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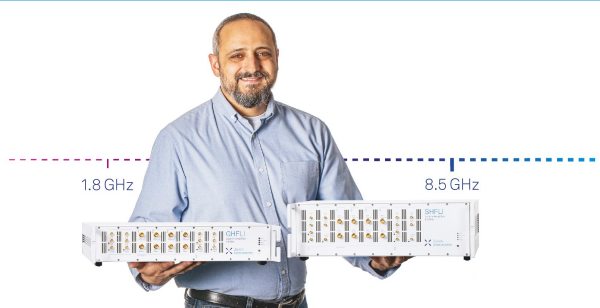
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# A unified formulation of the constant temperature molecular dynamics methods

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Three recently proposed constant temperature molecular dynamics methods by: (i) Nosé (Mol. Phys., to be published); (ii) Hoover *et al.* [Phys. Rev. Lett. **48**, 1818 (1982)], and Evans and Morriss [Chem. Phys. **77**, 63 (1983)]; and (iii) Haile and Gupta [J. Chem. Phys. **79**, 3067 (1983)] are examined analytically via calculating the equilibrium distribution functions and comparing them with that of the canonical ensemble. Except for effects due to momentum and angular momentum conservation, method (i) yields the rigorous canonical distribution in both momentum and coordinate space. Method (ii) can be made rigorous in coordinate space, and can be derived from method (i) by imposing a specific constraint. Method (iii) is not rigorous and gives a deviation of order  $N^{-1/2}$  from the canonical distribution ( $N$  the number of particles). The results for the constant temperature–constant pressure ensemble are similar to the canonical ensemble case.

## I. INTRODUCTION

Recently, the extension of molecular dynamics (MD) methods to treat ensembles other than the traditional microcanonical ensemble has attracted considerable attention.

The constant pressure MD method, first introduced by Andersen<sup>1</sup> and subsequently extended by Parrinello and Rahman<sup>2-4</sup> to allow for changes of the MD cell shape, has demonstrated its usefulness in applications to structural changes in the solid state.<sup>2-9</sup> Recently, Heyes<sup>10</sup> employed a similar approach to that of Anderson but used real variables instead of the scaled variables.<sup>1-4</sup> A constant pressure MD method based on nonequilibrium MD technique was also proposed by Hoover *et al.*<sup>11</sup>

Several constant temperature MD methods have been proposed. The purpose of the present article is to examine and compare these methods and to establish a unified formalism for their derivation. Emphasis is placed on the static properties and on the equilibrium distribution function.

The earliest method for the constant temperature MD is a momentum scaling procedure, in which the velocities of the particles are scaled at each time step to maintain the total kinetic energy at a constant value.<sup>12</sup> This method has been used without demonstrated justification. Haile and Gupta<sup>13</sup> discussed how to add the constraint of constant kinetic energy to the equations of motion. As a special case, they proposed a constraint method based on a momentum scaling procedure. This is a refinement of the earlier method. It will be shown in Sec. III C that the equilibrium distribution function in the momentum scaling method deviates from the canonical distribution by order  $N^{-1/2}$  ( $N$  the number of particles).

Anderson<sup>1</sup> proposed a hybrid of MD and Monte Carlo methods. In his approach, the particles change their velocities by stochastic collisions. The distribution of the velocities of the particles that collided is chosen to reproduce the canonical ensemble. Because of the sudden change of the velocities by collisions, the trajectory in the phase space is discontinuous.

Hoover *et al.*<sup>14,15</sup> and Evans<sup>16</sup> proposed a constraint MD method which was derived from a nonequilibrium MD formulation.<sup>17,18</sup> This method will be called the HLME method hereafter.

In this method, an additional term  $-\alpha \mathbf{p}_i$  is added to the force term in Eq. (1.2) ( $\mathbf{q}_i$ , coordinate;  $\mathbf{p}_i$ , momentum of particle  $i$ ),

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{p}_i/m_i, \quad (1.1)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi}{\partial\mathbf{q}_i} - \alpha\mathbf{p}_i. \quad (1.2)$$

Consequently, the equations are no longer in a canonical form. The parameter  $\alpha$  is determined from the requirement that the total kinetic energy is constant,

$$\sum_i \mathbf{p}_i^2/2m_i = gkT/2 \quad (1.3)$$

or

$$\sum_i \mathbf{p}_i \frac{d\mathbf{p}_i}{dt}/m_i = 0. \quad (1.4)$$

Thus, we get

$$\alpha = -\left(\sum_i \frac{\partial\phi}{\partial\mathbf{q}_i} \mathbf{p}_i/m_i\right) / \left(\sum_i \mathbf{p}_i^2/m_i\right). \quad (1.5)$$

This method can produce the canonical distribution in coordinate space if we set  $g = 3N - 1$ , where  $N$  is the number of particles (in the original papers<sup>14,16</sup>  $g = 3N$ ). Further, in Sec. III B, it will be shown that the HLME equations are derived from the extended system (ES) method<sup>19</sup> by imposing a particular constraint.

The extended system method by Nosé<sup>19</sup> introduced an additional degree of freedom  $s$ , which acts as an external system for the physical system of  $N$  particles. If we choose an appropriate potential  $gkT \ln s$ , for the variable  $s$ , the equilibrium distribution function, projected onto the physical system from the extended system of the particles and the variable  $s$ , is exactly that of the canonical ensemble. The parameter  $g$  is an integer, essentially equal to the number of degrees of freedom in the physical system, but the exact value depends on the particular procedure.

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In the present article, the basic formalism is that of the extended system method and other methods are analyzed in this formulation. The details of the ES method are given in Sec. II. The equations of motion of the ES method with a constraint and the derivation of the HLME method are given in Sec. III. Extension to the constant temperature-constant pressure (TP) ensemble is discussed in Sec. IV. The method by Evans and Morriss<sup>18</sup> is derived from the ES method<sup>19</sup> in a similar fashion as for the canonical ensemble case. Most of the discussion is exact only if we ignore the momentum and the angular momentum conservation laws. The correction for the momentum conservation as well as other comments are given in Sec. V.

## II. THE EXTENDED SYSTEM METHOD

### A. A virtual variable formulation

We start from a method which seems to be most convenient to obtain the equilibrium distribution function. In the ES method,<sup>19</sup> an additional degree of freedom  $s$  is introduced which acts as an external system on the physical system of  $N$  particles, with coordinates  $\mathbf{q}'_i$ , masses  $m_i$  and potential energy  $\phi(\mathbf{q}')$ . We also introduce *virtual* variables (coordinate  $\mathbf{q}_i$ , momentum  $\mathbf{p}_i$ , and time  $t$ ) which are related to the *real* variables ( $\mathbf{q}'_i, \mathbf{p}'_i, t'$ ) by

$$\mathbf{q}'_i = \mathbf{q}_i, \quad (2.1)$$

$$\mathbf{p}'_i = \mathbf{p}_i/s, \quad (2.2)$$

$$t' = \int \frac{dt}{s}. \quad (2.3)$$

The real velocity ( $d\mathbf{q}'_i/dt'$ ) is also expressed via a scaled form in the virtual variable formulation

$$\frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}'_i}{dt} = s \frac{d\mathbf{q}_i}{dt}. \quad (2.4)$$

Thus, a simple interpretation of these transformations is scaling the time by  $dt' = dt/s$ . This is similar to scaling the coordinates in the constant pressure MD method.<sup>1-4</sup>

The Hamiltonian of the extended system of the particles and the variable  $s$  in terms of the virtual variables is postulated as

$$H = \sum_i \mathbf{p}_i^2/2m_i s^2 + \phi(\mathbf{q}) + p_s^2/2Q + gkT \ln s, \quad (2.5)$$

$p_s$  is the conjugate momentum of  $s$ ;  $Q$  is a parameter of dimension energy·(time)<sup>2</sup> and behaves as a *mass* for the motion of  $s$ ;  $k$  is Boltzmann's constant;  $T$  the externally set temperature; the parameter  $g$  is essentially equal to the number of degrees of freedom of the physical system. However, its exact value will be chosen to satisfy the canonical distribution exactly at equilibrium. As we will discuss later, a logarithmic dependence of the potential on the variable  $s$ ,  $gkT \ln s$ , is essential for producing the canonical ensemble.

We assume the Hamiltonian formalism can be applied to Eq. (2.5) with the virtual variables. The equations of motion are

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \mathbf{p}_i/m_i s^2, \quad (2.6)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}_i}, \quad (2.7)$$

$$\frac{ds}{dt} = \frac{\partial H}{\partial p_s} = p_s/Q, \quad (2.8)$$

$$\frac{dp_s}{dt} = -\frac{\partial H}{\partial s} = \left( \sum_i \mathbf{p}_i^2/m_i s^2 - gkT \right)/s. \quad (2.9)$$

In Lagrangian form, these are

$$\frac{d}{dt} \left( m_i s^2 \frac{d\mathbf{q}_i}{dt} \right) = -\frac{\partial \phi}{\partial \mathbf{q}_i} \quad (2.10)$$

or

$$\frac{d^2 \mathbf{q}_i}{dt^2} = -\frac{1}{m_i s^2} \frac{\partial \phi}{\partial \mathbf{q}_i} - \frac{2}{s} \frac{ds}{dt} \frac{d\mathbf{q}_i}{dt} \quad (2.11)$$

and

$$\frac{d}{dt} \left( Q \frac{ds}{dt} \right) = \left[ \sum_i s^2 \left( \frac{d\mathbf{q}_i}{dt} \right)^2 / m_i - gkT \right] / s. \quad (2.12)$$

The conserved quantities are the Hamiltonian  $H$ , the total momentum  $\sum_i \mathbf{p}_i$ , and the angular momentum  $\sum_i \mathbf{q}_i \times \mathbf{p}_i$ .

$$\begin{aligned} \frac{dH}{dt} &= \sum_i \left( \frac{\partial H}{\partial \mathbf{p}_i} \frac{d\mathbf{p}_i}{dt} + \frac{\partial H}{\partial \mathbf{q}_i} \frac{d\mathbf{q}_i}{dt} \right) \\ &\quad + \frac{\partial H}{\partial p_s} \frac{dp_s}{dt} + \frac{\partial H}{\partial s} \frac{ds}{dt} = 0. \end{aligned}$$

The conservation laws for the last two quantities are derived from Eq. (2.7) and the properties satisfied by the potential

$$\sum_i \frac{\partial \phi}{\partial \mathbf{q}_i} = 0$$

and

$$\sum_i \mathbf{q}_i \times \frac{\partial \phi}{\partial \mathbf{q}_i} = 0.$$

However, it should be noted here that during the ordinary type of simulations with periodic boundary condition the angular momentum is not conserved.

Because of the momentum and angular momentum conservation, the ensembles produced by the MD method are slightly different from the usual statistical mechanical ensembles.<sup>20-22</sup> These small deviations are ignored in the discussion in Secs. II-IV.

The partition function  $Z$  for  $N$  identical particles is obtained by integration of the equilibrium distribution function  $\rho(x_1, x_2, \dots)$  over the whole phase space.

$$Z = \frac{1}{N! h^{3N}} \int dx_1 \int dx_2 \dots \rho(x_1, x_2, \dots),$$

where  $h$  is Planck's constant and  $x_i$  is a generalized coordinate (the constant factors for  $\rho$  and  $Z$  are ignored hereafter). The projection of the equilibrium distribution function from the space  $(x_1, x_2)$  onto the space  $(x_1)$  is carried out by integrating with respect to the variable  $x_2$ ,

$$\rho(x_1) = \int dx_2 \rho(x_1, x_2).$$

In particular, we need a distribution function  $\rho(\mathbf{p}', \mathbf{q}')$  that is projected from the extended system onto the physical system.

In the extended system, the total Hamiltonian of Eq. (2.5) is conserved. Therefore, this method produces a microcanonical ensemble and the distribution function  $\rho(\mathbf{p}, \mathbf{q}, p_s, s)$  is expressed as  $\delta(H-E)$ ;  $\delta(x)$  is the Dirac delta function. The shortened forms  $d\mathbf{p} = d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N$ ,  $d\mathbf{q} = d\mathbf{q}_1 d\mathbf{q}_2 \dots d\mathbf{q}_N$ , and  $H_0(\mathbf{p}, \mathbf{q}) = \sum_i \mathbf{p}_i^2/2m_i + \phi(\mathbf{q})$  are used. The partition function is

$$Z = \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{q} \times \delta[H_0(\mathbf{p}/s, \mathbf{q}) + p_s^2/2Q + gkT \ln s - E]. \quad (2.13)$$

The virtual momenta  $\mathbf{p}_i$  and coordinates  $\mathbf{q}_i$  are transformed to the real variables  $\mathbf{p}'_i = \mathbf{p}_i/s$ ,  $\mathbf{q}'_i = \mathbf{q}_i$ . The volume element is  $d\mathbf{p} d\mathbf{q} = s^{3N} d\mathbf{p}' d\mathbf{q}'$ . Hence

$$Z = \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N} \delta[H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q + gkT \ln s - E]. \quad (2.14)$$

Because the argument of the  $\delta$  function in the above equation has only one zero as a function of the variable  $s$ , we can employ the equivalence relation  $\delta[f(s)] = \delta(s - s_0)/|f'(s_0)|$ ;  $s_0$  is the zero of  $f(s)$ .

$$\begin{aligned} Z &= \frac{1}{gkT} \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N+1} \\ &\times \delta(s - \exp\{-[H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q - E]/gkT\}) \\ &= \frac{1}{gkT} \exp\left[\left(\frac{3N+1}{g}\right)E/kT\right] \int dp_s \\ &\times \exp\left[-\left(\frac{3N+1}{g}\right)p_s^2/2QkT\right] \int d\mathbf{p}' \int d\mathbf{q}' \\ &\times \exp\left[-\left(\frac{3N+1}{g}\right)H_0(\mathbf{p}', \mathbf{q}')/kT\right]. \end{aligned} \quad (2.15)$$

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

$$Z = C \int d\mathbf{p}' \int d\mathbf{q}' \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT],$$

and the equilibrium distribution function is

$$\rho(\mathbf{p}', \mathbf{q}') = \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT]. \quad (2.16)$$

With the quasiergodic hypothesis which relates the time average along the trajectory to the ensemble average, the averages of any static quantities expressed as functions of  $\mathbf{p}_i/s, \mathbf{q}_i$  along the trajectory determined by Eqs. (2.6)–(2.9), are exactly those in the canonical ensemble:

$$\lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} A(\mathbf{p}/s, \mathbf{q}) dt = \langle A(\mathbf{p}/s, \mathbf{q}) \rangle = \langle A(\mathbf{p}', \mathbf{q}') \rangle_c, \quad (2.17)$$

$\langle \dots \rangle$  and  $\langle \dots \rangle_c$  denote the ensemble average in the extended system and in the canonical ensemble, respectively. The first equivalence in Eq. (2.17) is achieved by sampling data points at integer multiples of the virtual time unit  $\Delta t$ . We call this *virtual time sampling*. In this sampling, the real time interval of each time step is unequal. If we sample using equal intervals in real time  $t'$  with  $t_1 = \int_0^{t_0} dt/s$  (we can use an interpola-

tion or the method in Sec. II B for this purpose), the result is a weighted average

$$\begin{aligned} \lim_{t_1 \rightarrow \infty} \frac{1}{t_1} \int_0^{t_1} A(\mathbf{p}/s, \mathbf{q}) dt' &= \lim_{t_1 \rightarrow \infty} \frac{t_0}{t_1} \frac{1}{t_0} \int_0^{t_0} A(\mathbf{p}/s, \mathbf{q}) \frac{dt}{s} \\ &= \left[ \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} A(\mathbf{p}/s, \mathbf{q}) \frac{dt}{s} \right] / \left( \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_0^{t_0} \frac{dt}{s} \right) \\ &= \langle A(\mathbf{p}/s, \mathbf{q})/s \rangle / \left\langle \frac{1}{s} \right\rangle. \end{aligned} \quad (2.18)$$

From comparison with Eq. (2.15), we find that if we choose  $g$  as  $g = 3N$ , the weighted average in the extended system [Eq. (2.18)] is identical to  $\langle A(\mathbf{p}', \mathbf{q}') \rangle_c$ . In virtual time sampling,  $g$  should be  $3N + 1$ , and in real time sampling,  $g$  must be  $3N$ .

## B. Equations in real variables

The equations of motion [Eqs. (2.6)–(2.9)] can be transformed into the equations for the real variables  $\mathbf{q}'_i = \mathbf{q}_i, \mathbf{p}'_i = \mathbf{p}_i/s, t' = \int dt/s, s' = s$ , and  $p'_s = p_s/s$ :

$$\frac{d\mathbf{q}'_i}{dt'} = s \frac{d\mathbf{q}_i}{dt} = \frac{d\mathbf{q}_i}{dt} = \mathbf{p}_i/m_i s = \mathbf{p}'_i/m_i, \quad (2.19)$$

$$\begin{aligned} \frac{d\mathbf{p}'_i}{dt'} &= s \frac{d\mathbf{p}_i}{dt} = s \frac{d}{dt}(\mathbf{p}_i/s) = \frac{d\mathbf{p}_i}{dt} - \frac{1}{s} \frac{ds}{dt} \mathbf{p}_i \\ &= -\frac{\partial \phi}{\partial \mathbf{q}'_i} - s' p'_s \mathbf{p}'_i/Q, \end{aligned} \quad (2.20)$$

$$\frac{ds'}{dt'} = s \frac{ds}{dt} = \frac{ds}{dt} = s'^2 p'_s/Q, \quad (2.21)$$

$$\begin{aligned} \frac{dp'_s}{dt'} &= s \frac{dp_s}{dt} = s \frac{d}{dt}(p_s/s) = \frac{dp_s}{dt} - \frac{1}{s} \frac{ds}{dt} p_s \\ &= \left( \sum_i p_s'^2/m_i - gkT \right) / s' - s' p_s'^2/Q. \end{aligned} \quad (2.22)$$

Equations (2.19)–(2.22) are no longer canonical, since Eqs. (2.20) and (2.22) have additional force terms.  $H$  of Eq. (2.5), in terms of the real variables,

$$H' = \sum_i p_s'^2/2m_i + \phi(\mathbf{q}') + s'^2 p_s'^2/2Q + gkT \ln s \quad (2.23)$$

is not a Hamiltonian. This is a disadvantage of the real variable method.  $H'$  is still conserved

$$\begin{aligned} \frac{dH'}{dt'} &= \sum_i \left( \frac{\partial H'}{\partial \mathbf{p}'_i} \frac{d\mathbf{p}'_i}{dt'} + \frac{\partial H'}{\partial \mathbf{q}'_i} \frac{d\mathbf{q}'_i}{dt'} \right) \\ &+ \frac{\partial H'}{\partial p'_s} \frac{dp'_s}{dt'} + \frac{\partial H'}{\partial s'} \frac{ds'}{dt'} = 0. \end{aligned}$$

The Lagrangian forms are

$$\frac{d}{dt'} \left( m_i s' \frac{d\mathbf{q}'_i}{dt'} \right) = -s' \frac{\partial \phi}{\partial \mathbf{q}'_i} \quad (2.24)$$

and

$$\frac{d}{dt'} \left( \frac{Q}{s'} \frac{ds'}{dt'} \right) = \sum_i m_i \left( \frac{d\mathbf{q}'_i}{dt'} \right)^2 - gkT. \quad (2.25)$$

The Lagrangian of the real time formulation is related to the original one by relation

$$L' = s(L + E), \quad (2.26)$$

$E$  is the conserved value of  $H$  of Eq. (2.5). These equations are to be solved in real time, so  $g$  must be  $g = 3N$ .

### C. Other potentials for the variable $s$

We can construct another class of constant temperature MD method by replacing the potential for  $s$  by (for example)  $gkTs^n$  [ $n > 0$ , an integer and  $g = (3N - n + 1)/n$ ]. The equilibrium distribution function can be readily obtained in a similar way.

$$\rho(\mathbf{p}', \mathbf{q}', p_s) = \{ [E - p_s^2/2Q - H_0(\mathbf{p}', \mathbf{q}')] / gkT \}^s \times h [E - p_s^2/2Q - H_0(\mathbf{p}', \mathbf{q}')], \quad (2.27)$$

where  $h(x)$  is the Heaviside function,  $h(x) = 1$  for  $x > 0$ , and  $h(x) = 0$  for  $x < 0$ . The Heaviside function is necessary to limit the range of the integration in phase space. This constraint arises because the potential  $gkTs^n$  is positive semi-definite; for some region in phase space  $(\mathbf{p}', \mathbf{q}', p_s)$ , the equation  $H = E$  does not have any real solution for  $s$ .

With the most favorable assumption  $\langle s^n \rangle = 1$ , the value of total energy  $E = \langle H_0(\mathbf{p}/s, \mathbf{q}) \rangle + \langle p_s^2/2Q \rangle + gkT$ . Using the definition  $H_1 = \langle H_0(\mathbf{p}/s, \mathbf{q}) \rangle - H_0(\mathbf{p}', \mathbf{q}') + \langle p_s^2/2Q \rangle - p_s^2/2Q$ , Eq. (2.27) is

$$\rho(\mathbf{p}', \mathbf{q}', p_s) = (1 + H_1/gkT)^s h(gkT + H_1).$$

Note that the distribution for the variable  $p_s$  cannot be separated from those of  $\mathbf{p}'$  and  $\mathbf{q}'$ . From the expansion of  $g \ln(1 + a/g)$  with respect to  $1/g$ ;  $g \ln(1 + a/g) = a - a^2/2g + a^3/3g^2 \dots$ ,  $\rho$  is approximated as

$$\rho = \exp[H_1/kT - \frac{1}{2}(H_1/kT)^2/g]. \quad (2.28)$$

Since  $H_1$  is a quantity of order  $N^{1/2}$ , the leading term of the deviation of  $\rho$  from the canonical distribution is of order  $N^{-1/2}$ .

As we can see from the derivation of the equilibrium distribution function [see Eqs. (2.14) and (2.15)], it is related to the inverse function of the potential for  $s$ .

$$\begin{aligned} \rho(\mathbf{p}', \mathbf{q}', p_s) &= \int ds s^{3N} \delta[H'' + f(s) - E] \\ &= \int ds s^{3N} \delta(s - s_0) / f'(s_0) = s_0^{3N} / f'(s_0); \end{aligned}$$

$s_0$  satisfies the relation  $f(s_0) = E - H''$ , thus  $s_0 = f^{-1}(E - H'')$ .  $H''$  is that part of the Hamiltonian  $H$  [Eq. (2.5)] which is independent of  $s$ . Therefore, a logarithmic form is essential to produce the canonical distribution.

## III. THE CONSTRAINT METHOD

### A. Virtual variable formulation

The distribution function in momentum space is usually simple and the contribution of this term can be easily calculated in the canonical ensemble. Therefore, any method that produces the canonical distribution, even if only in coordinate space, can be useful in some situations. The standard way for this approach is to constrain the total kinetic energy term

$$\sum_i \frac{m_i}{2} \left( \frac{d\mathbf{q}_i'}{dt'} \right)^2 = \frac{g}{2} kT. \quad (3.1)$$

However, fluctuations of the total kinetic energy are suppressed by imposing this constraint. The Hamiltonian [Eq. (2.5)]

$$H = \sum_i \mathbf{p}_i'^2 / 2m_i s^2 + \phi(\mathbf{q}) + p_s^2 / 2Q + gkT \ln s$$

is constrained by the conditions<sup>13</sup>

$$\frac{\partial H}{\partial s} = - \left[ \sum_i \mathbf{p}_i'^2 / m_i s^2 - gkT \right] / s \equiv 0 \quad (3.2)$$

and

$$\frac{\partial H}{\partial p_s} = p_s / Q \equiv 0. \quad (3.3)$$

Equation (3.3) is trivial, and we ignore the  $p_s^2/2Q$  term hereafter. The equations of motion for  $\mathbf{q}_i$  and  $\mathbf{p}_i$  maintain the same form as Eqs. (2.6) and (2.7):

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} + \frac{\partial H}{\partial s} \frac{\partial s}{\partial \mathbf{p}_i} = \frac{\partial H}{\partial \mathbf{p}_i} = \mathbf{p}_i / m_i s^2, \quad (3.4)$$

$$\frac{d\mathbf{p}_i}{dt} = - \frac{\partial H}{\partial \mathbf{q}_i} - \frac{\partial H}{\partial s} \frac{\partial s}{\partial \mathbf{q}_i} = - \frac{\partial H}{\partial \mathbf{q}_i} = - \frac{\partial \phi}{\partial \mathbf{q}_i}, \quad (3.5)$$

but the value of  $s$  must be determined from Eq. (3.2), i.e.,

$$s = \left[ (\sum_i \mathbf{p}_i'^2 / m_i) / gkT \right]^{1/2}. \quad (3.6)$$

The Hamiltonian [Eq. (2.5)] is still conserved:

$$\begin{aligned} \frac{dH}{dt} &= \sum_i \left( \frac{\partial H}{\partial \mathbf{p}_i} \frac{d\mathbf{p}_i}{dt} + \frac{\partial H}{\partial \mathbf{q}_i} \frac{d\mathbf{q}_i}{dt} \right) \\ &\quad + \frac{\partial H}{\partial p_s} \frac{dp_s}{dt} + \frac{\partial H}{\partial s} \frac{ds}{dt} = 0. \end{aligned}$$

The partition function in this case is [recall that  $H_0(\mathbf{p}, \mathbf{q}) = \sum_i \mathbf{p}_i'^2 / 2m_i + \phi(\mathbf{q})$ ]

$$\begin{aligned} Z &= \int ds \int d\mathbf{p} \int d\mathbf{q} \delta[H_0(\mathbf{p}/s, \mathbf{q}) + gkT \ln s - E] \\ &\quad \times \delta \left\{ s - \left[ (\sum_i \mathbf{p}_i'^2 / m_i) / gkT \right]^{1/2} \right\} \\ &= \int ds \int d\mathbf{p} \int d\mathbf{q} \delta[H_0(\mathbf{p}/s, \mathbf{q}) + gkT \ln s - E] s gkT \\ &\quad \times \delta(s^2 gkT / 2 - \sum_i \mathbf{p}_i'^2 / 2m_i). \end{aligned}$$

With the transformation  $\mathbf{p}_i' = \mathbf{p}_i / s$ ,  $\mathbf{q}_i' = \mathbf{q}_i$ , we get

$$\begin{aligned} Z &= \left[ \int d\mathbf{p}' \delta(\sum_i \mathbf{p}_i'^2 / 2m_i - gkT / 2) \right] \int d\mathbf{q}' \int ds s^{3N-1} gkT \\ &\quad \times \delta[gkT / 2 + \phi(\mathbf{q}') + gkT \ln s - E] \\ &= \left[ \int d\mathbf{p}' \delta(\sum_i \mathbf{p}_i'^2 / 2m_i - gkT / 2) \right] \int d\mathbf{q}' \\ &\quad \times \exp \left\{ - \frac{3N}{g} [gkT / 2 + \phi(\mathbf{q}') - E] / kT \right\}. \end{aligned}$$

With  $g = 3N$ , we obtain the equilibrium distribution function

$$\rho(\mathbf{p}', \mathbf{q}') = \delta(\sum_i \mathbf{p}_i'^2 / 2m_i - gkT / 2) \exp[-\phi(\mathbf{q}') / kT]. \quad (3.7)$$

Equations (3.4)–(3.6) produce the canonical distribution in

coordinate space. Note that if we sample in real time,  $g$  must be  $3N - 1$ .

### B. Equations in real variables

The equations for the real variables  $\mathbf{q}_i'$ ,  $\mathbf{p}_i'$ ,  $t'$  are

$$\frac{d\mathbf{q}_i'}{dt'} = s \frac{d\mathbf{q}_i}{dt} = \mathbf{p}_i/m_i s = \mathbf{p}_i'/m_i, \quad (3.8)$$

$$\frac{d\mathbf{p}_i'}{dt'} = s \frac{d}{dt}(\mathbf{p}_i/s) = -\frac{\partial\phi}{\partial\mathbf{q}_i'} - \frac{ds}{dt'} \mathbf{p}_i'. \quad (3.9)$$

These are formally equivalent to Eqs. (2.19) and (2.20). The derivative  $ds/dt$  is obtained via the differentiation of Eq. (3.2),

$$\sum_i \mathbf{p}_i \frac{d\mathbf{p}_i}{dt} / m_i = gkTs \frac{ds}{dt}$$

or

$$\frac{ds}{dt} = -\left(\sum_i \frac{\partial\phi}{\partial\mathbf{q}_i'} \mathbf{p}_i' / m_i\right) / gkT. \quad (3.10)$$

Equation (3.10) can be changed to

$$\begin{aligned} \frac{ds}{dt} &= -\left(\sum_i \frac{\partial\phi}{\partial\mathbf{q}_i'} \mathbf{p}_i' / m_i\right) / gkT \\ &= -\left(\sum_i \frac{\partial\phi}{\partial\mathbf{q}_i'} \frac{d\mathbf{q}_i'}{dt'}\right) / gkT = -\frac{d\phi}{dt'} / gkT. \end{aligned} \quad (3.11)$$

If one sets the parameter  $\alpha = ds/dt$ , Eqs. (3.8)–(3.10) are identical to Eqs. (1.1), (1.2), and (1.5) of the HLME method.<sup>14–18</sup> These equations are based on real time sampling, so that if  $g$  is set equal to  $3N - 1$  we recover the canonical distribution. In the original papers,<sup>14,16</sup>  $g = 3N$  was used.

As shown above, the HLME method is equivalent to the ES method with the additional constraint of Eq. (3.2).

### C. Another constraint method

Any other choice but the logarithmic form for the potential function of  $s$  used in Eq. (2.5) leads to an ensemble different from the canonical one. As an example, we derive the equilibrium distribution function of the refined form of the momentum scaling (HG) method by Haile and Gupta.<sup>13</sup>

The starting Hamiltonian is ( $s$  corresponds to  $1-\xi$  of Ref. 13)

$$H = \sum_i \mathbf{p}_i^2 / 2m_i s + \phi(\mathbf{q}) + \frac{g}{2} kTs. \quad (3.12)$$

With the constraint

$$\frac{\partial H}{\partial s} = -\sum_i \mathbf{p}_i^2 / 2m_i s^2 + \frac{g}{2} kT \equiv 0 \quad (3.13)$$

or

$$s = \left[ \left( \sum_i \mathbf{p}_i^2 / m_i \right) / gkT \right]^{1/2},$$

the equations of motion are

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{p}_i / m_i s = \mathbf{p}_i' / m_i, \quad (3.14)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi}{\partial\mathbf{q}_i}. \quad (3.15)$$

The momenta  $\mathbf{p}_i' = \mathbf{p}_i/s$  are considered to be the real momenta. These equations are identical to the traditional momentum scaling equations.<sup>12,23</sup> The partition function is

$$\begin{aligned} Z &= \int ds \int d\mathbf{p} \int d\mathbf{q} \delta \left[ \sum_i \mathbf{p}_i^2 / 2m_i s + \phi(\mathbf{q}) + \frac{g}{2} kTs - E \right] \\ &\quad \times \delta \left\{ s - \left[ \sum_i (\mathbf{p}_i^2 / m_i) / gkT \right]^{1/2} \right\}. \end{aligned}$$

With the transformation  $\mathbf{p}_i' = \mathbf{p}_i/s$ , we get

$$\begin{aligned} Z &= \left[ \int d\mathbf{p}' \delta \left( \sum_i \mathbf{p}_i'^2 / 2m_i - gkT/2 \right) \right] \int d\mathbf{q} \int ds s^{3N-1} \\ &\quad \times \delta [gkTs + \phi(\mathbf{q}) - E] \\ &= \left[ \int d\mathbf{p}' \delta \left( \sum_i \mathbf{p}_i'^2 / 2m_i - gkT/2 \right) \right] \int d\mathbf{q} \\ &\quad \times \{ [E - \phi(\mathbf{q})] / gkT \}^{3N-1} h [E - \phi(\mathbf{q})]. \end{aligned} \quad (3.16)$$

Assuming the most favorable case:  $\langle s \rangle = 1$ ,  $g = 3N - 1$ , and  $E = gkT + \langle \phi \rangle$ , the equilibrium distribution function of this method is

$$\begin{aligned} \rho(\mathbf{p}', \mathbf{q}) &= \delta \left( \sum_i \mathbf{p}_i'^2 / 2m_i - gkT/2 \right) \\ &\quad \times \{ 1 + [\langle \phi \rangle - \phi(\mathbf{q})] / gkT \}^s \\ &\quad \times h [gkT + \langle \phi \rangle - \phi(\mathbf{q})]. \end{aligned} \quad (3.17)$$

In the same way as in Sec. II C, Eq. (3.17) deviates from  $\exp[-\phi(\mathbf{q})/kT]$  by order  $N^{-1}$ . The coordinate part of  $\rho(\mathbf{p}', \mathbf{q})$  in Eq. (3.17) is similar to the equilibrium distribution function of the microcanonical ensemble projected onto coordinate space,

$$\begin{aligned} \rho_{mc}(\mathbf{q}) &= \int d\mathbf{p} \delta \left( \sum_i \mathbf{p}_i^2 / 2m_i + \phi - E \right) \\ &= \int dP \delta(P^2 + \phi - E) \int d\mathbf{p} \delta \left[ P - \left( \sum_i \mathbf{p}_i^2 / 2m_i \right)^{1/2} \right] \\ &= C \int dP P^{3N-1} \delta(P^2 + \phi - E) \\ &= C' \int dP P^{3N-2} \delta[P - (E - \phi)^{1/2}] \\ &= C'' (E - \phi)^{\frac{3}{2}N-1} = C'' \left( 1 + \frac{\langle \phi \rangle - \phi}{3NkT/2} \right)^{\frac{3}{2}N-1}, \end{aligned} \quad (3.18)$$

where  $P$  is a radius of a  $3N$  dimension sphere and  $E = \frac{3}{2}NkT + \langle \phi \rangle$ . Therefore, the difference between the canonical ensemble and the ensemble generated by the HG method<sup>13</sup> is the same order as we expect between the microcanonical and the canonical ensembles. The ensemble corrections of order  $N^{-1}$  for first order quantities (energy, virial, ...) and those of order one for quantities relating to fluctuation formulas (heat capacity, compressibility, ...) are generally expected.<sup>21,22</sup> For example, the fluctuation of the potential energy in the HG method is

$$\langle (\delta\phi)^2 \rangle = N(kT)^2 3c_v^* / (3 + c_v^*) + O(1), \quad (3.19)$$

where  $c_v^* = (1/Nk)(d\langle \phi \rangle/dT)$  is a heat capacity of the coordinate part.

#### IV. THE CONSTANT TEMPERATURE-CONSTANT PRESSURE (TP) ENSEMBLE

##### A. The extended system method

Combined with the constant pressure MD method of Anderson,<sup>1</sup> the canonical ensemble MD method can be readily extended to the TP ensemble.<sup>19</sup> Here we use the formulation for uniform dilation given by Anderson,<sup>1</sup> but the extension to the generalized form of the constant pressure simulation method by Parrinello and Rahman can be derived in a similar way.<sup>2-4</sup>

In the TP ensemble, the virtual variables ( $\mathbf{q}_i, \mathbf{p}_i, s, V, t$ ) are related to the real variables ( $\mathbf{q}'_i, \mathbf{p}'_i, s, V, t'$ ) via scaling of the coordinates by  $V^{1/3}$  and scaling of the time by  $s$  ( $V$ , the volume of a MD cell),

$$\mathbf{q}'_i = V^{\frac{1}{3}} \mathbf{q}_i, \quad (4.1)$$

$$\mathbf{p}'_i = \mathbf{p}_i / V^{\frac{1}{3}} s, \quad (4.2)$$

$$t' = \int \frac{dt}{s}. \quad (4.3)$$

The values of the components of the scaled coordinates  $\mathbf{q}_i$  are limited to the range of 0 to 1. The Hamiltonian is

$$H = \sum_i \mathbf{p}_i^2 / 2m_i V^{\frac{2}{3}} s^2 + \phi(V^{\frac{1}{3}} \mathbf{q}) + p_s^2 / 2Q + gkT \ln s + p_V^2 / 2W + P_{\text{ex}} V, \quad (4.4)$$

where  $p_V$  is the conjugate momentum of  $V$ ,  $W$  is a mass for the volume motion, and  $P_{\text{ex}}$  is the externally set pressure.

The equations of motion are

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i} = \mathbf{p}_i / m_i V^{\frac{2}{3}} s^2, \quad (4.5)$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}'_i} V^{\frac{1}{3}}, \quad (4.6)$$

$$\frac{ds}{dt} = \frac{\partial H}{\partial p_s} = p_s / Q, \quad (4.7)$$

$$\frac{dp_s}{dt} = -\frac{\partial H}{\partial s} = \left[ \sum_i \mathbf{p}_i^2 / m_i V^{\frac{2}{3}} s^2 - gkT \right] / s, \quad (4.8)$$

$$\frac{dV}{dt} = \frac{\partial H}{\partial p_V} = p_V / W, \quad (4.9)$$

$$\frac{dp_V}{dt} = -\frac{\partial H}{\partial V} = \left[ \sum_i (\mathbf{p}_i^2 / m_i V^{\frac{2}{3}} s^2 - \frac{\partial \phi}{\partial \mathbf{q}'_i} \mathbf{q}'_i) \right] / 3V - P_{\text{ex}}. \quad (4.10)$$

In Lagrangian form, these are

$$\frac{d}{dt} \left( m_i V^{\frac{2}{3}} s^2 \frac{d\mathbf{q}_i}{dt} \right) = -\frac{\partial \phi}{\partial \mathbf{q}_i} = -\frac{\partial \phi}{\partial \mathbf{q}'_i} V^{\frac{1}{3}}, \quad (4.11)$$

$$\frac{d}{dt} \left( Q \frac{ds}{dt} \right) = \left[ \sum_i V^{\frac{2}{3}} s^2 \left( \frac{d\mathbf{q}_i}{dt} \right)^2 / m_i - gkT \right] / s, \quad (4.12)$$

$$\frac{d}{dt} \left( W \frac{dV}{dt} \right) = \left\{ \sum_i \left[ V^{\frac{2}{3}} s^2 \left( \frac{d\mathbf{q}_i}{dt} \right)^2 / m_i - \frac{\partial \phi}{\partial \mathbf{q}'_i} \mathbf{q}'_i \right] \right\} / 3V - P_{\text{ex}}. \quad (4.13)$$

The equilibrium distribution function is obtained in the same way as in Secs. II and III. We define  $H_0(\mathbf{p}, \mathbf{q}) = \sum_i \mathbf{p}_i^2 / 2m_i + \phi(\mathbf{q})$  as before. Then

$$Z = \int dp_V \int dV \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{q} \delta[H_0(\mathbf{p}/V^{\frac{1}{3}}s, V^{\frac{1}{3}}\mathbf{q}) + p_s^2/2Q + gkT \ln s + p_V^2/2W + P_{\text{ex}}V - E].$$

The transformations equations (4.1) and (4.2) lead to

$$\begin{aligned} Z &= \int dp_V \int dp_s \int dV \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N} \delta[H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q + gkT \ln s + p_V^2/2W + P_{\text{ex}}V - E] \\ &= C \int dp_V \int dp_s \int dV \int d\mathbf{p}' \int d\mathbf{q}' \exp \left[ -\left( \frac{3N+1}{g} \right) \cdot (H_0(\mathbf{p}', \mathbf{q}') + p_s^2/2Q + p_V^2/2W - P_{\text{ex}}V - E) / kT \right] \\ &= C \int dV \int d\mathbf{p}' \int d\mathbf{q}' \int \exp \left[ -\left( \frac{3N+1}{g} \right) \cdot (H_0(\mathbf{p}', \mathbf{q}') + P_{\text{ex}}V) / kT \right]. \end{aligned}$$

For virtual time sampling, with  $g = 3N + 1$ , the equilibrium distribution function is

$$\rho(\mathbf{p}', \mathbf{q}', V) = \exp[-(H_0(\mathbf{p}', \mathbf{q}') + P_{\text{ex}}V) / kT] \quad (4.14)$$

and the averages of any function of  $\mathbf{p}', \mathbf{q}', V$  are identical with those in the TP ensemble.

$$\begin{aligned} \lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_{t_0}^{t_0+t} A(\mathbf{p}/V^{\frac{1}{3}}s, V^{\frac{1}{3}}\mathbf{q}, V) dt \\ = \langle A(\mathbf{p}/V^{\frac{1}{3}}s, V^{\frac{1}{3}}\mathbf{q}, V) \rangle \\ = \langle A(\mathbf{p}', \mathbf{q}', V) \rangle_{\text{TP}}, \end{aligned} \quad (4.15)$$

$\langle \dots \rangle_{\text{TP}}$  denotes the average in the TP ensemble. For real time sampling,  $g$  must be  $3N$  in order to produce the TP ensemble.

In the same fashion as in Sec. II B, we can also get the equations for real variables.

##### B. The constraint method

The equations for the constraint method are Eqs. (4.5) and (4.6) and the constraints

$$\frac{\partial H}{\partial s} = -\left( \sum_i \mathbf{p}_i^2 / m_i V^{\frac{2}{3}} s^2 - gkT \right) / s = 0, \quad (4.16)$$

$$\frac{\partial H}{\partial V} = -\left[ \sum_i \left( \mathbf{p}_i^2 / m_i V^{\frac{2}{3}} s^2 - \frac{\partial \phi}{\partial \mathbf{q}'_i} \mathbf{q}'_i \right) - 3P_{\text{ex}}V \right] / 3V = 0, \quad (4.17)$$

$$\frac{\partial H}{\partial p_s} = p_s / Q = 0, \quad \text{and} \quad \frac{\partial H}{\partial p_V} = p_V / W = 0.$$

The partition function is

$$Z = C \int d\mathbf{p}' \delta \left( \sum_i \mathbf{p}_i'^2 / 2m_i - gkT/2 \right) \int dV \int d\mathbf{q}' \times \exp \left\{ - \left( \frac{3N}{g} \right) [gkT/2 + \phi(\mathbf{q}') + P_{ex} V] / kT \right\} \delta \left[ (gkT - \sum_i \frac{\partial \phi}{\partial \mathbf{q}_i'} \mathbf{q}_i') / 3 - P_{ex} V \right], \quad (4.18)$$

$g$  is  $3N$  for virtual time sampling and  $3N - 1$  for real time sampling.

The equations for real variables ( $\mathbf{p}_i' = \mathbf{p}_i / V^{1/2}$ ,  $\mathbf{q}_i' = V^{1/3} \mathbf{q}_i$ , and  $t' = \int dt / s$ ) are

$$\frac{d\mathbf{q}_i'}{dt'} = \mathbf{p}_i' / m_i + \left( \frac{1}{3V} \frac{dV}{dt'} \right) \mathbf{q}_i' \quad (4.19)$$

and

$$\frac{d\mathbf{p}_i'}{dt'} = - \frac{\partial \phi}{\partial \mathbf{q}_i'} - \left( \frac{1}{3V} \frac{dV}{dt'} \right) \mathbf{p}_i' - \left( \frac{ds}{dt} \right) \mathbf{p}_i'. \quad (4.20)$$

The derivatives  $ds/dt$ ,  $1/3V dV/dt'$ , are obtained via differentiation of Eqs. (4.16) and (4.17),

$$\frac{ds}{dt} + \frac{1}{3V} \frac{dV}{dt'} = - \left( \sum_i \frac{\partial \phi}{\partial \mathbf{q}_i'} \frac{\mathbf{p}_i'}{m_i} \right) / gkT \quad (4.21)$$

and

$$\frac{1}{3V} \frac{dV}{dt'} = - \left( \sum_i \frac{\partial \phi}{\partial \mathbf{q}_i'} \frac{\mathbf{p}_i'}{m_i} + \sum_i \sum_j \frac{\partial^2 \phi}{\partial \mathbf{q}_i' \partial \mathbf{q}_j'} \mathbf{q}_j' \frac{\mathbf{p}_i'}{m_i} \right) / \left( 9P_{ex} V + \sum_i \frac{\partial \phi}{\partial \mathbf{q}_i'} \mathbf{q}_i' + \sum_i \sum_j \frac{\partial^2 \phi}{\partial \mathbf{q}_i' \partial \mathbf{q}_j'} \mathbf{q}_i' \mathbf{q}_j' \right). \quad (4.22)$$

If we define parameters  $\alpha = ds/dt$  and  $\epsilon = 1/3V dV/dt'$ , Eqs. (4.19)–(4.22) are identical to the equations given by Evans and Morriss<sup>18</sup> except that in this derivation the total kinetic energy  $\sum_i \mathbf{p}_i'^2 / 2m_i$  has to be set equal to  $(3N - 1)kT/2$  and not to  $3NkT/2$ .

## V. DISCUSSION

### A. Comparison of the extended system method and the constraint method

The constant temperature MD methods for the canonical and the TP ensembles are reviewed in Secs. II–IV. The

relation of these equations is listed in Table I. The HLME method<sup>14–18</sup> and Evans–Morriss method<sup>18</sup> were derived as a special case of the ES method.<sup>19</sup> Other methods except those mentioned here and that by Anderson<sup>1</sup> do not seem to give the rigorous canonical distribution.

The methods were first presented in the virtual variable formulation, then transformed to the real variable case. The virtual variable formulation is the backbone of the constant temperature method. In this form, the equations remain canonical and the proof of equivalence with the canonical ensemble is straightforward. However, the unequal time intervals are not convenient for simulations. The real time formulation is recommended for applications. It should be remembered that in this case the equations are no longer canonical.

Both constant temperature methods (the ES and the HLME) are still not ideal. The number of independent variables are listed in Table II. The ES method has more independent variables than the equivalent statistical mechanical ensemble. This is the reason why the ES method gives correct results for the static quantities, but the time evolution of  $s$  and/or  $V$  are dependent on the adjustable parameters  $Q$  and/or  $W$ . This arbitrariness is both a disadvantage and an advantage of this method. The calculation of the velocity autocorrelation functions in the constant pressure MD method<sup>7</sup> and in the constant temperature method<sup>13,24,25</sup> show no significant difference from that of the ordinary MD method. If the effects on the dynamics of the physical system are negligible, we can select the parameters  $Q$  and  $W$  to optimize the efficiency of the calculations.

In the constraint method, the number of independent variables is less than those of the statistical mechanical formulation, due to the addition of the constraints. Some of the static quantities in the constraint method are not exactly those appropriate to the canonical distribution. In the canonical ensemble, only the quantities dependent on the momentum are affected. In the TP ensemble, the pressure constraint depends both on the volume and on coordinate space.

If we define the instantaneous temperature  $T_i$  and pressure  $P_i$  by

$$\sum_j \mathbf{p}_j^2 / 2m_j = \frac{3N}{2} kT_i, \quad (5.1)$$

and

TABLE I. Relation between the various constant temperature methods.

	Extended system method		Constraint method
Virtual variable equations	Sec. II A, Nosé <sup>a</sup> Eqs. (2.5)–(2.12)	→ constraint Eq. (3.2)	Sec. III A Eqs. (3.2)–(3.6)
	↓ transformation Eqs. (2.1)–(2.3)		↓ transformation [Eqs. (2.1)–(2.3)]
Real variable equations	Sec. II B Eqs. (2.19)–(2.25)		Sec. III B, HLME <sup>b</sup> Eqs. (3.8)–(3.10)

<sup>a</sup> Reference 19.

<sup>b</sup> References 14–18.



TABLE II. The number of independent variables in the various constant temperature MD methods. The numbers in brackets explicitly consider the momentum and angular momentum conservation.

	Extended system method	Statistical mechanics	Constraint method
Canonical Ensemble	$6N + 1$ ( $6N - 5$ )	$6N$	$6N - 1$ ( $6N - 7$ )
TP Ensemble	$6N + 3$ ( $6N - 3$ )	$6N + 1$	$6N - 1$ ( $6N - 7$ )

$$\left[ \sum_j (\mathbf{p}_j^2/2m_j - \frac{\partial \phi}{\partial \mathbf{q}_j} \mathbf{q}_j) \right] / 3V = P_i, \quad (5.2)$$

the averages and the fluctuations of these quantities in the canonical and the TP ensemble are

$$\langle T_i \rangle = T, \quad (5.3)$$

$$\langle (T_i - T)^2 \rangle = \frac{2}{3N} T^2, \quad (5.4)$$

$$\langle P_i \rangle = P_{\text{ex}}, \quad (5.5)$$

and

$$\begin{aligned} \langle (P_i - P_{\text{ex}})^2 \rangle &= -kT \left\langle \frac{\partial P_i}{\partial V} \right\rangle \\ &= \frac{kT}{9} \left\langle \left( 5 \sum_j \mathbf{p}_j^2/m_j - 2 \sum_j \frac{\partial \phi}{\partial \mathbf{q}_j} \mathbf{q}_j \right. \right. \\ &\quad \left. \left. + \sum_j \sum_k \frac{\partial^2 \phi}{\partial \mathbf{q}_j \partial \mathbf{q}_k} \mathbf{q}_j \mathbf{q}_k \right) / V^2 \right\rangle. \end{aligned} \quad (5.6)$$

The fluctuations of  $T_i$  and  $P_i$  [Eqs. (5.4) and (5.6)] are suppressed in the constraint method. In the formulation of statistical mechanics,  $T$  and  $P_{\text{ex}}$  are the temperature and pressure of the external system, and the values of the temperature and pressure in the physical system are defined only in an averaged sense by Eqs. (5.3) and (5.5).

## B. Some comments

The proper choices for the values of the parameter  $g$  in the potential energy function for the variable  $s$ ,  $gkT \ln s$ , are listed in Table III. These values depend on the nature of the method as well as on the type of sampling.

In the rigid molecule case, the kinetic energy term for the molecular rotation  $\sum_i \frac{1}{2} s^2 \omega_i I_i \omega_i$  or  $\sum_i \frac{1}{2} \mathbf{p}_{\omega_i} I_i^{-1} \mathbf{p}_{\omega_i} / s^3$  ( $\omega_i$ , angular velocity;  $I_i$ , moment of inertia tensor;  $\mathbf{p}_{\omega_i}$ , the conjugate momentum of  $\omega_i$ ) are added to the Hamiltonian [Eq.

TABLE III. Proper values of the parameter  $g$  in the potential function for  $s$ ,  $gkT \ln s$ .

	Extended system method	Constraint method
Sampling in virtual time	$3N + 1$	$3N$
Sampling in real time	$3N$	$3N - 1$

(2.5)] and the number of degrees of freedom of the rotation must be added to  $g$  value.

The constant pressure MD method deviates by order  $N^{-1}$  from the constant enthalpy-constant pressure ensemble in any case, due to the kinetic energy term for the volume motion  $p_V^2/2W$ . Therefore, the effects of using different functional forms for this term [e.g.,  $A(V)p_V^2$ ] are much less significant.<sup>4</sup> However, in the canonical and the TP ensemble, methods, there are no intrinsic deviation of order  $N^{-1}$  to start with, so different forms for these kinetic terms (e.g.,  $p_s^2/2Q$  or  $p_s^2/2Qs^2$ ,  $p_V^2 V^2/2W$ ) can give rise to deviations of order  $N^{-1}$ . A careful choice of the functional form for the additional kinetic energy terms is important in these types of calculations.

Due to the conservation of the total momentum and angular momentum, MD methods produce ensembles that deviate slightly from the statistical mechanical ensembles.<sup>20-22</sup> The true number of independent variables (when the above conservation laws are taken into account) are bracketed in Table II. In practice, the angular momentum is not conserved in MD simulations if we employ periodic boundary conditions. Here, we only discuss the effect of the momentum conservation law.

The momentum conservation law holds when it is expressed in terms of virtual variables

$$\sum_i p_{ix} = p_x, \quad \sum_i p_{iy} = p_y, \quad \text{and} \quad \sum_i p_{iz} = p_z, \quad (5.7)$$

where  $p_x, p_y, p_z$  are constants. The partition function in the extended system is modified

$$\begin{aligned} Z &= \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{q} \delta(H - E) \\ &\quad \delta(\sum_i p_{ix} - p_x) \delta(\sum_i p_{iy} - p_y) \delta(\sum_i p_{iz} - p_z). \end{aligned}$$

With the transformation to real variables, it becomes

$$\begin{aligned} Z &= \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N} \delta(H' - E) \delta(s \sum_i p'_{ix} - p_x) \\ &\quad \times \delta(s \sum_i p'_{iy} - p_y) \delta(s \sum_i p'_{iz} - p_z) \\ &= \int dp_s \int d\mathbf{p}' \int d\mathbf{q}' \int ds s^{3N-3} \delta(H' - E) \delta(\sum_i p'_{ix} - p_x/s) \\ &\quad \times \delta(\sum_i p'_{iy} - p_y/s) \delta(\sum_i p'_{iz} - p_z/s). \end{aligned}$$

If the total momentum  $p_x = p_y = p_z = 0$ , momentum space and coordinate space can be separated. Hence,

$$\begin{aligned} Z &= \int dp_s \int d\mathbf{p}' \delta(\sum_i p'_{ix}) \delta(\sum_i p'_{iy}) \delta(\sum_i p'_{iz}) \\ &\quad \times \int d\mathbf{q}' \int ds s^{3N-3} \delta(H' - E). \end{aligned} \quad (5.8)$$

From above equation, if  $g = 3N + 3$ , the equilibrium distribution function is

$$\rho(\mathbf{p}', \mathbf{q}') = \exp[-H_0(\mathbf{p}', \mathbf{q}')/kT] \delta(\sum_i p'_{ix}) \delta(\sum_i p'_{iy}) \delta(\sum_i p'_{iz}). \quad (5.9)$$

In momentum space, there is restriction due to momentum

conservation, but that has no effect in coordinate space. The instantaneous temperature should be defined as

$$\sum_i p_i'^2/2m_i = (3N - 3)kT/2. \quad (5.10)$$

This follows from a decrease of the number of independent variables. In the case of the TP ensemble, the weight factor for the volume also changes.

Theoretically, static quantities are independent of the value chosen for the parameter  $Q$ . However, in practice because of the finite number of time steps, the equivalence equation (2.17) is not always satisfied. With small  $Q$  values, the degree of freedom associated with  $s$  tends to decouple from the physical system. On the other hand, large  $Q$  values lead to inefficient sampling of phase space. The most efficient calculation will be done by choosing same order of time scales for the physical system and the variable  $s$ . If we only consider the fluctuation of  $s$  around the averaged value  $\langle s \rangle$ ,  $s = \langle s \rangle + \delta s$ ,<sup>19</sup> Eq. (2.12) can be simplified as

$$Q \frac{d^2}{dt^2} \delta s = - \frac{2gkT}{\langle s \rangle^2} \delta s. \quad (5.11)$$

The frequency of this harmonic equation is

$$\omega^2 = \left( \frac{2gkT}{Q \langle s \rangle^2} \right). \quad (5.12)$$

We can choose a  $Q$  value such that  $\omega^2$  in Eq. (5.12) gives the same order of magnitude as the second moment of the frequency spectrum of the velocity autocorrelation function of the physical system.

This time scale approximately corresponds to the time taken for a sound wave to travel the nearest neighbor distance.

## VI. SUMMARY

Three constant temperature MD methods are examined analytically. Except for effects due to momentum and angular momentum conservation, the ES method<sup>19</sup> gives rigorous equilibrium distribution functions in the canonical and in the TP ensembles. The HLME constraint method<sup>14-18</sup> give the canonical distribution only in coordinate space. Both the HLME and the Evans-Morriss method have been derived from the formulation of the ES method by imposing constraints. The Haile-Gupta method<sup>13</sup> on the other hand does not give the rigorous canonical distribution.

The virtual variable formulation is best suited for proof of the equivalence with the statistical mechanical ensembles. The equations based on the real variable formulations [Eqs. (2.19)-(2.25) or the HLME method] are recommended for applications.

The extension of the MD method to ensembles other than the microcanonical ensemble is formulated in a unified fashion. By introducing real variables and virtual variables the constant pressure MD method is generated from a scaling of the coordinates. The constant temperature MD method is obtained from a scaling of the time.

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