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Constant-temperature molecular dynamics

Shuichi Nosé

Department of Physics, Faculty of Science and Technology, Keio University, 3-14-1
Hiyoshi, Kohokoku, Yokohama, 223 Japan

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Abstract. A review is given of how molecular dynamics methods have been modified to perform simulations in the constant-temperature condition. We usually consider a system which is thermally connected with a huge external system (a heat reservoir) to describe a canonical ensemble in statistical mechanics. The way in which this situation is reflected is a key factor for simulations under isothermal conditions. The total kinetic energy is kept to a constant value in constraint methods. In stochastic methods, interactions with a heat bath are treated as random collisions with hypothetical atoms or random forces acting on particles. In the extended-system method, a degree of freedom which mimics a heat bath is introduced, and the total energy of a physical system is allowed to fluctuate.

Molecular dynamics simulations are one of commonly used methods to study many-particle systems. Consider a classical system of N particles in a fixed volume. The movement of particles in this system is governed by the equations of motion of classical mechanics, i.e. Newton's equations.

$$m_i d^2 \mathbf{q}_i / dt^2 = \mathbf{F}_i = -\partial \Phi / \partial \mathbf{q}_i \quad (1)$$

where \mathbf{q}_i is a coordinate of particle i . We also express this equation in a canonical form using coordinate \mathbf{q}_i and momentum \mathbf{p}_i for later use:

$$d\mathbf{q}_i / dt = \mathbf{p}_i / m_i \quad d\mathbf{p}_i / dt = \mathbf{F}_i = -\partial \Phi / \partial \mathbf{q}_i. \quad (2)$$

We solve these equations numerically by the aid of computers and follow the trajectory of every particle in a system. Thermodynamical and structural properties are calculated from the trajectory thus obtained. In the classical mechanical sense, we can obtain all the information about a system. We can also obtain dynamical properties in molecular dynamics simulations, which is an advantage over the Monte Carlo method.

The equations of motion conserve the total energy of a system. Thus, in molecular dynamics simulations, we can obtain properties of a system at a constant energy. A statistical mechanical ensemble corresponding to this situation is the microcanonical or constant- EVN ensemble, where E is the total energy, V is the volume and N is the number of particles in a system. These three quantities are controllable parameters in the microcanonical ensemble.

In molecular dynamics simulations, we often encounter limitations and inconveniences which come from the use of the microcanonical ensemble. Ordinary laboratory experiments are carried out at constant temperature and constant pressure, but molecular dynamics simulations are done at constant energy and constant volume. The

difference in these conditions makes direct comparison with experiments difficult. Perhaps, the most inconvenient feature of the molecular dynamics method is that we cannot carry out simulations exactly at a specific temperature and pressure. This problem arises because we cannot obtain the temperature value until the simulations are finished. Usually, we relate the temperature T to the average of the kinetic energy:

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

Only after we carry out simulations and calculate the average of the kinetic energy, do we know the temperature at which the simulations are carried out. Constant-temperature molecular dynamics methods are developed to resolve this frustrating situation.

We review how the temperature is controlled in the canonical ensemble. Consider a physical system surrounded by a large external system. The exchange of particles is not allowed, but energy transfer is allowed between these two systems. The external system is very large in comparison with a physical system and is called a heat reservoir or heat bath. The temperature of this external system is fixed at T . In fact, the temperature of our physical system in a thermodynamical sense is the temperature T of the external system. If we define an internal temperature by an average of the total kinetic energy in equation (3), the temperature is maintained at a constant value by thermal contact with a heat bath. Several methods have been proposed to realize the constant-temperature condition in the molecular dynamics method. They are the constraint, stochastic and extended-system methods. The way in which the thermal contact between a physical system and a heat bath is taken into consideration is a key factor in distinguishing between these methods.

In the constraint method, the total kinetic energy is kept to a constant value. As a result of thermal contact with a heat bath, the total kinetic energy is almost maintained at an averaged value in the canonical ensemble. The kinetic energy should fluctuate in the canonical ensemble, but the relative deviation from an averaged value becomes very small in a large system (in the thermodynamic limit). Thus, we ignore the fluctuations of the total kinetic energy and keep it to a constant value.

One legitimate constraint method is now known as the Gaussian thermostat [1–3]. It has been proved in this case that the equilibrium distribution function has a canonical form. The equations of motion are modified as follows to satisfy the imposed constraint of a constant kinetic energy:

$$dq_i/dt = p_i/m_i \quad dp_i/dt = -\partial\Phi/\partial q_i - \zeta p_i = F_i - \zeta p_i. \quad (4)$$

A term similar to a friction term is added to the force. However, the coefficient ζ (which is a Lagrangian undetermined multiplier) is not a constant and is determined to satisfy the constraint. We require that the equations of motion (4) should satisfy a differential form of this constraint

$$\sum_i \frac{p_i}{m_i} \cdot \dot{p}_i = 0. \quad (5)$$

Then, the Lagrangian multiplier ζ becomes

$$\zeta = - \left(\sum_i \frac{p_i}{m_i} \cdot \frac{\partial\Phi}{\partial q_i} \right) / \sum_i \frac{p_i^2}{m_i} = - \frac{d\Phi}{dt} / \sum_i \frac{p_i^2}{m_i}. \quad (6)$$

The equilibrium distribution function $f(\mathbb{P}, \mathbb{Q})$ can be obtained analytically [4] as

$$f(\mathbf{p}, \mathbf{q}) = \delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m_i} - \frac{3N-4}{2} kT\right) \exp\left(-\frac{\Phi(\mathbf{q})}{kT}\right). \quad (7)$$

The momentum part has a delta-function form, as expected because of imposition of a constraint. In coordinate space, the distribution function coincides with a canonical distribution. Thus, we can obtain correct canonical ensemble averages in quantities which are a function of the coordinate only.

The momentum-scaling algorithm, first proposed by Woodcock [5] in 1971 is another constraint method. In this procedure, an estimate of velocity is scaled in every time step to keep the kinetic energy at a constant value. For a long time after its proposal, it was not clear whether we can obtain a canonical ensemble average with this algorithm. Only after the proposal of new constant-temperature methods, has an analysis of the momentum-scaling algorithm become possible. Now, this is considered as an approximate algorithm to solve the Gaussian thermostat equations, assuming that the scaling procedure is carried out in every time step.

In the stochastic method, we consider the interaction between a physical system and a heat bath to be very complicated, and there is no way of knowing it in detail, but the effect of this thermal contact is random. A heat bath works as a source of random forces acting on particles. Schneider and Stoll [6] employed a fluctuation-dissipation theorem and added a Gaussian random force \mathbf{R}_i and a friction term $-\zeta\dot{\mathbf{q}}_i$ to the force. Andersen considered the collisions of physical particles with hypothetical heat bath particles and changed the velocity of a particle to a randomly selected new velocity which follows a Maxwell-Boltzmann distribution of temperature T . Both methods can produce the equilibrium distribution function in the canonical ensemble.

The extended-system method [8, 9] tries to mimic a situation which is written in a textbook on statistical mechanics. A physical system is connected to an external system, but in the extended-system method the external system consists of only one degree of freedom and not a huge system as we expect in a statistical mechanical treatment. The addition of an external system allows the total energy of a physical system to fluctuate.

The extended-system method has been reformulated in a set of simple equations by Hoover [10]. This approach is now called the Nosé-Hoover form. The equations of motion in this form are

$$d\mathbf{q}_i/dt = \mathbb{p}_i/m_i \quad d\mathbb{p}_i/dt = -\partial\Phi/\partial\mathbf{q}_i - \zeta\mathbb{p}_i \quad (8)$$

$$\frac{Q}{2} \frac{d\zeta}{dt} = \sum_i \frac{\mathbb{p}_i^2}{2m_i} - \frac{3}{2} NkT. \quad (9)$$

The changes from Newton's equation are that a term similar to a friction term is added to the force in equation (8), and an equation which governs the change in the coefficient ζ is given by equation (9). ζ is a variable related to the heat bath. A feedback mechanism works to keep the average of kinetic energy to a constant value. Assume that the kinetic energy is larger than the averaged value $\frac{3}{2}NkT$. In this case, $\dot{\zeta} > 0$. Thus ζ increases. Even if ζ is negative, some time later ζ becomes positive. The equation of motion with positive ζ is equivalent to an equation with a frictional force, the velocity of particles decreases, and this continues until the kinetic energy becomes smaller than $\frac{3}{2}NkT$. If the kinetic energy is smaller than $\frac{3}{2}NkT$, this mechanism increases the kinetic energy. Thus, the kinetic energy fluctuates around the averaged value, and the temperature is controlled to T .

If we introduce one more variable s by

$$d(\ln s)/dt = \zeta \quad (10)$$

then

$$\sum_i \frac{\mathbb{p}_i^2}{2m_i} + \Phi(\mathbf{q}) + \frac{Q}{2} \zeta^2 + 3NkT \ln s \quad (11)$$

becomes a conserved quantity. In this form, it is clear that an extended system consists of a physical system (first two terms) and an external system which mimics a heat bath. These two systems are coupled via the friction term in equation (8).

It can be proved that the equilibrium distribution function has a canonical form starting from a generalized Liouville equation in a phase space $\Gamma = (\mathbf{p}, \mathbf{q}, \zeta)$ [10, 11]. The distribution function $f(\mathbf{p}, \mathbf{q}, \zeta)$ expresses a probability that trajectories pass through a phase space point $(\mathbf{p}, \mathbf{q}, \zeta)$. The generalized Liouville equation states that the probability should be conserved.

$$\partial f / \partial t + (\partial / \partial \Gamma) \cdot (\dot{\Gamma} f) = 0. \quad (12)$$

The first term is a change inside a volume element, and the second term expresses the change passing through the surface of a volume element. If we define a time derivative along a phase space trajectory by

$$d/dt = \partial / \partial t + \dot{\Gamma} \cdot \partial / \partial \Gamma$$

then equation (12) can be re-expressed as

$$df/dt = -[(\partial / \partial \Gamma) \cdot \dot{\Gamma}] f. \quad (13)$$

In ordinary mechanics, the right-hand side of the above equation is zero, and this means that the equilibrium distribution function does not change. In our case, $(\partial / \partial \Gamma) \cdot \dot{\Gamma}$ is equal to $3N\zeta f$. If we define a function

$$H_T = \sum_i \frac{\mathbb{p}_i^2}{2m_i} + \Phi(\mathbf{q}) + \frac{Q}{2} \zeta^2 \quad (14)$$

the time derivative of H_T is

$$\frac{dH_T}{dt} = \sum_i \left(\dot{\mathbb{p}}_i \cdot \frac{\partial H_T}{\partial \mathbb{p}_i} + \mathbb{q}_i \cdot \frac{\partial H_T}{\partial \mathbf{q}_i} \right) + \dot{\zeta} \frac{\partial H_T}{\partial \zeta} = -3NkT\zeta. \quad (15)$$

Thus, the generalized Liouville equation reduces to

$$df/dt = -(1/kT) (dH_T/dt) f. \quad (16)$$

A solution of this equation is easily obtained and is

$$f(\mathbf{p}, \mathbf{q}, \zeta) = c \exp(-H_T/kT)$$

which has a canonical distribution form.

Finally, I would like to comment on recent developments in constant-temperature methods. The formulation of Nosé–Hoover-type [10, 11] methods is quite general in comparison with the original formulation based on a Hamiltonian [8, 9]. In a simple case in which the kinetic energy of all the particles are controlled uniformly by one variable ζ , the two formulations are completely equivalent. However, the method based on a Hamiltonian is very hard to extend to the multiple- ζ case. In the Nosé–Hoover form,

there is no problem in introducing many ζ for separate groups of coordinates or to limit temperature control to some regions.

A general extension of the Nosé–Hoover equations is given in [12]. From this extension, the essence of the Nosé–Hoover equations becomes clear. Consider two quantities. The ratio of averages in the canonical ensemble of these two quantities is kT . If one sets the derivative of the friction coefficient ζ equal to the difference in these two quantities, the canonical distribution is realized. As a special case, they also give an important extension [13] of the Nosé–Hoover thermostat to a system which does not have a kinetic energy term. The classical Heisenberg spin system is a typical example.

References

- [1] Evans D J, Hoover W G, Failor B H, Moran B and Ladd A J C 1983 *Phys. Rev. A* **28** 1016
- [2] Hoover W G, Ladd A J C and Moran B 1982 *Phys. Rev. Lett.* **48** 1818
- [3] Evans D J 1983 *J. Chem. Phys.* **78** 3297
- [4] Evans D J and Morriss G P 1983 *Phys. Lett.* **98A** 433
- [5] Woodcock L V 1971 *Chem. Phys. Lett.* **10** 257
- [6] Schneider T and Stoll E 1978 *Phys. Rev. B* **17** 1302
- [7] Andersen H C 1980 *J. Chem. Phys.* **72** 2384
- [8] Nosé S 1984 *Mol. Phys.* **52** 255
- [9] Nosé S 1984 *J. Chem. Phys.* **81** 511
- [10] Hoover W G 1985 *Phys. Rev. A* **31** 1695
- [11] Nosé S 1986 *Mol. Phys.* **57** 187
- [12] Kusnezov D, Bulgac A and Bauer W 1990 *Ann. Phys., NY* at press
- [13] Kusnezov D and Bulgac A 1990 private communication