Remarks on "Constant-temperature molecular dynamics with momentum conservation"

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In a recent paper [K. Cho, J. D. Joannopoulos, and L. Kleinmann, Phys. Rev. E **47**, 3145 (1993)], the Nosé-Hoover canonical dynamics method was shown to generate the canonical ensemble in systems with no external forces only for the special case of zero total linear momentum. Here, it is demonstrated that this is not a general failing of Nosé-Hoover–type methods but a specific feature of the simple Nosé-Hoover scheme. The slightly more complex Nosé-Hoover chain method which includes a linear chain of coupled variables to control the temperature rather than a single variable is sufficient to yield the canonical ensemble for the case of nonzero linear momentum.

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In their paper, Cho, Joannopoulos, and Kleinmann [1] show that for systems with no external forces ($\sum_{i=1}^{N}\mathbf{F}_i=0$), the Nosé-Hoover canonical dynamics method [2–4] only gives rise to the canonical distribution if the total linear momentum is taken to be zero. It will be demonstrated that this constraint is eliminated under Nosé-Hoover chain dynamics [5], a simple extension of the Nosé-Hoover scheme that also corrects other deficiencies of the original approach [5].

The Nosé-Hoover chain method employs the equations of motion

$$\dot{\mathbf{r}}_i=\frac{\mathbf{p}_i}{m_i}\ ,$$

$$\dot{\mathbf{p}}_i=-\nabla_i V(\mathbf{r})-\mathbf{p}_i\frac{p_{\eta_1}}{Q_1}\ ,$$

$$\dot{s}_1=\frac{dN\,s_1 p_{\eta_1}}{Q_1}\ ,$$

$$\dot{s}_i=\frac{s_i p_{\eta_i}}{Q_i}\ , \tag{1}$$

$$\dot{p}_{\eta_1}=\left[\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{m_i}-dN\,kT_{\rm ext}\right]-p_{\eta_1}\frac{p_{\eta_2}}{Q_2}\ ,$$

$$\dot{p}_{\eta_j}=\left[\frac{p_{\eta_{j-1}}^2}{Q_{j-1}}-kT_{\rm ext}\right]-p_{\eta_j}\frac{p_{\eta_{j+1}}}{Q_{j+1}}\ ,$$

$$\dot{p}_{\eta_M}=\left[\frac{p_{\eta_{M-1}}^2}{Q_{M-1}}-kT_{\rm ext}\right]\ ,$$

where each thermostat variable ($\mathbf{s}_i$) is in turn thermostatted to form a chain. The dynamics conserves

$$H'(\mathbf{p},\mathbf{r},\mathbf{s},\mathbf{p}_\eta)=V(\mathbf{r})+\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}+\sum_{i=1}^{M}\frac{p_{\eta_i}^2}{2Q_i}+\sum_{i=1}^{M}kT_{\rm ext}\ln(s_i)\ . \tag{2}$$

However, if $\sum_{i=1}^{N}\nabla_i V(\mathbf{r})=\mathbf{0}$, then $\mathbf{P}'(t)=\mathbf{P}(t)s_1^{1/dN}(t)$ is also conserved where $\mathbf{P}(t)=\sum_{i=1}^{N}\mathbf{p}_i(t)$ is the total linear momentum. The factor $s_1^{1/dN}(t)$ appears in the conservation law due to the nonstandard but convenient definition of $\dot{s}_1$. In general, Nosé-Hoover dynamics is recovered for $M=1$.

The partition function generated by Nosé-Hoover chain dynamics ($M>1$) for an ergodic system with $\sum_{i=1}^{N}\nabla_i V(\mathbf{r})=0$ is

$$Z=\int\prod_{i=1}^{N}d\mathbf{r}_i\prod_{i=1}^{N-1}d\mathbf{p}_i'\prod_{i=1}^{M}p_{\eta_i}\prod_{i=1}^{M}ds_i\,d\mathbf{P}\,\delta^3\left[s_1^{1/dN}\mathbf{P}-\mathbf{P}'\right]$$
$$\times\delta\left[V(\mathbf{r})+\sum_{i=1}^{N-1}\frac{\mathbf{p}_i'^2}{2m_i'}+\frac{\mathbf{P}^2}{2M}+\sum_{i=1}^{M}\frac{p_{\eta_i}^2}{2Q_i}+kT_{\rm ext}\ln(s_1)+kT_{\rm ext}\sum_{i=2}^{M}\ln(s_i)-E\right]\ , \tag{3}$$

$$Z\propto\int\prod_{i=1}^{N}d\mathbf{r}_i\prod_{i=1}^{N-1}d\mathbf{p}_i'\prod_{i=1}^{M}p_{\eta_i}\int_0^\infty dP\,P^{d-1}\exp\left\{-\frac{1}{kT_{\rm ext}}\left[V(\mathbf{r})+\sum_{i=1}^{N}\frac{\mathbf{p}_i'^2}{2m_i'}+\frac{P^2}{2M}+\sum_{i=1}^{M}\frac{p_{\eta_i}^2}{2Q_i}\right]\right\}\ ,$$

where an alternative set of variables (normal modes) $\{\mathbf{p}',\mathbf{P}\}$ has been used [1] and the integrals over the thermostat variables (the $\{\mathbf{s}\}$) range from zero to infinity. The canonical ensemble is therefore generated by the dynamics with

$$\mathbf{P}(0)=\mathbf{P}'s_1^{-1/dN}(0)\neq 0 \quad (M>1) .$$

It should be noted that this result and the result of Cho, Joannopoulos, and Kleinman are, in some sense, a consequence of the fact that for a single one-dimensional free particle, Nosé-Hoover chain dynamics ($M>1$) generates the canonical distribution, while the basic Nosé-Hoover dynamics ($M=1$) does not [5].

In the canonical partition function produced by chain dynamics ($M>1$), only the magnitude of the total linear momentum, P, appears ($P^{d-1}\exp[-P^2/2MkT]$). The individual components of the total linear momentum are not resolved because the dynamics of the system only depends on $P(t)$ and hence $P(0)$. The individual components of the linear momentum can be recovered if the diagonal components of the kinetic-energy tensor,

$$K_{\alpha\alpha}=\sum_i (\mathbf{p}_i)_\alpha(\mathbf{p}_i)_\alpha/m_i ,$$

are each thermostatted with an independent Nosé-Hoover chain ($M>1$). This gives $1/2^d$ of the total space as the individual components of the linear momenta still cannot change sign (the one-dimensional analog of direction). To produce the full distribution, each component of the kinetic-energy tensor must be independently thermostatted.

The preceding results demonstrate that there is no formal difficulty in generating the canonical ensemble for

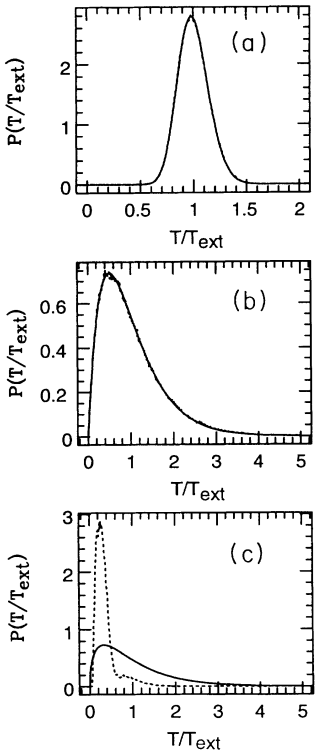

FIG. 1. Calculated temperature distribution functions of a system of 32 Lennard-Jones particles ($d=3$, $N=32$, $M=4$, $T^*=1.5$, $\rho^*=0.8$, $Q^*=1$) under Nosé-Hoover chain dynamics compared to the exact results of the canonical ensemble $P(T/T_{\rm ext})\propto(T/T_{\rm ext})^{(N_f-2)/2}\exp[-N_f(T/2T_{\rm ext})]$. (a) The calculated particle temperature distribution function (dotted line) compared to the exact results (solid line) $[T=(1/dN\,k_B)\sum_k m_k\mathbf{v}_k^2,\ N_f=3N]$. (b) The calculated thermostat temperature distribution function (dotted line) compared to the exact results (solid line) $[T=(1/Mk_B)\sum_k Q_k v_{\eta_k}^2,\ N_f=4]$. (c) The calculated temperature distribution function of the center of mass (dotted line) compared to the exact results (solid line) $[T=(1/dk_B)m_{\rm c.m.}\mathbf{v}_{\rm c.m.}^2,\ N_f=d]$. The numerical data may be indistinguishable in the plots due to the good agreement with the exact result.

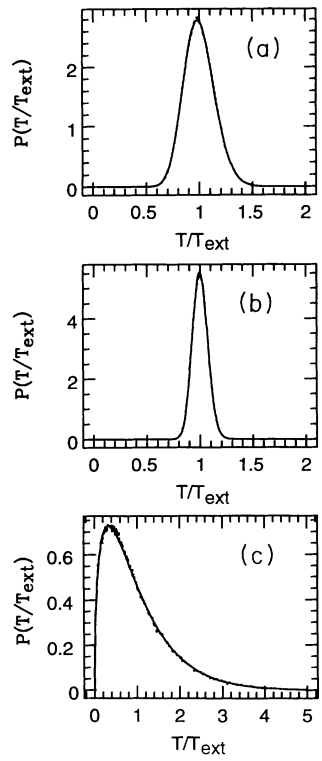

FIG. 2. Calculated temperature distribution functions of a system of 32 Lennard-Jones particles ($d=3$, $N=32$, $M=4$, $T^*=1.5$, $\rho^*=0.8$, $Q^*=1$) under massive Nosé-Hoover chain dynamics compared to the exact results of the canonical ensemble, $P(T/T_{\rm ext})\propto(T/T_{\rm ext})^{(N_f-2)/2}\exp[-N_f(T/2T_{\rm ext})]$. (a) The calculated particle temperature distribution function (dotted line) compared to the exact results (solid line) $[T=(1/dN\,k_B)\sum_k m_k\mathbf{v}_k^2,\ N_f=3N]$. (b) The calculated thermostat temperature distribution function (dotted line) compared to the exact results (solid line) $[T=(1/Mk_B)\sum_k Q_k v_{\eta_k}^2$, $N_f=12N$, $3N$ chains of $M=4]$. (c) The calculated temperature distribution function of the center of mass (dotted line) compared to the exact results (solid line) $[T=(1/dk_B)m_{\rm c.m.}\mathbf{v}_{\rm c.m.}^2$, $N_f=d)]$. The numerical data may be indistinguishable in the plots due to the good agreement with the exact result.

the case of nonzero linear momentum. However, the thermostatting scheme as formulated, above, is only sensitive to the total kinetic energy. Therefore, local heating of any weakly coupled degree of freedom, for instance, the center of mass, can easily occur. The massive method, an independent thermostat on every degree of freedom [6,7], was developed to ensure good equipartition for all degrees of freedom. (A single one-dimensional free particle is ergodic under Nosé-Hoover chain dynamics [5]. Others have produced a similar result using a different method [8].) That the massive method gives rise to the canonical distribution can be verified using the techniques described above. Therefore the formal difficulties with nonzero total momentum have been overcome but problems related to ergodicity, in general, must be carefully considered. Nonetheless, the standard scheme, Eq. (1), was tested on a Lennard-Jones fluid ($d=3$, $N=32$, $M=4$, $T^*=1.5$, $\rho^*=0.8$, $Q^*=1$) where an inverse sixth power lattice sum was employed [9] to calculate the potential energy and the forces (due to the small system size). A reasonable initial kinetic energy $K \sim 3kT_{\text{ext}}/2$ was assigned to the center of mass. Good agreement with the exact results of the classical canonical ensemble was observed (see Fig. 1). Full ergodicity is achieved by the massive method (see Fig. 2).

For completeness, the zero total linear momentum condition will be considered. Taking $\mathbf{P}'(0)=\mathbf{0}$, $s_1(0)\neq 0$ gives $\mathbf{P}(t)=\mathbf{0}$ for all time (the fixed point of the dynamics). This is formally equivalent to changing the equation of motion for the particle velocities presented in Eq. (1) to

$$\dot{\mathbf{p}}_i = -\nabla_i V(\mathbf{r}) - (\mathbf{p}_i - \mathbf{P}_{\text{c.m.}}) \frac{p_{\xi_1}}{Q_1} , \tag{4}$$

which can be shown to generate a canonical ensemble, with the zero total linear momentum condition, for all values of M, provided the parameter N in Eq. (1) is decreased by 1. The zero total linear momentum condition is convenient as the position of the center of mass of the system remains fixed. In the more general method ($\mathbf{P}'\neq\mathbf{0}$), the center of mass will monotonically increase (it is a free particle) unless the full kinetic tensor is thermostatted as described above. Therefore, the zero total linear momentum simulations are to be preferred and are, in fact, generally performed in systems coupled to a single thermostat/chain [4].

It has been shown that under the Nosé-Hoover chain dynamics ($M>1$), the canonical ensemble, in principle, can be generated in systems with no external forces using an arbitrary initial condition for the total linear momentum. The result of Cho, Joannopoulos, and Kleinmann that the total momentum must be zero applies only to the Nosé-Hoover method ($M=1$) which does not produce the canonical ensemble for the related problem of a one-dimensional free particle. In practice, the ergodicity of systems with weakly coupled degree of freedom under a single chain scheme, Eq. (1), is problematic and care must be taken. Other recent work employing the Nosé-Hoover chains, including the massive scheme that leads to improved ergodicity, has demonstrated that the method is generally useful and not just a formal device [6,7,10–12].

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