathbf{P}_0 = C \exp[H_T/gkT] \mathbf{P}_0, \quad (5 \cdot 19)$$

$$\mathbf{L} = \sum_i \mathbf{q}_i \times \mathbf{p}_i = \exp \left[-\int^t \zeta dt' \right] \mathbf{L}_0 = C \exp[H_T/gkT] \mathbf{L}_0. \quad (5 \cdot 20)$$

\mathbf{P}_0 and \mathbf{L}_0 are constant vectors. The momentum \mathbf{P} and the angular momentum \mathbf{L} are not the conserved quantities in the Nosé-Hoover thermostat method. Modified quantities $\mathbf{P}_0 = \exp[-H_0/gkT] \mathbf{P}$ and $\mathbf{L}_0 = \exp[-H_0/gkT] \mathbf{L}$ are conserved. In most simulations, the total linear momentum is set equal to zero. In this situation, the total momentum is always kept to zero. The angular momentum is generally not conserved in simulations which employ the periodic boundary conditions.

5.3. Multiple temperature control variables⁵⁹⁾

The Nosé-Hoover thermostat equations can be easily extended to various situations which the original Hamiltonian formulation cannot apply to. The separate temperature control for different degrees of freedom is a typical example. The coupling between different kinds of molecular motions (e.g., translations, rotations or vibrations) is often not so strong to assure a quick equilibration among them. This situation occurs especially when the typical times of each motion are very different. The change in the molecular rotations and the intramolecular vibrations are usually quicker than that in the translation of the molecule as a whole for a simple molecule. The total kinetic energy reaches an objective value rapidly, but the temperatures of the translational motion and the rotation may still disagree. It will take quite a long time to equilibrate in a whole system.

The introduction of several temperature control variables for different degrees of freedom is useful in such a situation. This extension is intractable in the virtual variable formulation based on a Hamiltonian. More than one different virtual times will appear. Also, there is an ambiguity how to determine appropriate values for g 's.

In the Nosé-Hoover form, the method is naturally extended to multiple temperature controls.⁵⁹⁾ The degrees of freedom are classified into n groups. We denote the momentum \mathbf{p}_{ij} and the coordinate \mathbf{q}_{ij} ($1 \leq i \leq g_j, 1 \leq j \leq n$), of the particle ij which contacts with j -th bath, g_j is the number of degrees of freedom connected to j -th bath. Masses Q_j are also different in each bath.

Equations (5·1)~(5·3) are generalized to

$$\frac{d\mathbf{q}_{ij}}{dt} = \frac{\mathbf{p}_{ij}}{m_{ij}}, \quad (5 \cdot 21)$$

$$\frac{d\mathbf{p}_{ij}}{dt} = -\frac{\partial \Phi}{\partial \mathbf{q}_{ij}} - \zeta_j \mathbf{p}_{ij}, \quad (5 \cdot 22)$$

$$\frac{d\zeta_j}{dt} = \left(\sum_i \frac{\mathbf{p}_{ij}^2}{m_{ij}} - g_j kT \right) / Q_j. \quad (5 \cdot 23)$$

Equation (5.12) is extended to

$$H_T(\mathbf{p}, \mathbf{q}, \boldsymbol{\zeta}) = \sum_j \sum_i \frac{\mathbf{p}_{ij}^2}{2m_{ij}} + \Phi(\mathbf{q}) + \sum_j \frac{Q_j}{2} \zeta_j^2. \quad (5.24)$$

The canonical distribution in $(\mathbf{p}, \mathbf{q}, \zeta_1, \dots, \zeta_n)$ space

$$f(\mathbf{p}, \mathbf{q}, \boldsymbol{\zeta}) = C \exp[-H_T(\mathbf{p}, \mathbf{q}, \boldsymbol{\zeta})/kT]. \quad (5.25)$$

is realized. A mechanism realizing the canonical distribution is clarified if we set different temperatures T_j for each bath. Then, Eq. (5.10) becomes

$$\frac{df}{dt} = -\left(\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}}\right) f = \left(\sum_j g_j \zeta_j\right) f. \quad (5.26)$$

On the other hand, Eq. (5.13) is

$$\frac{dH_T}{dt} = -k\left(\sum_j g_j \zeta_j T_j\right). \quad (5.27)$$

A proportional relation between the flux $(\partial/\partial \mathbf{\Gamma}) \dot{\mathbf{\Gamma}}$ in the phase space and the dissipation of the pseudo total energy H_T is a key factor connecting Eqs. (5.26) and (5.27). The replacement of the flux term by dH_T/dt is only possible when all temperatures T_j are equal. This relation is broken when T_j are different. This is a natural conclusion. When a physical system is connected to heat baths with different temperatures, the heat flow from high to low baths occurs and the system is not in equilibrium. This type of nonequilibrium situations was studied by Holian et al.,⁶⁰ in relation with the origin of the irreversibility.

We must pay attention to the momentum conservation law in multiple temperature controls. Equation (5.17) changes to

$$\begin{aligned} \frac{d}{dt} \sum_j \sum_i \mathbf{p}_{ij} &= \sum_j \left[\sum_i -\frac{\partial \Phi}{\partial \mathbf{q}_{ij}} - \zeta_j \sum_i \mathbf{p}_{ij} \right] \\ &= -\sum_j \zeta_j \left(\sum_i \mathbf{p}_{ij} \right). \end{aligned} \quad (5.28)$$

This cannot be integrated because the weight ζ_j is different in each bath. The total momentum is not conserved in this case. Therefore, separate temperature controls for each species of particles are not recommended. A similar problem is also known in the velocity scaling algorithm.

Separate controls for the translational and rotational temperatures of rigid molecules and separate controls of x, y, z components of kinetic energy do not produce such problems.

A generalization to limit the temperature control in a certain region of a system is also possible.⁶¹⁾ Consider a function of the coordinate $G(\mathbf{q}_i)$. The friction coefficient ζ in Eq. (5.2) is replaced by $\zeta G(\mathbf{q}_i)$. The restriction of the temperature control in a certain region is expressed as a special case of this generalization: $G(\mathbf{q}_i) = 1$, when \mathbf{q}_i is included in the region, and $G(\mathbf{q}_i) = 0$, when \mathbf{q}_i is not. The gradual cutoff of the coupling with a heat bath is also possible. Choose a continuous function for $G(\mathbf{q}_i)$.

The equations in this case are modified as

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m_i}, \quad (5.29)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\Phi}{\partial\mathbf{q}_i} - \zeta G(\mathbf{q}_i)\mathbf{p}_i, \quad (5.30)$$

$$\frac{d\zeta}{dt} = \left(\sum_i G(\mathbf{q}_i) \left\{ \frac{\mathbf{p}_i^2}{m_i} - gkT \right\} \right) / Q. \quad (5.31)$$

The right-hand side of Eq. (5.31) is an average of the kinetic energy weighted by a coordinate dependent function $G(\mathbf{q}_i)$.

5.4. The extension by Bulgac and Kusnezov

The most general extension of the extended system method is presented in a recent paper by Bulgac and Kusnezov,⁴²⁾ and Bulgac et al.⁴⁵⁾ This extension clarifies an essence of the Nosé-Hoover thermostat method which generates the canonical distribution.

Consider an extended phase space $\Gamma = (\mathbf{p}, \mathbf{q}, \xi, \zeta)$ in which two additional variables ξ and ζ behaving as frictional coefficients are included. The generalization will be expressed as four requirements.

(1) A distribution function f in the extended phase space Γ should satisfy a generalized Liouville's equation,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma}. \quad (5.32)$$

It is reexpressed in terms of a total time derivative as

$$\begin{aligned} \frac{df}{dt} &= - \left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} \right) f \\ &= - \left[\sum_i \left(\frac{\partial}{\partial \mathbf{p}_i} \cdot \dot{\mathbf{p}}_i + \frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i \right) + \frac{\partial}{\partial \xi} \dot{\xi} + \frac{\partial}{\partial \zeta} \dot{\zeta} \right] f. \end{aligned} \quad (5.33)$$

(2) The solution of Eq. (5.33) is the canonical distribution in terms of a pseudo total energy H_T ,

$$H_T = H(\mathbf{p}, \mathbf{q}) + g_2(\xi)/\beta + g_1(\zeta)/\alpha, \quad (5.34)$$

$$f(\mathbf{p}, \mathbf{q}, \xi, \zeta) = \exp[-H_T/kT]. \quad (5.35)$$

$g_2(\xi)$ and $g_1(\zeta)$ correspond to the kinetic energy term of the heat bath in the original formulation, and their functional form must be chosen so that the integration of Eq. (5.35) with respect to ξ or ζ converges. α and β are the inverse of the heat bath mass.

(3) In the equations of motion for particles, supplemental terms are added to the original canonical equation. It is important that the modification is chosen in an additional form but not a multiplicative form as in the virtual variable equations,

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} - h_2(\xi) \mathbf{F}_i(\mathbf{p}, \mathbf{q}), \quad (5.36)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} - h_1(\zeta) \mathbf{G}_i(\mathbf{p}, \mathbf{q}). \quad (5.37)$$

\mathbf{F}_i and \mathbf{G}_i are some arbitrary function of \mathbf{p} and \mathbf{q} , and $h_1(\zeta)$ and $h_2(\xi)$ is related to $g_1(\zeta)$ and $g_2(\xi)$ by

$$h_1(\zeta) = \frac{d g_1(\zeta)}{d \zeta}, \quad (5.38)$$

$$h_2(\xi) = \frac{d g_2(\xi)}{d \xi}. \quad (5.39)$$

(4) Supplemental equations for ξ and ζ are

$$\frac{d\zeta}{dt} = \alpha \sum_i \left[\frac{\partial H}{\partial \mathbf{p}_i} \cdot \mathbf{G}_i - kT \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} \right], \quad (5.40)$$

$$\frac{d\xi}{dt} = \beta \sum_i \left[\frac{\partial H}{\partial \mathbf{q}_i} \cdot \mathbf{F}_i - kT \frac{\partial \mathbf{F}_i}{\partial \mathbf{q}_i} \right]. \quad (5.41)$$

The functional forms for $d\zeta/dt$ and $d\xi/dt$ are chosen not to depend on ζ and ξ ,

$$\frac{\partial}{\partial \xi} \dot{\xi} = \frac{\partial}{\partial \zeta} \dot{\zeta} = \frac{\partial}{\partial \xi} \dot{\xi} = \frac{\partial}{\partial \zeta} \dot{\zeta} = 0. \quad (5.42)$$

The equations of motion for frictional coefficients are proportional to the difference of two quantities whose ratio of the canonical ensemble averages is kT . The quantities on the right-hand side of Eqs. (5.40) and (5.41) satisfy this relation. It is shown by the partial integration,

$$\begin{aligned} kT \left\langle \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} \right\rangle_c &= C \int kT \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} \exp[-H/kT] d\mathbf{p}d\mathbf{q} \\ &= -C \int kT \mathbf{G}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \exp[-H/kT] d\mathbf{p}d\mathbf{q} \\ &= C \int \mathbf{G}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} \exp[-H/kT] d\mathbf{p}d\mathbf{q} = \left\langle \mathbf{G}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} \right\rangle_c. \end{aligned} \quad (5.43)$$

An essence in this generalization is that a constant temperature condition and the canonical distribution could be realized by merely controlling the ratio of two quantities. We can choose any pair of quantities, the ratio of whose canonical ensemble averages is kT . The control of the kinetic energy in the original formulation is only a special case of them. In the Nosé-Hoover thermostat equations, $\mathbf{F}_i = \xi = g_2 = 0$, $\mathbf{G}_i = \mathbf{p}_i$, $g_1 = \zeta^2/2$ and $\alpha = 1/Q$. The kinetic energy and a constant are a pair of quantities used for temperature control.

These four requirements are consistent. From three requirements (1), (3) and (4), the canonical distribution Eq. (5.35) (requirement (2)) is derived in the same way as in § 5.2.

$$\begin{aligned} \frac{dH_T}{dt} &= \sum_i \left(\dot{\mathbf{p}}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} + \dot{\mathbf{q}}_i \cdot \frac{\partial H}{\partial \mathbf{q}_i} \right) + \frac{\partial g_2}{\partial \xi} \frac{1}{\beta} \dot{\xi} + \frac{\partial g_1}{\partial \zeta} \frac{1}{\alpha} \dot{\zeta} \\ &= -kT \left[h_1 \sum_i \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} + h_2 \sum_i \frac{\partial \mathbf{F}_i}{\partial \mathbf{q}_i} \right], \end{aligned} \quad (5.44)$$

$$\begin{aligned} \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} &= \sum_i \left(\frac{\partial}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i + \frac{\partial}{\partial \mathbf{q}_i} \dot{\mathbf{q}}_i \right) + \frac{\partial}{\partial \xi} \dot{\xi} + \frac{\partial}{\partial \zeta} \dot{\zeta} \\ &= -h_1 \sum_i \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} - h_2 \sum_i \frac{\partial \mathbf{F}_i}{\partial \mathbf{q}_i} = \frac{1}{kT} \frac{dH_T}{dt}. \end{aligned} \quad (5.45)$$

Equation (5.44) is proportional to Eq. (5.45). This is a sufficient condition to derive the canonical distribution.

On the other hand, if we assume the canonical distribution (requirement (2)) and Eqs. (5.36) and (5.37), the equations for ξ and ζ are determined to Eqs. (5.40) and (5.41). The time derivative of H_T is

$$\begin{aligned} \frac{dH_T}{dt} &= \sum_i \left(\dot{\mathbf{p}}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} + \dot{\mathbf{q}}_i \cdot \frac{\partial H}{\partial \mathbf{q}_i} \right) + h_1 \frac{1}{\alpha} \dot{\zeta} + h_2 \frac{1}{\beta} \dot{\xi} \\ &= -h_1 \sum_i \frac{\partial H}{\partial \mathbf{p}_i} \cdot \mathbf{G}_i - h_2 \sum_i \frac{\partial H}{\partial \mathbf{q}_i} \cdot \mathbf{F}_i + h_1 \frac{1}{\alpha} \dot{\zeta} + h_2 \frac{1}{\beta} \dot{\xi}. \end{aligned} \quad (5.46)$$

Equation (5.33) becomes

$$\begin{aligned} \frac{df}{dt} &= -\frac{1}{kT} \frac{dH_T}{dt} f = -\left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} \right) f \\ &= \left[h_1 \sum_i \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} + h_2 \sum_i \frac{\partial \mathbf{F}_i}{\partial \mathbf{q}_i} + \frac{\partial}{\partial \xi} \dot{\xi} + \frac{\partial}{\partial \zeta} \dot{\zeta} \right] f. \end{aligned} \quad (5.47)$$

Comparing Eqs. (5.46) and (5.47), and employing Eq. (5.42), we obtain

$$\begin{aligned} h_1(\zeta) \left[\dot{\zeta} - \alpha \sum_i \left\{ \frac{\partial H}{\partial \mathbf{p}_i} \cdot \mathbf{G}_i - kT \frac{\partial \mathbf{G}_i}{\partial \mathbf{p}_i} \right\} \right] \\ + h_2(\xi) \left[\dot{\xi} - \beta \sum_i \left\{ \frac{\partial H}{\partial \mathbf{q}_i} \cdot \mathbf{F}_i - kT \frac{\partial \mathbf{F}_i}{\partial \mathbf{q}_i} \right\} \right] = 0. \end{aligned} \quad (5.48)$$

The terms in square brackets are independent of ζ and ξ . From this identity, the requirement (4), Eqs. (5.40) and (5.41) are derived.

5.5. The extension to classical spin systems⁴²⁾

The generalization in § 5.4 clarifies how a constant temperature condition and the canonical distribution are attained. The canonical equations are supplemented by a term or terms similar to frictional force. The time derivative of the temperature control variables is postulated to be proportional to the difference of two quantities. The ratio of their canonical ensemble averages is kT . It is no longer necessary to stick to the kinetic energy for temperature control.

This paves a way to the application of the constant temperature molecular dynamics method to a system which does not have terms corresponding to the kinetic energy. A classical spin system is a typical example. The equations of motion for

a spin $\mathbf{S}=(S_x, S_y, S_z)$ is derived from a Hamiltonian $H(\mathbf{S})$ as

$$\frac{d}{dt}\mathbf{S}=\frac{\partial H}{\partial \mathbf{S}}\times \mathbf{S}, \quad (5.49)$$

in a vector form, or in expression for each component, it will be

$$\frac{d}{dt}S_j=\varepsilon_{jkl}\frac{\partial H}{\partial S_k}S_l. \quad (5.50)$$

ε_{jkl} is the Levi-Civita tensor. Consider a simple example of the Larmor precession. A classical spin in a magnetic field $\mathbf{h}=(0, 0, h)$ rotates around the magnetic field. In this motion, the Hamiltonian of the system $H(\mathbf{S})=-hS_z$ is kept to a constant value. This does not seem to have a term allowing a temperature control.

Equation (5.49) is modified to a constant temperature form as

$$\frac{d}{dt}\mathbf{S}=\frac{\partial H}{\partial \mathbf{S}}\times \mathbf{S}-\zeta\left[\mathbf{A}-\mathbf{S}\frac{(\mathbf{A}\cdot \mathbf{S})}{S^2}\right]. \quad (5.51)$$

\mathbf{A} is an arbitrary vector function of \mathbf{S} . The length of a classical spin \mathbf{S} is conserved.

$$S^2=\mathbf{S}\cdot \mathbf{S}=S_x^2+S_y^2+S_z^2. \quad (5.52)$$

Therefore, a partial derivative is modified to a form compatible with the constraint Eq. (5.52).

$$\frac{\mathcal{D}\mathbf{A}}{\mathcal{D}\mathbf{S}_j}=\frac{\partial \mathbf{A}}{\partial \mathbf{S}_j}-\frac{S_j}{S^2}\left(\frac{\partial \mathbf{A}}{\partial \mathbf{S}}\cdot \mathbf{S}\right). \quad (5.53)$$

The generalized Liouville equation in (\mathbf{S}, ζ) space is

$$\frac{\partial f}{\partial t}+\sum_j\frac{\mathcal{D}}{\mathcal{D}\mathbf{S}_j}(\dot{S}_j f)+\frac{\partial}{\partial \zeta}(\dot{\zeta} f)=0. \quad (5.54)$$

The total time derivative is defined as before,

$$\frac{df}{dt}=\frac{\partial f}{\partial t}+\sum_j\dot{S}_j\frac{\mathcal{D}f}{\mathcal{D}\mathbf{S}_j}+\dot{\zeta}\frac{\partial f}{\partial \zeta}. \quad (5.55)$$

Equation (5.54) becomes

$$\frac{df}{dt}=-\left[\sum_j\left(\frac{\mathcal{D}}{\mathcal{D}\mathbf{S}_j}\dot{S}_j\right)+\frac{\partial}{\partial \zeta}\dot{\zeta}\right]f. \quad (5.56)$$

If we require that the canonical distribution $f(\mathbf{S}, \zeta)$

$$f(\mathbf{S}, \zeta)=\exp[-\{H(\mathbf{S})+\zeta^2/2a\}/kT], \quad (5.57)$$

is a stationary solution of Eq. (5.56), an additional equation for ζ is obtained as

$$\begin{aligned} \frac{d\zeta}{dt}=a\left[\left\{\left(\frac{\partial H}{\partial \mathbf{S}}\cdot \mathbf{S}\right)+\frac{1}{S^2}\left(\frac{\partial H}{\partial \mathbf{S}}\cdot \mathbf{S}\right)(\mathbf{A}\cdot \mathbf{S})\right\}\right. \\ \left.-kT\left\{\frac{\partial}{\partial \mathbf{S}}\cdot \mathbf{A}-\frac{1}{S^2}\left(\mathbf{S}\cdot \left(\mathbf{S}\cdot \frac{\partial}{\partial \mathbf{S}}\right)\mathbf{A}\right)-\frac{2}{S^2}(\mathbf{A}\cdot \mathbf{S})\right\}\right]. \end{aligned} \quad (5.58)$$

$\partial \dot{\zeta} / \partial \zeta = 0$ is assumed in deriving process. We can also derive the canonical distribution Eq. (5.57) from Eqs. (5.56), (5.51) and (5.58). The ratio of two quantities in braces in Eq. (5.58) is controlled by ζ .

A general extension to a system described by higher Lie algebra is also presented in Ref. 42).

As an illustration of the extension in this subsection, consider a simple example; a classical spin in a magnetic field $\mathbf{h} = (0, 0, h)$. The Hamiltonian is $H = -\mathbf{h} \cdot \mathbf{S} = -hS_z$. A vector $\mathbf{A} = (0, 0, 1)$ is chosen. Then, the equations of motion are

$$\dot{S}_x = hS_y + \zeta S_x S_z / S^2, \quad (5.59)$$

$$\dot{S}_y = -hS_x + \zeta S_y S_z / S^2, \quad (5.60)$$

$$\dot{S}_z = -\zeta(1 - S_z^2 / S^2), \quad (5.61)$$

$$\dot{\zeta} = \alpha[-h(1 - S_z^2 / S^2) + kT(2S_z / S^2)]. \quad (5.62)$$

The canonical ensemble averages of two terms on the right-hand side of Eq. (5.62) are

$$\langle S_z \rangle_c = S L\left(\frac{hS}{kT}\right), \quad (5.63)$$

where $L(x) = \coth x - 1/x$ is the Langevin function, and

$$1 - \langle S_z^2 \rangle_c / S^2 = 2 \frac{kT}{hS} L\left(\frac{hS}{kT}\right), \quad (5.64)$$

and they satisfy the relation,

$$h(1 - \langle S_z^2 \rangle_c / S^2) / (2 \langle S_z \rangle_c / S^2) = kT. \quad (5.65)$$

Without additional terms, Eqs. (5.59)~(5.61) describe the Larmor precession of \mathbf{S} around the magnetic field. The friction term for S_z works so that S_z fluctuates around

$$\bar{S}_z = S \left[\left\{ 1 + \left(\frac{kT}{hS} \right)^2 \right\}^{1/2} - \frac{kT}{hS} \right], \quad (5.66)$$

which is the solution of Eq. (5.62) when $\dot{\zeta} = 0$.

The canonical distribution $f(\mathbf{S}) = C \exp[hS_z / kT]$ is realized by Eqs. (5.59)~(5.62).

§ 6. The dynamical properties

The correct canonical ensemble averages for thermodynamical quantities are obtained in the constant temperature method. Because the equations of motion are solved numerically, the dynamical properties of the system can be studied in the molecular dynamics simulations. This is a feature of the molecular dynamics method. Therefore, it is a natural question whether the correct dynamical behaviors are also obtainable or not at constant temperature. If the simulations are carried out in an appropriate condition, the answer is affirmative in most cases.

The relaxation from a nonequilibrium state to equilibrium in constant temperature simulations does not correspond to any realistic process in the experiments. The relaxation process is introduced artificially to control the temperature. The speed of the relaxation is determined by the value of mass Q in the extended system method. The response is quick with a small mass, and a system relaxes slowly with a large mass. Also a large amplitude slowly decaying continuous oscillation of the heat bath variable s is often observed. In a certain condition, the coupling between the variable s and a physical system is not so strong. It takes quite a long time for the damping of this oscillation. All behaviors mentioned above are artifacts introduced by the extended system method. The rate of collision with hypothetical particles or the random forces acting on a particle in the stochastic constant temperature method also affect the relaxation. The correct dynamical behavior in nonequilibrium state cannot be obtained by modified simulation methods.

In this section, we consider several problems relating to dynamical behaviors in the constant temperature methods. In § 6.1, the response speed of a heat bath in equilibrium is studied. This is necessary for determining an appropriate mass value for the heat bath variable. A good choice is important to realize a thermal equilibrium between a physical system and a heat bath. The general dynamical behavior in equilibrium is discussed in § 6.2.

6.1. Choice of values for mass parameters

An artificial kinetic energy term for the external system is introduced to derive an equation for the heat bath variable in the extended system formulation. The mass parameter appearing in this term controls the speed of response of a heat bath. How can we choose an appropriate value for this parameter?

It should not be too small. In the study of the lattice vibration in a system containing impurities, it is known that a localized isolated mode appears when the mass of the impurities is smaller than that of host atoms. A similar situation occurs in our system when Q is small. The heat bath variable becomes an isolated mode and it continues an oscillation independently. The behavior resembles that of a harmonic oscillator. The distribution of the total kinetic energy deviates significantly from the Gaussian distribution in this situation as shown schematically in Fig. 5(a). The distribution of a harmonic oscillator has two peaks at turning points. These correspond to two peaks at high and low temperature in the kinetic energy distribution. The variable s oscillates independently from other degrees of freedom. The system does not reach an equilibrium state during the

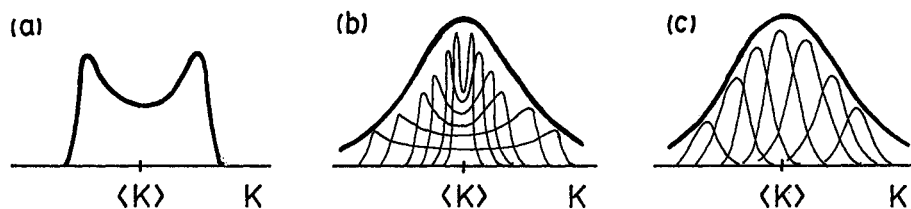


Fig. 5. Change of the distribution of the total kinetic energy with different Q values; (a) very small Q , (b) small Q , (c) large Q . Thin lines indicate the distribution during a short period.

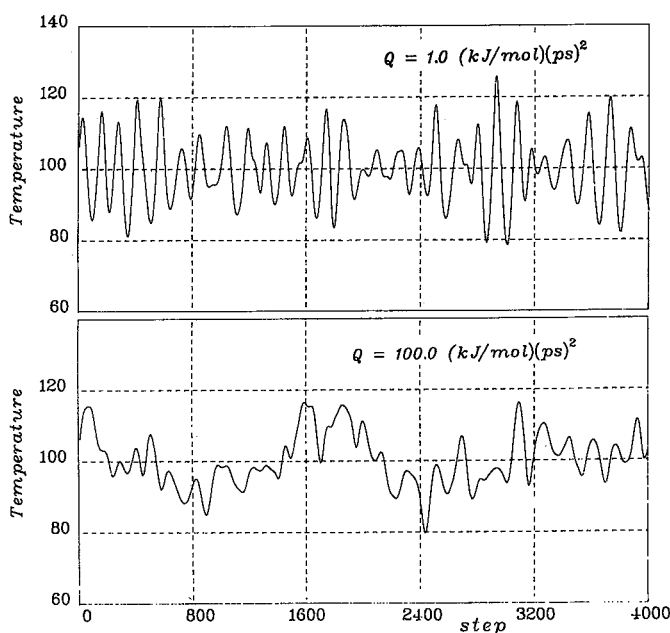


Fig. 6. Comparison of the temperature fluctuations with different Q values. A 108 Lennard-Jones system at $T=100$ K. Above: $Q=1.0$ (kJ/mol)(ps)², below: $Q=100.0$ (kJ/mol)(ps)².

simulation, and the ergodic hypothesis is not satisfied.

With a larger mass, the behavior changes. Typical examples of the time evolution of the temperature (kinetic energy) are depicted in Fig. 6. The results are obtained in a 108 particle Lennard-Jones system with parameters; the energy depth $\epsilon = 125$ K, the radius $\sigma = 3.446$ Å, the mass $m = 39.9$ g/mol at 100 K. With a smaller mass ($Q=1.0$ in Fig. 6), the change of the kinetic energy is still mostly driven by the fast oscillation due to the heat bath variable s . The amplitude of the oscillation beats by a coupling between a bath and a physical system. In this case, the accumulation of the distribution of harmonic oscillators with various amplitudes forms a Gaussian type distribution with a single peak at an average value (Fig. 5(b)). At larger mass (see Fig. 6 (below)), we observe the fast thermal fluctuations of the kinetic energy around a slow systematic change due to the heat bath variable oscillation. A distribution of Gaussian type but narrower than the Maxwell distribution at temperature T is expected in a short period. The situation is similar to that in the microcanonical ensemble because the exchange of the heat is slow. The centers of mass of the distribution oscillate synchronizing the oscillation of the variable s . An envelope of these distribution becomes the Maxwell distribution (Fig. 5(c)). A large number of time steps are necessary to get a reliable average value with large Q .

We must choose an intermediate value for the mass Q . To obtain a criterion for it, we analyze the period of oscillation of s by linearizing Eq. (4·27).²⁴⁾ We express the equation explicitly with the heat bath variable s . A virtual frame expression for momentum, $\mathbf{p}'_i = \mathbf{p}_i/s$, is used.

$$Q \frac{d}{dt} \left(\frac{1}{s} \frac{ds}{dt} \right) = \sum_i \frac{\mathbf{p}_i^2}{m_i s^2} - gkT. \quad (6.1)$$

We consider a fluctuation δs of the variable s around an average $\langle s \rangle$,

$$s = \langle s \rangle + \delta s. \quad (6.2)$$

At a small mass limit, the change of s is much faster than that of the particles, and we can ignore the change of the momentum in a virtual frame. The constant temperature condition is mainly maintained by the motion of s ,

$$\sum_i \frac{\mathbf{p}_i^2}{m_i \langle s \rangle^2} = gkT. \quad (6.3)$$

Linearizing Eq. (6.1), an equation for δs is obtained,

$$\begin{aligned} Q \frac{1}{\langle s \rangle} \frac{d^2 \delta s}{dt^2} &= \sum_i \frac{\mathbf{p}_i^2}{m_i \langle s \rangle^2} \left(1 - \frac{2\delta s}{\langle s \rangle} \right) - gkT \\ &= -\frac{2}{\langle s \rangle} \left(\sum_i \frac{\mathbf{p}_i^2}{m_i \langle s \rangle^2} \right) \delta s = -\frac{2gkT}{\langle s \rangle} \delta s. \end{aligned} \quad (6.4)$$

This is equivalent to the equation of a harmonic oscillator. Its frequency is,

$$\omega_1 = \left[\frac{2gkT}{Q} \right]^{1/2}, \quad (6.5)$$

and the period T_1 is

$$T_1 = \frac{2\pi}{\omega_1} = 2\pi \left[\frac{Q}{2gkT} \right]^{1/2}. \quad (6.6)$$

The period is proportional to the square root of the mass Q , and inversely proportional to the square roots of the number of degree of freedom g and the temperature T .

On the other hand, at a large mass, if we average thermal fluctuations during a short period and define a time dependent temperature $T(t)$, Eq. (6.1) is reduced to

$$Q \frac{1}{\langle s \rangle} \frac{d^2 \delta s}{dt^2} = gk(T(t) - T) = -gk \left[-\frac{T(t) - T}{\delta s} \right] \delta s. \quad (6.7)$$

The change of the fluctuation $\delta T = T(t) - T$ is proportional to the fluctuation of s . The ratio $A = -\delta T / \delta s$ can be estimated by the ratio of the standard deviation of two fluctuations,

$$A = [\langle (\delta T)^2 \rangle / \langle (\delta s)^2 \rangle]^{1/2}. \quad (6.8)$$

The whole fluctuation of the kinetic energy should be that in the canonical ensemble. The fluctuation around $T(t)$ will be that in the microcanonical ensemble. Therefore, the fluctuation of δT is the difference between that in the canonical and microcanonical ensembles. The fluctuations in both ensembles are given in Eq. (2.23).

Table I. The oscillation period of the variable s . 256 particle Lennard-Jones system at $T=60$ K. $\epsilon=125$ K, $\sigma=3.446$ A, $m=39.9$ g/mol.

Q ((kJ/mol)(ps) ²)	T_1 (ps)	$T_2^a)$ (ps)	T_{obs} (ps)
1.0	0.227	0.321	0.22
4.0	0.455	0.643	0.45
16.0	0.909	1.286	1.24
64.0	1.819	2.572	2.23
256.0	3.637	5.143	5.26

^{a)} The heat capacity is assumed to be $3Nk$.

$$\begin{aligned} \langle(\delta T)^2\rangle &= \langle(\delta T)^2\rangle_c - \langle(\delta T)^2\rangle_{\text{mc}} \\ &= \frac{2T^2}{g} - \frac{2T^2}{g} \left(1 - \frac{gk}{2C_V}\right) = \frac{kT^2}{C_V}. \end{aligned} \quad (6.9)$$

C_V is the heat capacity. The fluctuation of the heat bath variable s is also related to the heat capacity Eq. (4.44),²⁴⁾

$$\langle(\delta s)^2\rangle = \frac{\langle s \rangle^2 C_V}{g^2 k}. \quad (6.10)$$

The ratio A is

$$A = \left[\left(\frac{kT^2}{C_V} \right) / \left(\frac{\langle s \rangle^2 C_V}{g^2 k} \right) \right]^{1/2} = \frac{gkT}{\langle s \rangle C_V}. \quad (6.11)$$

Therefore, we get the frequency and the period at large mass,

$$\omega_2 = \left[\frac{2gkT}{Q} \frac{gk}{2C_V} \right]^{1/2}, \quad (6.12)$$

$$T_2 = \frac{2\pi}{\omega_2} = 2\pi \left[\frac{Q}{2gkT} \frac{2C_V}{gk} \right]^{1/2}. \quad (6.13)$$

The comparison of the oscillation period of the variable s with various mass Q is given in Table I. The simulations are carried out in a 256 atom Lennard-Jones system in a supercooled liquid state at $T=60$ K. The heat capacity in T_2 is assumed as $C_V=3Nk$, the Dulong-Petit law. $T_2=\sqrt{2}T_1$ in this case. T_1 agrees very well with T_{obs} at $Q=1.0$ and 4.0. At large Q , T_2 exhibits a better agreement. We can estimate the oscillation period over a wide range of Q by Eqs. (6.6) and (6.13).

We will give a criterion for an appropriate value of the heat bath mass Q . It should be an intermediate value. A small Q does not guarantee the equilibration in a whole system. A large Q is inefficient. The most economical choice is to agree the oscillation of s with a typical oscillation period of a physical system. A maximum coupling is generally expected at a resonant condition. The characteristic time T_0 of a system does not depend much on a system size. An appropriate choice for Q will be calculated from the dependence of Q on the system size and the temperature. The mass Q is proportional to the number of particle ($g=3N$) and the temperature T .

$$Q \propto (gkT)(T_0)^2. \quad (6.14)$$

6.2. *A general discussion on dynamical properties in equilibrium*

The modified equations must have a quasi-Newtonian form as mentioned in § 4.5. Otherwise, a reasonable dynamical behavior is not expected. The modification in an additional form as in Eqs. (5·36) and (5·37) always guarantees a quasi-Newtonian form. The effect of introduction of a heat bath is negligibly small in equilibrium in a large system limit in the extended and constraint methods with a quasi-Newtonian form.

We will estimate the intensity of the extra force term in Eqs. (3·7), (4·25) and (5·2). The coefficient of these velocity dependent term becomes small in a large system. For example, we consider the extended system method for temperature. The average of the kinetic energy for the heat bath variable $(Q/2)\zeta^2$ is equal to $kT/2$ from the equipartition theorem. The amplitude of ζ fluctuation decreases with the dependence of $Q^{-1/2}$. Q increases linearly with the number of particles N in an appropriate choice given in Eq. (6·14). Therefore, the ζ is proportional to $N^{-1/2}$. The inverse-square-root dependence on N is a general behavior for quantities relating to fluctuations. The driving force for ζ is the fluctuation of the temperature. In the constraint method, the numerator part $\sum_i \mathbf{v}_i(t) \cdot \mathbf{F}_i(t)$ of the undetermined multiplier ζ (Eq. (3·9)) is a fluctuating term. The inner product of the velocity and the force increases with only $N^{1/2}$ dependence, where the denominator increases linearly with N . Thus $\lambda \propto N^{-1/2}$. The effect on a single particle dynamics is very small in a large system.

The same system size dependence has been obtained by Evans and Morriss from the perturbational expansions of the response function.⁶²⁾ They also investigated the response of a thermostated system to external perturbations in the Gaussian thermostat case.⁶³⁾ The result is simple. The expression of the response function does not change formally from that in the ordinary Newtonian dynamics when the time propagator of the Gaussian thermostat is used instead of that of the Newtonian dynamics. Similar results are also obtained in the Nosé-Hoover thermostat case.⁴¹⁾ Therefore, not only the static quantities but the dynamical response are correctly calculated in the constant temperature methods.

Summing up the discussion in this subsection, the coupling with a heat bath prevents the shift of the temperature as a whole and keeps the kinetic energy around a certain value. But the effect on each particle is very mild in a large system. Therefore, any significant difference will not be recognized for ordinary dynamical properties, especially for single particle dynamics.

However, we should be careful for collective dynamical quantities such as sound waves. We assumed that the effect for each particle is random. This assumption does not hold for collective quantities. A typical example is the total kinetic energy. We control this by an additional variable or by imposition of a constraint. The dynamical behavior of the kinetic energy depends on the mass Q explicitly.

§ 7. Conclusions

The developments of two deterministic constant temperature dynamical simula-

tion methods are reviewed. They are the constraint method (or the Gaussian thermostat) and the extended system method (or the Nosé-Hoover thermostat). Time reversal dynamical equations of motion can produce the canonical distribution in the coordinate part (Gaussian thermostat) or in the extended phase space of $(\mathbf{p}, \mathbf{q}, \zeta)$ (Nosé-Hoover thermostat). We can obtain correct thermodynamical quantities and dynamical responses in simulations at constant temperature.

The behaviors of the equations of motion in both methods are essentially non-canonical. They do not conserve the volume of the phase space. Rather, the breaking of the conservation relates directly the canonical distribution. In fact, the volume along a phase space trajectory changes in proportion to the Boltzmann factor $\exp[-H(\mathbf{p}, \mathbf{q})/kT]$. A state in the phase space passes through a phase space point with a weight of the canonical distribution. The constraint force in the Gaussian thermostat and the feedback term in the Nosé-Hoover thermostat changes the dynamical behaviors from the adiabatic Newtonian type to the isothermal dynamics.

An essence of the feedback mechanism in the Nosé-Hoover thermostat is clarified in a recent paper by Bulgac and Kusnezov.⁴²⁾ The canonical distribution can be derived only controlling a pair of quantities to the ratio in the canonical ensemble averages by an appropriate feedback mechanism. This is a surprising simple conclusion to the problem which was once considered almost intractable.

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