

A molecular dynamics method for simulations in the canonical ensemble†

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A molecular dynamics simulation method which can generate configurations belonging to the canonical (T, V, N) ensemble or the constant temperature constant pressure (T, P, N) ensemble, is proposed. The physical system of interest consists of N particles (f degrees of freedom), to which an external, macroscopic variable and its conjugate momentum are added. This device allows the total energy of the physical system to fluctuate. The equilibrium distribution of the energy coincides with the canonical distribution both in momentum and in coordinate space. The method is tested for an atomic fluid (Ar) and works well.

1. Introduction

The molecular dynamics (MD) method has become an important technique for the study of fluids and solids. In the standard MD method, the newtonian equations of motion of the particles in a fixed MD cell of volume V are solved numerically. The total energy E is conserved, and thus the ensemble generated by the simulation is the microcanonical or (E, V, N) ensemble.

With the MD method, not only the static quantities but also the dynamic quantities can be obtained. This is one advantage over the Monte Carlo (MC) method. However, a disadvantage of the MD method is that the conditions of the simulations are not the same as those normally encountered in experiments (constant temperature, constant pressure or (T, P, N) conditions).

In this regard, Andersen's introduction of the constant pressure MD method represented a significant breakthrough [1]. In his modified MD method, the volume becomes a variable and is allowed to fluctuate. The average volume is determined by the balance between the internal pressure and the externally set pressure P_{ex} . The enthalpy of the system is approximately conserved, so this method generates the constant enthalpy, constant pressure (H, P, N) ensemble. Parrinello and Rahman subsequently extended the method to allow for changes of the MD cell shape [2, 3]. The usefulness of this latter method has been

demonstrated by numerous applications to structural changes in the solid state [2–7].

To perform MD simulations at constant temperature, one can simply keep the kinetic energy constant by scaling the velocities at each time step and this approach is now widely employed [8, 9]. However, there seems to be no rigorous proof that the latter approach produces configurations belonging to the canonical ensemble.

Hoover *et al.* proposed a constraint method in which an additional velocity dependent term is added to the forces to keep the total kinetic energy constant [10]. Their method produces the canonical distribution for the potential energy term. The fluctuations of the kinetic energy are suppressed.

A method for constant temperature MD simulations was also proposed by Andersen [1]. This is effectively a hybrid of MD and MC methods since the velocities of the particles are changed stochastically to produce the Boltzmann distribution. It also lacks a well defined conserved quantity. Tanaka *et al.* applied Andersen's method to a Lennard-Jones system and also to a water system [11]. They found that if the probability of the stochastic collision exceeds a certain value, the diffusion coefficient decreases appreciably. To prevent the decrease of the diffusion coefficient and at the same time to maintain the temperature constant, it seems to be necessary to select the collision probability in a certain range.

In the present article, a new molecular dynamics method at constant temperature is proposed. By introduction of an additional degree of freedom s , the total energy of the physical system is allowed to fluctuate. A special choice of the potential for the variable s guaran-

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tees that the averages of static quantities in this method are equal to those in the canonical ensemble. This method is purely dynamical. In the extended system of the particles and the coordinate s , the total hamiltonian is conserved and all the equations of motion are solved without introducing any stochastic process.

The formulation of the method is presented in §2. As an example, an application to a system of argon atoms is given in §3. If the present method is combined with the constant pressure MD method, then simulations at conditions of a constant temperature and constant pressure are also possible. The formulation for the (T, P, N) ensemble is given in the Appendix.

2. A canonical ensemble molecular dynamics method

2.1. Equations of motion

We formulate the system which produces configurations following the canonical distribution. We limit the discussion to the case of atoms, but the extension to molecular systems is straightforward. First, consider a physical system; N particles with coordinates $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ in a fixed volume V ; and potential energy $\phi(\mathbf{r})$. An additional degree of freedom s is introduced, which acts as an external system. The interaction between the physical system and s is expressed via the scaling of the velocities of the particles,

$$\mathbf{v}_i = s\dot{\mathbf{r}}_i, \quad (2.1)$$

and \mathbf{v}_i is considered as the real velocity of particle i . We can interpret this as an exchange of heat between the physical system and the external system (heat reservoir).

We associate a potential energy $(f+1)kT_{\text{eq}} \ln s$ with the variable s , where f is the number of degrees of freedom in the physical system, k Boltzmann's constant, and T_{eq} the externally set temperature value. As we shall see, this choice of potential energy ensures that canonical ensemble averages are recovered.

The lagrangian of the extended system of particles and s is thus postulated to be

$$\mathcal{L} = \sum_i \frac{m_i}{2} s^2 \dot{\mathbf{r}}_i^2 - \phi(\mathbf{r}) + \frac{Q}{2} \dot{s}^2 - (f+1)kT_{\text{eq}} \ln s. \quad (2.2)$$

The kinetic energy term, $\frac{1}{2}Q\dot{s}^2$ is introduced in order to be able to construct a dynamic equation for s . The parameter Q has the dimensions of energy \cdot (time)² and determines the time scale of the temperature fluctuation. The equations of motion for \mathbf{r}_i and s are derived from the lagrangian equation

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{A}} \right) = \frac{\partial \mathcal{L}}{\partial A}, \quad (2.3)$$

where A stands for one of the variables mentioned above.

The equations for the particles are

$$\frac{d}{dt} (m_i s^2 \dot{\mathbf{r}}_i) = - \frac{\partial \phi}{\partial \mathbf{r}_i}, \quad (2.4)$$

or

$$\ddot{\mathbf{r}}_i = - \frac{1}{m_i s^2} \frac{\partial \phi}{\partial \mathbf{r}_i} - \frac{2\dot{s}}{s} \dot{\mathbf{r}}_i. \quad (2.5)$$

The equation for s is

$$Q\ddot{s} = \sum_i m_i s \dot{\mathbf{r}}_i^2 - \frac{(f+1)kT_{\text{eq}}}{s}. \quad (2.6)$$

If we denote the average in the extended system by $\langle \dots \rangle$, the relation

$$\left\langle \frac{\sum_i m_i s^2 \dot{\mathbf{r}}_i^2}{s} \right\rangle = (f+1)kT_{\text{eq}} \left\langle \frac{1}{s} \right\rangle \quad (2.7)$$

is obtained from (2.6) because the time average of a time derivative (e.g. $Q\ddot{s}$) vanishes. This suggests that the average of the kinetic energy coincides with the externally set temperature T_{eq} .

The momenta are given by

$$\mathbf{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i \quad (2.8)$$

and

$$p_s = \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q\dot{s}. \quad (2.9)$$

The conserved quantities in this extended system are the hamiltonian

$$\mathcal{H}_1 = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1)kT_{\text{eq}} \ln s, \quad (2.10)$$

the total momentum

$$\mathbf{P} = \sum_i \mathbf{p}_i = \sum_i (m_i s^2 \dot{\mathbf{r}}_i), \quad (2.11)$$

and the total angular momentum

$$\mathbf{M} = \sum_i \mathbf{r}_i \times \mathbf{p}_i = \sum_i \mathbf{r}_i \times (m_i s^2 \dot{\mathbf{r}}_i). \quad (2.12)$$

2.2. Proof of the equivalence of the present method and the canonical ensemble

Now we prove that the equations of motion derived from (2.2) produce configurations in the canonical ensemble at temperature T_{eq} . Our extended system produces a microcanonical ensemble of $(f+1)$ degree of freedom. The partition function of this ensemble is defined by

$$Z = \frac{1}{N!} \int dp_s \int ds \int d\mathbf{p} \int d\mathbf{r} \times \delta \left(\sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1)kT_{\text{eq}} \ln s - E \right). \quad (2.13)$$

Here, $\delta(x)$ denotes the Dirac δ function, and the shortened forms $d\mathbf{p} = d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N$, $d\mathbf{r} = d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$ are used.

The momentum \mathbf{p}_i is transformed as

$$\frac{\mathbf{p}_i}{s} = \mathbf{p}'_i, \quad (2.14)$$

and the volume element becomes $d\mathbf{p} = s^f d\mathbf{p}'$ (f is the number of degrees of freedom in the physical system). There is no upper limit in momentum space, so we can change the order of integration of $d\mathbf{p}'$ and ds ;

$$Z = \frac{1}{N!} \int dp_s \int d\mathbf{p}' \int d\mathbf{r} \int ds s^f \times \delta \left(\sum_i \frac{\mathbf{p}'_i^2}{2m_i} + \phi(\mathbf{r}) + \frac{p_s^2}{2Q} + (f+1)kT_{\text{eq}} \ln s - E \right).$$

Using the equivalence relation for δ function $\delta(g(s)) = \delta(s - s_0)/g'(s)$ where s_0 is the zero of $g(s) = 0$, and the shortened form

$$\mathcal{H}(\mathbf{p}', \mathbf{r}) = \sum_i \mathbf{p}'_i^2 / 2m_i + \phi(\mathbf{r}),$$

we get

$$\begin{aligned} Z &= \frac{1}{N!} \int dp_s \int d\mathbf{p}' \int d\mathbf{r} \int ds \frac{s^{f+1}}{(f+1)kT_{\text{eq}}} \\ &\times \delta \left(s - \exp \left[- \frac{(\mathcal{H}(\mathbf{p}', \mathbf{r}) + (p_s^2/2Q) - E)}{(f+1)kT_{\text{eq}}} \right] \right) \\ &= \frac{1}{(f+1)kT_{\text{eq}}} \frac{1}{N!} \int dp_s \int d\mathbf{p}' \int d\mathbf{r} \\ &\times \exp \left[- \left(\mathcal{H}(\mathbf{p}', \mathbf{r}) + \frac{p_s^2}{2Q} - E \right) / kT_{\text{eq}} \right]. \end{aligned}$$

The integration with respect to p_s can be carried out immediately, so we get the final result

$$Z = \frac{1}{(f+1)} \left(\frac{2\pi Q}{kT_{\text{eq}}} \right)^{1/2} \exp(E/kT_{\text{eq}}) Z_c. \quad (2.15)$$

Z_c is the partition function of the canonical ensemble

$$Z_c = \frac{1}{N!} \int d\mathbf{p}' \int d\mathbf{r} \exp[-\mathcal{H}(\mathbf{p}', \mathbf{r})/kT_{\text{eq}}]. \quad (2.16)$$

The average of some static quantity which is an arbitrary function of \mathbf{p}_i/s and \mathbf{r}_i in the extended system is exactly the same as that in the canonical ensemble,

$$\left\langle A \left(\frac{\mathbf{p}}{s}, \mathbf{r} \right) \right\rangle = \langle A(\mathbf{p}', \mathbf{r}) \rangle_c, \quad (2.17)$$

where $\langle \dots \rangle_c$ means the average in the canonical ensemble.

The above result is derived from the assumption that the only conserved quantity is the total hamiltonian \mathcal{H}_1 . In fact, the system has other conserved quantities: total momentum and angular momentum. These deviate by an order $O(1/N)$ from the canonical ensemble averages. A similar result was already pointed out by Hoover and Alder for the microcanonical ensemble [12].

The correction for total momentum conservation in this method can be achieved by using $f-3$ in place of f in the definition of both the lagrangian and the instantaneous temperature.

2.3. Some average quantities in the canonical ensemble MD method

If the instantaneous temperature T is defined as

$$\sum_i \frac{\mathbf{p}'_i^2}{2m_i s^2} = \frac{f}{2} kT,$$

the average and the fluctuation of T are, respectively

$$\langle T \rangle = \langle T \rangle_c = T_{\text{eq}} \quad (2.18)$$

and

$$\langle (T - T_{\text{eq}})^2 \rangle = \langle (T - T_{\text{eq}})^2 \rangle_c = T_{\text{eq}}^2 \frac{2}{f}. \quad (2.19)$$

The formula for the heat capacity c_v is derived from the fluctuation of the total energy

$$\begin{aligned} E_T &= \sum_i \frac{\mathbf{p}'_i^2}{2m_i s^2} + \phi(\mathbf{r}); \\ c_v &= \frac{\langle E_T^2 \rangle_c - \langle E_T \rangle_c^2}{NkT_{\text{eq}}^2} = \frac{1}{kT_{\text{eq}}^2} \left[\frac{f}{2} \frac{(kT_{\text{eq}})^2}{N} + \frac{\langle \phi^2 \rangle_c - \langle \phi \rangle_c^2}{N} \right] \\ &= \frac{fk}{2N} + \frac{\langle \phi^2 \rangle_c - \langle \phi \rangle_c^2}{NkT_{\text{eq}}^2}. \end{aligned} \quad (2.20)$$

We can also obtain averages of quantities depending on s , (see equation (2.21) on bottom of next page).

Some special case of (2.21) are

$$\langle s^m \rangle = \exp \left[\frac{mE}{(f+1)kT_{\text{eq}}} \right] \left(\frac{f+1}{f+1+m} \right)^{(f+1)/2} \times \left\langle \exp \left[-\frac{m}{f+1} \cdot \frac{\phi}{kT_{\text{eq}}} \right] \right\rangle_c, \quad (2.22)$$

$$\left\langle \frac{\mathbf{p}_i^2}{m_i s^3} \right\rangle = \left\langle \frac{\mathbf{p}_i'^2}{m_i s} \right\rangle = \left\langle \frac{1}{s} \right\rangle \frac{f+1}{f} kT_{\text{eq}}.$$

This last equation is identical to (2.7).

The fluctuation of s is

$$\left\langle \left(\frac{s - \langle s \rangle}{\langle s \rangle} \right)^2 \right\rangle = \left\{ \left(\frac{(f+2)^2}{(f+1)(f+3)} \right)^{(f+1)/2} \times \frac{\langle \exp\{-[2/(f+1)](\phi/kT_{\text{eq}})\} \rangle_c}{\langle \exp\{-[1/(f+1)](\phi/kT_{\text{eq}})\} \rangle_c^2} - 1 \right\}. \quad (2.23)$$

For large f , (2.23) tends to

$$\left\langle \left(\frac{s - \langle s \rangle}{\langle s \rangle} \right)^2 \right\rangle = \frac{N c_v}{f^2 k}. \quad (2.24)$$

2.4. An interpretation of the variable s

To obtain the dynamical quantities, the variable s can be interpreted as a scaling factor for the time step Δt in the simulations. The real time step $\Delta t'$ is obtained by the relation

$$\Delta t' = \frac{\Delta t}{s}. \quad (2.25)$$

The length of each time step $\Delta t'$ is now unequal.

Equation (2.25) is deduced as follows. In simultaneously transforming $s' = s/a$, and $t' = t/a$ by a constant a , the coordinates and their time derivatives change as

$$\left. \begin{aligned} \mathbf{r}' &= \mathbf{r}, & \dot{\mathbf{r}}' &= a\dot{\mathbf{r}}, & \ddot{\mathbf{r}}' &= a^2\ddot{\mathbf{r}}, \dots, \\ \mathbf{p}' &= \mathbf{p}/a, & t' &= t/a, \\ s' &= s/a, & \dot{s}' &= \dot{s}, & \ddot{s}' &= a\ddot{s}, \dots; \end{aligned} \right\} \quad (2.26)$$

the hamiltonian \mathcal{H}_1 is invariant except for a constant term

$$\mathcal{H}'_1 = \mathcal{H}_1 - (f+1)kT_{\text{eq}} \ln a. \quad (2.27)$$

So only the ratio $t/s = t'/s'$ has any real meaning, and in the case of $s' = 1$, the hamiltonian recovers its normal, unscaled form. The time in this case is considered to correspond to the real time. The velocity in (2.1) is re-expressed as

$$\mathbf{v}_i = \frac{d\mathbf{r}_i}{dt'} = s \frac{d\mathbf{r}_i}{dt}.$$

The length of the time step is unequal in the canonical ensemble MD method. For calculation of time dependent quantities, it is convenient to sample at intervals that are integer multiples of a unit time step. This can be done very easily by interpolation. At equilibrium, the fluctuation of s is of order $N^{-1/2}$ (see 2.24), so in practice, the differences in the lengths of individual time steps can sometimes be ignored. An averaged real time can be obtained by multiplying the simulation time with $\langle s^{-1} \rangle$.

The detailed nature of the dynamics depends upon the value of Q chosen. However, some dynamic quantities (especially, one body quantities) of the system are, we believe, less sensitive to the value of Q . If this is the case, we can get information on both static and dynamic quantities.

The frequency of the s oscillation can be estimated from (2.5),

$$Q\ddot{s} = \sum_i \frac{\mathbf{p}_i^2}{m_i s^3} - \frac{(f+1)}{s} kT_{\text{eq}}.$$

We assume the system is in equilibrium, and s fluctuates around the averaged value $\langle s \rangle$, $s = \langle s \rangle + \delta s$. Then the above equation can be simplified as

$$Q(\delta\ddot{s}) = fkT_{\text{eq}} \left(\frac{\langle s \rangle^2}{s^3} - \frac{1}{s} \right) = -\frac{2fkT_{\text{eq}}}{\langle s \rangle^2} \delta s. \quad (2.28)$$

This is the equation for a harmonic oscillator, with frequency

$$\begin{aligned} \left\langle B \left(\frac{\mathbf{p}}{s}, r \right) s^m \right\rangle &= \frac{\int dp_s \int d\mathbf{p}' \int d\mathbf{r} B(\mathbf{p}', r) \int ds \cdot s^{f+1+m} \delta \left(s - \exp \left[-\frac{\mathcal{H}(\mathbf{p}', r) + (p_s^2/2Q) - E}{(f+1)kT_{\text{eq}}} \right] \right)}{\int dp_s \int d\mathbf{p}' \int d\mathbf{r} \int ds \cdot s^{f+1} \delta \left(s - \exp \left[-\frac{\mathcal{H}(\mathbf{p}', r) + (p_s^2/2Q) - E}{(f+1)kT_{\text{eq}}} \right] \right)} \\ &= \exp \left[\frac{mE}{(f+1)kT_{\text{eq}}} \right] \left(\frac{f+1}{f+1+m} \right)^{1/2} \left\langle B(\mathbf{p}', r) \exp \left[-\frac{m}{(f+1)} \cdot \frac{\mathcal{H}(\mathbf{p}', r)}{kT_{\text{eq}}} \right] \right\rangle_c. \end{aligned} \quad (2.21)$$

$$\omega = \left(\frac{2fkT_{\text{eq}}}{Q\langle s \rangle^2} \right)^{1/2}. \quad (2.29)$$

The period of the oscillation is

$$t_0 = \frac{2\pi}{\omega} = 2\pi \left(\frac{Q\langle s \rangle^2}{2fkT_{\text{eq}}} \right)^{1/2}. \quad (2.30)$$

A typical value of Q for a 108 particle system, at $T_{\text{eq}} = 150$ K and for $t_0 = 1$ ps is $20 \text{ (kJ mol}^{-1}\text{) (ps)}^2$.

The transformation (2.26) can be used to change the length of time step. Without this control, the real time step in the simulations may become too small or too large. For a small time step, the calculation is inefficient; for a large one, the precision of the calculation cannot be maintained.

3. An application

The canonical ensemble MD method was tested on a system of 108 argon atoms (mass 39.9 g mol^{-1}), interacting with a Lennard-Jones 12–6 potential ($\varepsilon = 1.039 \text{ kJ mol}^{-1}$, $\sigma = 3.446 \text{ \AA}$) which was truncated at 8.5 \AA . The MD cell was a cube of edge length 17.5 \AA (or volume $29.88 \text{ cm}^3 \text{ mol}^{-1}$) and as usual, the periodic boundary condition was adopted. A 5th order predictor–corrector algorithm was employed for integration of the equations of motion. A time step $\Delta t = 2.5 \times 10^{-15} \text{ s}$ was used, except for the runs with $Q = 100 \text{ (kJ mol}^{-1}\text{) (ps)}^2$ for which $\Delta t = 5.0 \times 10^{-15} \text{ s}$. Each run consisted of the calculation of 2500 time steps, the first 500 steps being discarded from the averaging.

In all applications, differences in the length of individual time steps were ignored and the real time was calculated by multiplying the time of simulation by the factor $\langle s^{-1} \rangle$.

The simulations were carried out by the following scheme. First, starting from an initial configuration (f.c.c. structure) a standard MD run (No. 1) was carried out at about 150 K. This was followed by a constant

temperature simulation at $T_{\text{eq}} = 100$ K (No. 2). Then, the temperature was reset to $T_{\text{eq}} = 150$ K (No. 3) and finally the effects of using different Q values 1, 10, and 100 ($\text{kJ mol}^{-1}\text{) (ps)}^2$ were compared at 100 K and 150 K (No. 4–9). The results are listed in table 1. The deviations of the temperature from T_{eq} are less than 1 K. The runs with $Q = 1$ show especially good agreement. The averages of the potential energy and pressure give almost the same results for different Q values. The run No. 9 clearly did not reach equilibrium because the temperature fluctuation is too large. The sudden increase in the value of Q at the beginning of the run gave a huge amount of kinetic energy to the variable s , which could not relax to equilibrium in the 2500 timesteps.

Figure 1 shows the evolution of the instantaneous temperature through the first 3 runs. In the constant temperature method, the temperature reaches T_{eq} quickly and fluctuates around this value. The approximate formula for the fluctuation of temperature in the microcanonical ensemble [13, 14].

$$\langle (\delta T)^2 \rangle_{E,V,N} = T_{\text{eq}}^2 \frac{2}{3N} \left(1 - \frac{3}{2c_v} \right) \quad (3.1)$$

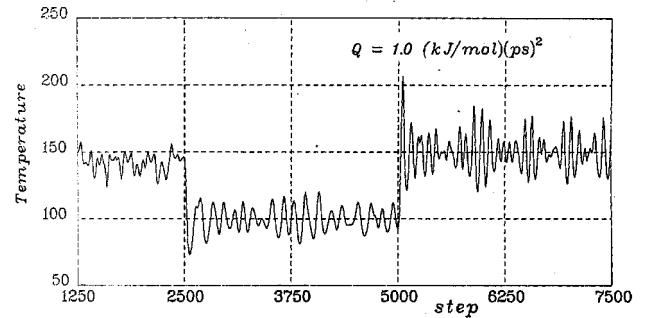


Figure 1. Evolution of the temperature. The first 1250 steps shown (1250–2500 step) are carried out with the standard MD method. At step 2500, the simulation is changed to the constant temperature method with $T_{\text{eq}} = 100$ K. At step 5000, T_{eq} is changed to 150 K.

Table 1. Results of the constant temperature MD simulations for system of 108 argon atoms, $V = 29.88 \text{ cm}^3 \text{ mol}^{-1}$.

Run	Initial condition	T_{eq} K	Q ($\text{kJ mol}^{-1}\text{) (ps)}^2$	$\langle T \rangle$ K	ΔT K	$\langle \phi \rangle$ kJ mol^{-1}	P GPa	$\langle s \rangle$	$\left\langle \frac{1}{s} \right\rangle$	c_v R	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$
1	f.c.c.		standard MD	143.3	6.8	−5.188	0.123	1.0	1.0		4.1
2	run 1	100	1	99.6	8.3	−5.520	0.049	1.419	0.706	2.54	1.6
3	run 2	150	1	149.3	12.4	−5.115	0.137	1.071	0.936	2.36	4.9
4	run 2	100	1	99.9	9.0	−5.525	0.045	1.418	0.707	2.82	1.6
5	run 2	100	10	99.3	6.9	−5.549	0.039	1.437	0.697	1.89	2.3
6	run 2	100	100	100.2	7.4	−5.537	0.042	1.425	0.703	2.04	1.9
7	run 3	150	1	149.8	12.7	−5.094	0.140	1.064	0.943	2.42	4.2
8	run 3	150	10	149.1	12.0	−5.151	0.132	1.101	0.910	2.63	3.3
9	run 3	150	100	148.7	25.9	−5.099	0.140	1.118	0.908	9.25	3.5

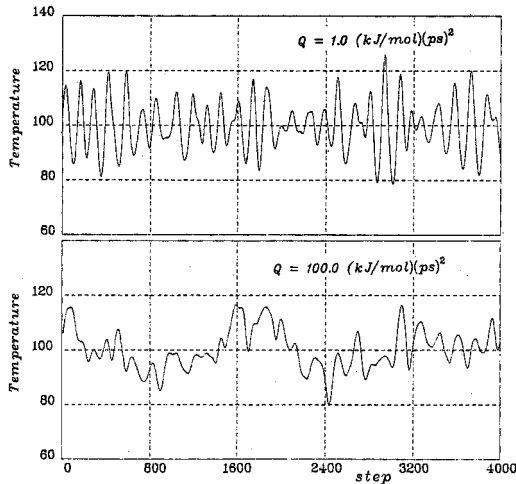


Figure 2. Comparison of the temperature fluctuations in runs with different Q values at 100 K. Above: $Q = 1$ ($\text{kJ mol}^{-1})(\text{ps})^2$, Below: $Q = 100$ ($\text{kJ mol}^{-1})(\text{ps})^2$. The total real time is about 7 ps.

(c_v heat capacity) shows that the temperature fluctuations in the canonical ensemble are larger than those in the microcanonical ensemble. We can readily recognize this in figure 1. The values of $\Delta T = ((\delta T)^2)^{1/2}$, 8.3 K at 100 K and 12.4 K at 150 K are comparable with those given by (2.19), 7.9 K at 100 K and 11.8 K at 150 K. As expected, the value of ΔT , and the heat capacity which is calculated from ΔT and the fluctuation of the potential energy, are less accurate than the energy or pressure results.

The comparison of temperature fluctuations in the run with $Q = 1$ and 100 ($\text{kJ mol}^{-1})(\text{ps})^2$ is given in figure 2. With $Q = 1$, the time scale of the fluctuation of s and that of the temperature are almost the same. On the other hand, with $Q = 100$, the temperature fluctuation can be decomposed into two components: the intrinsic temperature fluctuation of the physical system and a slow modulation due to fluctuation in s .

The time periods of fluctuations in s are $t_0 = 0.34$ ps for $Q = 1$ and $t_0 = 2.99$ ps for $Q = 100$. The estimates given by (2.30) are $t_0 = 0.38$ ps for $Q = 1$ and $t_0 = 3.8$ ps for $Q = 100$.

As a check on some dynamic quantity, the diffusion coefficient D was calculated from the mean square displacement.

$$D = \lim_{t \rightarrow \infty} \frac{\langle |r_i(t) - r_i(0)|^2 \rangle}{6t}. \quad (3.2)$$

The plot of the time evolution of the mean square displacement for different Q values is given in figure 3. All values for D for a given temperature seem to agree reasonably well. Even run No. 9 gives almost the same result as the other $T_{\text{eq}} = 150$ K runs, in spite of the large deviation from a straight line.

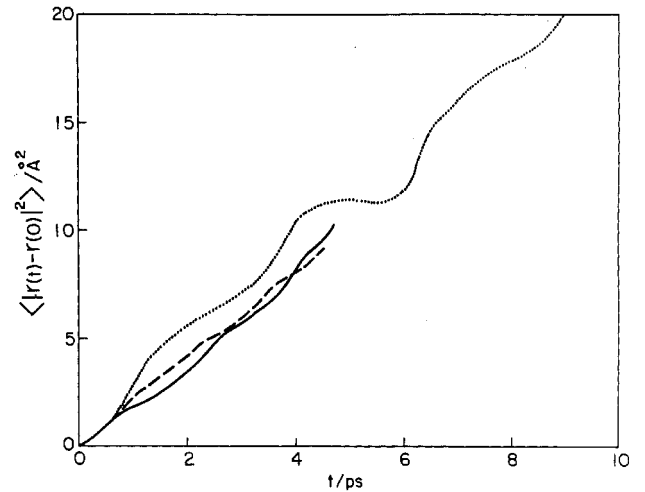


Figure 3. Comparison of the mean square displacements for different Q values at 150 K. Solid line $Q = 1$, dashed line $Q = 10$, and dotted line $Q = 100$ ($\text{kJ mol}^{-1})(\text{ps})^2$.

4. Conclusion

An MD method for constant temperature simulations has been presented. One can see from the derivation in §2 that different kinds of constant temperature simulation methods can be constructed by changing the functional form of the potential for the variable s . However, the equilibrium distribution function thus obtained is related to the inverse function of the potential for s , so that any other choice but a logarithmic form, results in an ensemble different from the canonical one. Therefore, a constant temperature method does not always imply that the calculation samples from the canonical ensemble.

The present method gives static quantities in the canonical ensemble. If we employ the interpretation that s is a scaling factor of time and that the real unit time $\Delta t'$ is related to the simulation unit time Δt by $\Delta t' = \Delta t/s$, calculation of dynamical quantities also seems to be possible. Of course, we have rigorously proved nothing concerning with the dynamic quantities, but it will be worth trying to determine under what conditions can one obtain the dynamical quantities reasonably well.

Main features of the present method are

- (1) The extended system of the particles and the variable s conserves the total hamiltonian. This gives a powerful error checking method in the process of programming and a useful precision control method in the simulations [7].
- (2) Since the present method employs a similar technique as the constant pressure MD method, it can readily be extended to the constant temperature constant pressure ensemble.
- (3) The scaling of the velocities can be interpreted as a scaling of the time variable. At the same time,

the constant pressure MD method is derived by scaling the coordinates. The extension of the MD method to ensembles other than the microcanonical ensemble is formulated in a unified fashion.

- (4) This method gives the rigorous canonical distribution both in momentum and in coordinate space.

If a structural change occurs during the simulation, the temperature necessarily changes and the standard MD method cannot produce the data at the required external conditions. The constant temperature method, especially the (T, P, N) ensemble method given in the Appendix, will be particularly useful in this situation.

During the preparation of the present paper, other constant temperature MD methods were proposed by Evans [15], by Evans and Morriss [16], and by Haile and Gupta [17]. The present method is the only one which gives the rigorous canonical distribution both in momentum and in coordinate space. The comparison with other methods will be presented in a forthcoming paper.

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Appendix

Formulation for the constant temperature constant pressure (T, P, N) ensemble

The constant temperature MD method is readily extended to the (T, P, N) ensemble.

In this Appendix, we use the formulation for uniform dilation by Andersen [1], but the extension to the generalized form of the constant pressure simulation method by Parrinello and Rahman can be done in a similar way [2, 3, 7].

In the case of the (T, P, N) ensemble, the MD cell is considered to be a cube of edge length $V^{1/3}$, the coordinate \mathbf{r}_i being expressed as

$$\mathbf{r}_i = V^{1/3} \mathbf{x}_i, \quad (\text{A } 1)$$

where \mathbf{x}_i is a scaled coordinate and the values of its components are limited to the range of 0 to 1. The velocity is also expressed by a scaled form

$$\dot{\mathbf{r}}_i = V^{1/3} \dot{\mathbf{x}}_i. \quad (\text{A } 2)$$

The lagrangian is

$$\begin{aligned} \mathcal{L} = & \sum_i \frac{m_i}{2} s^2 V^{2/3} \dot{\mathbf{x}}_i^2 - \phi(V^{1/3} \mathbf{x}) + \frac{Q}{2} \dot{s}^2 \\ & - (f+1)kT_{\text{eq}} \ln s \frac{W}{2} \dot{V}^2 - P_{\text{ex}} V. \end{aligned} \quad (\text{A } 3)$$

P_{ex} is the externally set pressure. The kinetic energy term for the volume is $\frac{1}{2}W\dot{V}^2$. The equations of motion are

$$\frac{d}{dt}(m_i s^2 V^{2/3} \dot{\mathbf{x}}_i) = -\frac{\partial \phi}{\partial \mathbf{x}_i} = -V^{1/3} \frac{\partial \phi}{\partial \mathbf{r}_i} \quad (\text{A } 4)$$

or

$$\ddot{\mathbf{x}}_i = -\frac{1}{m_i s^2 V^{1/3}} \frac{\partial \phi}{\partial \mathbf{r}_i} - \left(\frac{2\dot{s}}{s} + \frac{2\dot{V}}{3V} \right) \dot{\mathbf{x}}_i \quad (\text{A } 5)$$

$$Q\dot{s} = \sum_i m_i s V^{2/3} \dot{\mathbf{x}}_i^2 - \frac{(f+1)}{s} kT_{\text{eq}} \quad (\text{A } 6)$$

and

$$W\ddot{V} = \frac{1}{3} \frac{1}{V} \left(\sum_i m_i s^2 V^{2/3} \dot{\mathbf{x}}_i^2 - \sum_i \mathbf{r}_i \cdot \frac{\partial \phi}{\partial \mathbf{r}_i} \right) - P_{\text{ex}}. \quad (\text{A } 7)$$

With the momenta

$$\mathbf{p}_i = m_i s^2 V^{2/3} \dot{\mathbf{x}}_i, \quad p_V = W\dot{V}, \quad \text{and} \quad p_s = Q\dot{s},$$

the hamiltonian becomes

$$\begin{aligned} \mathcal{H}_2 = & \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2 V^{2/3}} + \phi(V^{1/3} \mathbf{x}) + \frac{p_s^2}{2Q} \\ & + (f+1)kT_{\text{eq}} \ln s + \frac{p_V^2}{2W} + P_{\text{ex}} V. \end{aligned} \quad (\text{A } 8)$$

The partition function of this system is

$$Z = \frac{1}{N!} \int dp_s \int ds \int dp_V \int dV \int d\mathbf{p} \int d\mathbf{x} (\delta \mathcal{H}_2 - E) \quad (\text{A } 9)$$

By scaling \mathbf{p} and \mathbf{x} as $\mathbf{p}/sV^{1/3} = \mathbf{p}'$, $V^{1/3} \mathbf{x} = \mathbf{r}$, we get

$$Z = \frac{1}{N!} \int dp_s \int dp_V \int dV \int d\mathbf{p}' \int d\mathbf{r} \int ds s^f \delta(\mathcal{H}_2 - E).$$

Following the steps in §2, one derives the result

$$\begin{aligned} Z = & \frac{1}{(f+1)} ((2\pi)^2 QW)^{1/2} \exp \left[\frac{E}{kT_{\text{eq}}} \right] \frac{1}{N!} \int dV \int d\mathbf{p}' \int d\mathbf{r} \\ & \times \exp \left[- \left(\sum_i \frac{\mathbf{p}'_i^2}{2m_i} + \phi(\mathbf{r}) + P_{\text{ex}} V \right) / kT_{\text{eq}} \right] \\ = & \frac{1}{(f+1)} ((2\pi)^2 QW)^{1/2} \exp \left[\frac{E}{kT_{\text{eq}}} \right] Z_{TPN}. \end{aligned} \quad (\text{A } 10)$$

Z_{TPN} is the partition function of the (T, P, N) ensemble. The averages of static quantities which are functions of \mathbf{p}' , \mathbf{r} , V are the same as those in the (T, P, N) ensemble:

$$\left\langle A \left(\frac{\mathbf{p}}{sV^{1/3}}, V^{1/3} \mathbf{x}, V \right) \right\rangle = \langle A(\mathbf{p}', \mathbf{r}, V) \rangle_{TPN}. \quad (\text{A } 11)$$

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