

Constant pressure molecular dynamics algorithms

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Modularly invariant equations of motion are derived that generate the isothermal–isobaric ensemble as their phase space averages. Isotropic volume fluctuations and fully flexible simulation cells as well as a hybrid scheme that naturally combines the two motions are considered. The resulting methods are tested on two problems, a particle in a one-dimensional periodic potential and a spherical model of C_{60} in the solid/fluid phase.

I. INTRODUCTION

In the past decade, equations of motion have been developed that generate many-body thermodynamic ensembles as their phase space averages.^{1–6} Alternatives to Monte Carlo methods are, now, available to study systems in the canonical, isothermal–isobaric, and isoenthalpic–isobaric ensembles.

Recently, the isobaric methods have been reexamined.⁶ It was observed that while isobaric ensembles are produced, the trajectories have an unphysical dependence on the choice of basis lattice vectors.^{7,8} This behavior arises because the equations of motion are not modularly invariant.^{7,8} However, modular invariance can be incorporated naturally into isobaric schemes using the formalism developed by Hoover.^{4,6,9} In this paper, the inconsistencies of prior schemes are removed^{2,4–6,9} and a new hybrid method which combines both isotropic volume fluctuations and full flexibility of the simulation cell is introduced. The methods are tested on two model problems, a particle in a one-dimensional periodic potential and C_{60} molecules in the solid/fluid phase.

II. ISOTHERMAL–ISOBARIC ENSEMBLE

In this section, three different approaches that generate the isothermal–isobaric ensemble are explored: uniform dilation, full flexibility of the simulation cell, and a hybrid scheme.

A. Uniform dilation

The equations of motion proposed by Hoover have the following basic form for a d -dimensional system of N particles (N_f degrees of freedom; $N_f = dN$ if there are no constraints):^{4,9,10}

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i, & \dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i, \\ \dot{V} &= \frac{dV p_\epsilon}{W}, & \dot{p}_\epsilon &= dV(P_{\text{int}} - P_{\text{ext}}) - \frac{p_\xi p_\epsilon}{Q}, \\ \dot{\xi} &= \frac{p_\xi}{Q}, & \dot{p}_\xi &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT.\end{aligned}\quad (2.1)$$

Here, \mathbf{r}_i and \mathbf{p}_i are the position and momentum of the i th particle, V is the volume, p_ϵ is the barostat momentum, ξ and p_ξ are the thermostat position and momentum, $\mathbf{F}_i = -\nabla_{\mathbf{r}_i} \phi(\mathbf{r}, V)$ is the force, P_{ext} is the external/applied pressure, and

$$P_{\text{int}} = \frac{1}{dV} \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i - (dV) \frac{\partial \phi(\mathbf{r}, V)}{\partial V} \right] \quad (2.2)$$

is the internal pressure. A possible explicit dependence of the potential energy on the volume has been considered. Such terms will occur when long-range interactions [$\phi(r) \propto 1/r^n, n \leq 3$] or long-range corrections to short-range potentials are present. Cutting off long-range interactions or neglecting long-range corrections in small systems can give rise to incorrect results.¹¹ Note that the barostat momentum p_ϵ has been coupled to the thermostat momentum p_ξ .

Hoover's equations have the advantage that they automatically and naturally satisfy the constraint that the volume be greater than or equal to zero, namely, $V(t) = V(0) \times \exp[d/W \int_0^t p_\epsilon(t') dt']$. The equations also have the conserved quantity

$$\begin{aligned}H' &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V) + (N_f + 1)kT\xi \\ &\quad + P_{\text{ext}}V, \\ \frac{dH'}{dt} &= \sum_{i=1}^N [\nabla_{\mathbf{p}_i} H' \cdot \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} H' \cdot \dot{\mathbf{r}}_i] + \frac{\partial H'}{\partial p_\epsilon} \dot{p}_\epsilon + \frac{\partial H'}{\partial \xi} \dot{\xi} \\ &\quad + \frac{\partial H'}{\partial p_\epsilon} \dot{p}_\epsilon + \frac{\partial H'}{\partial V} \dot{V} = 0,\end{aligned}\quad (2.3)$$

and Jacobian,¹²

$$\begin{aligned}\frac{dJ(t)}{dt} &= -J(t) \left[\frac{d\xi}{d\xi} + \frac{d\dot{p}_\xi}{dp_\xi} + \frac{d\dot{V}}{dV} + \frac{d\dot{p}_\epsilon}{dp_\epsilon} \right. \\ &\quad \left. + \sum_{i=1}^N (\nabla_{\mathbf{p}_i} \dot{\mathbf{p}}_i + \nabla_{\mathbf{r}_i} \dot{\mathbf{r}}_i) \right], \\ J(t) &= V^{-1} \exp[(N_f + 1)\xi].\end{aligned}\quad (2.4)$$

The Jacobian is the weight associated with the phase space volume and is unity for systems that obey Liouville's theorem.¹² It represents the transform to a set of variables where $J=1$, here, simply, $\{s=N_f s p_\xi\}$ or equivalently, $\{\log s=N_f \xi\}$. Using the assumption of ergodicity, the Jacobian, and the conserved quantity, the partition function associated with the dynamics can be constructed:¹²

$$\Delta = \int dp_\xi dp_\epsilon d\xi dV \int_{D(V)} d\mathbf{p} d\mathbf{r} V^{-1} \times \exp[(N_f+1)\xi] \delta(H'-E), \quad (2.5)$$

$$\Delta = \frac{\exp[E/kT]}{(N_f+1)kT} \int dp_\xi dp_\epsilon dV \int_{D(V)} d\mathbf{p} d\mathbf{r} V^{-1} \times \exp\left[-\frac{H''}{kT}\right],$$

where

$$H'' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V) + P_{\text{ext}} V \quad (2.6)$$

and $D(V)$ is the domain defined by the volume. Unfortunately, Δ is not the isothermal-isobaric partition function (within a constant) as was made clear by Hoover in the original derivation.^{4,9}

In an effort to correctly generate the isothermal-isobaric ensemble, it has been suggested that Hoover's equations of motion be slightly modified:⁶

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} (\mathbf{r}_i - \mathbf{r}_{\text{c.m.}}), \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i,$$

$$\dot{V} = \frac{dV p_\epsilon}{W}, \quad \dot{p}_\epsilon = dV(\tilde{P}_{\text{int}} - P_{\text{ext}}) - \frac{p_\xi p_\epsilon}{Q}, \quad (2.7)$$

$$\dot{\xi} = \frac{p_\xi}{Q}, \quad \dot{p}_\xi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f+1)kT,$$

where $\mathbf{r}_{\text{c.m.}} = (1/M) \sum_i m_i \mathbf{r}_i$ is the center of mass (c.m.) and

$$\tilde{P}_{\text{int}} = \frac{1}{dV} \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{\text{c.m.}}) \cdot \mathbf{F}_i - (dV) \frac{\partial \phi(\mathbf{r}, V)}{\partial V} \right]. \quad (2.8)$$

These equations have the same conserved quantity as the original set, but the Jacobian is $J = \exp[(N_f+1)\xi]$. The isothermal-isobaric ensemble is, therefore, in principle, generated. For the special case of no external forces, $\mathbf{F}_{\text{c.m.}} = 0$, considered in the original paper,⁶ the choice $P_{\text{int}} = \tilde{P}_{\text{int}}$ was made. Note, another, possible but nonseparable choice is $P_{\text{int}} = \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{\text{c.m.}})' \cdot \mathbf{F}_i'$, where a prime indicates that a given term must be consistent with the periodic boundary conditions. For the more restrictive case of a set of free particles, both choices reduce to, $P_{\text{int}} = \tilde{P}_{\text{int}}$. Most generally, however, the two functions, P_{int} and \tilde{P}_{int} , are not equal. If the thermostats are decoupled from the dynamics, the

isoenthalpic-isobaric ensemble is produced to within the fluctuations of Wp_ϵ^2 , the barostat kinetic energy.

In this paper, the alternative equations of motion are proposed:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \frac{p_\epsilon}{W} \mathbf{r}_i, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \left(1 + \frac{d}{N_f}\right) \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i,$$

$$\dot{V} = \frac{dV p_\epsilon}{W}, \quad \dot{p}_\epsilon = dV(P_{\text{int}} - P_{\text{ext}}) + \frac{d}{N_f} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon, \quad (2.9)$$

$$\dot{\xi} = \frac{p_\xi}{Q}, \quad \dot{p}_\xi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f+1)kT.$$

Like the prior modification, Eqs. (2.7), the new equations, Eqs. (2.9), have the same conserved quantity as Hoover's original set, Jacobian, $J = \exp[(N_f+1)\xi]$ and, in principle, generate the isothermal-isobaric partition function (within a constant). Again, if the thermostats are removed, the isoenthalpic-isobaric ensemble is produced to within the fluctuations of Wp_ϵ^2 .

The relative merits of the modified equations of motion, Eqs. (2.7), and the new equations of motion, Eqs. (2.9), must be assessed. A simple physical argument based on the conditions for equilibrium in a dynamical system will be given in the text. A complete and rigorous analysis of the phase space is provided in Appendix A.

If a dynamical system is at equilibrium, the time average of the force on each of the independent variables will be zero. Furthermore, if the system is ergodic than the time average can be taken to the trajectory average. Application of this principle to Hoover dynamics, Eqs. (2.1), yields

$$\langle \dot{p}_\epsilon \rangle = d \langle (P_{\text{int}} - P_{\text{ext}}) V \rangle = 0, \quad (2.10)$$

a statement of a pressure virial theorem obeyed by the Hoover ensemble, Eq. 2.5 (see Appendix B for a discussion of pressure virial theorems). Unsurprisingly, there is a feedback between the equations of motion and the equilibrium/limiting distribution function. Similarly, the equations of motion proposed in this paper, Eqs. (2.9), generate

$$\langle \dot{p}_\epsilon \rangle = d \left\{ \left\langle \frac{2}{N_f} \sum_i \frac{\mathbf{p}_i^2}{2m_i} \right\rangle + \langle (P_{\text{int}} - P_{\text{ext}}) V \rangle \right\} = 0,$$

$$\langle \dot{p}_\epsilon \rangle = d \{ kT + \langle (P_{\text{int}} - P_{\text{ext}}) V \rangle \} = 0,$$

a virial theorem obeyed by the isothermal-isobaric ensemble (see Appendix B). The rather strong condition, the kinetic virial theorem, is used to produce the necessary factor of kT . The modified equations, Eqs. (2.7), give

$$\langle \dot{p}_\epsilon \rangle = d \{ \langle (\tilde{P}_{\text{int}} - P_{\text{int}}) V \rangle + \langle (P_{\text{int}} - P_{\text{ext}}) V \rangle \} = 0. \quad (2.11)$$

Here, $\langle (\tilde{P}_{\text{int}} - P_{\text{int}}) V \rangle = (1/d) \langle \mathbf{r}_{\text{c.m.}} \cdot \mathbf{F}_{\text{c.m.}} \rangle$ (the definition of the \tilde{P}_{int} from the original paper⁶) is relied upon to generate the crucial factor of kT . If this term is zero, then in order to achieve a stable equilibrium the Hoover ensemble, Eq. (2.5), must be produced.

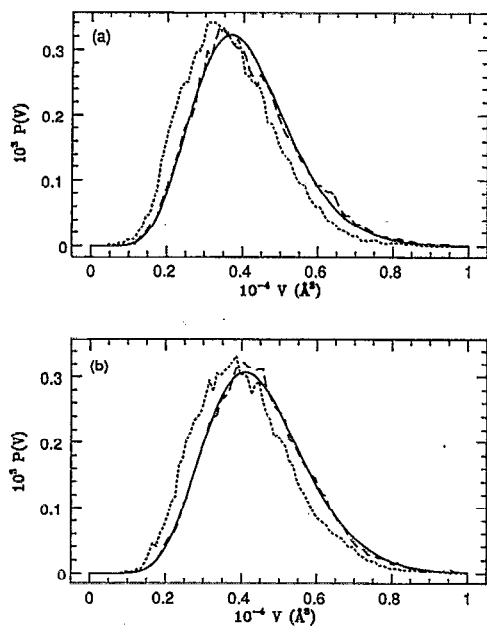


FIG. 1. (a) Volume distribution function of a system of ten free particles ($T=300$ K, $P_{\text{ext}}=100$ atm, $M=3$) with total linear momentum conservation. (b) Volume distribution function of a system of ten free particles without momentum conservation. The solid line is the exact result, the short dashed line is the result of Eq. (2.1) or (2.7), the long dot dashed line is the result of Eqs. (2.9).

The analysis based on the virial theorem seemingly contradicts the proof based on the Liouville equation (see above) for the modified equations of motion if $\mathbf{F}_{\text{c.m.}}=0$, $\tilde{P}_{\text{int}}=P_{\text{int}}$. However, under these conditions, the position of the center of mass of the particles is an auxiliary variable, i.e., the dynamics of the $\mathbf{r}_{\text{c.m.}}$ depend on all the other variables but not vice versa. In such dynamical systems, satisfying the Liouville equation for the entire distribution is insufficient to guarantee that the individual pieces are properly generated. In Appendix A, it is shown that for systems with no external forces, the volume distribution generated by Eqs. (2.7) is reduced by one factor of the volume. In Fig. 1, the pathology is illustrated numerically, for a system of free particles, with and without the imposition of a zero linear momentum constraint, $\mathbf{p}_{\text{c.m.}}=0$. In the numerical calculations, the Nosé–Hoover thermostatting scheme, which is insufficient to handle the condition $\{\mathbf{p}_{\text{c.m.}}(t) \neq 0, \mathbf{F}_{\text{c.m.}}=0\}$,^{13,24} is replaced by the more general Nosé–Hoover chain method¹⁴ (see Appendix C).

The results presented above and in Appendix A suggest that the new equations of motion, Eqs. (2.9), will be robust while the modified equations, Eqs. (2.7), may fail to generate the isothermal–isobaric ensemble under certain circumstances, particularly, if the separable definition of \tilde{P}_{int} (Ref. 6) is employed. Therefore, the new equations of motion, Eqs. (2.9), appear to be superior. Tests of the new method on more realistic problems are described in Sec. IV.

B. Fully flexible cells

It is often useful to consider not only isotropic relaxation but full relaxation of the simulation cell.^{2,5} In order to accomplish this, an ensemble with anisotropic cell fluctuations must be introduced. The general result

$$\Delta = \int dV \exp[-\beta P_{\text{ext}} V] \tilde{Q}(V), \quad (2.12)$$

where $\tilde{Q}(V)$ is a canonical partition function, can be rewritten as

$$\Delta = \int dV d\vec{\mathbf{h}}_0 \exp[-\beta P_{\text{ext}} V] Q(V, \vec{\mathbf{h}}_0) \delta(\det[\vec{\mathbf{h}}_0] - 1). \quad (2.13)$$

Here,

$$\begin{aligned} \tilde{Q}(V) &= \int d\vec{\mathbf{h}}_0 Q(V, \vec{\mathbf{h}}_0) \delta(\det[\vec{\mathbf{h}}_0] - 1) \\ &= \int d\vec{\mathbf{h}}_0 \int_{D(\vec{\mathbf{h}}_0, V)} d\mathbf{p} d\mathbf{r} \exp[-\beta H(\mathbf{p}, \mathbf{r})] \\ &\quad \times \delta(\det[\vec{\mathbf{h}}_0] - 1), \end{aligned} \quad (2.14)$$

where the domain of integration is determined by the transformation $\mathbf{r} = V^{1/d} \vec{\mathbf{h}}_0 \mathbf{s}$, where \mathbf{s} are the scaled/reduced coordinates. The assumption, consistent with the isothermal–isobaric ensemble, is that all cells with the same volume occur with equal *a priori* probability weighted by the appropriate Boltzman factor $Q(V, \vec{\mathbf{h}}_0)$. Therefore, the virial theorem is always obeyed, i.e., the external pressure P_{ext} is directly related to the average of the usual expression for the internal pressure and the correct isotropic limit is obtained.

It is possible to transform the proposed partition function, Eq. (2.13), to a more familiar form. By introducing the normal matrix of cell parameters, $\vec{\mathbf{h}} = V^{1/d} \vec{\mathbf{h}}_0$, and eliminating the volume using the delta function, one finds

$$\Delta = \int d\vec{\mathbf{h}} \exp[-\beta P_{\text{ext}} \det(\vec{\mathbf{h}})] Q(\vec{\mathbf{h}}) \det[\vec{\mathbf{h}}]^{1-d}. \quad (2.15)$$

In this form, it is possible to show that the tensorial virial theorem

$$\begin{aligned} \langle P_{\alpha\beta} - P_{\text{ext}} \delta_{\alpha\beta} \rangle &= \left\langle \frac{kT}{\det[\vec{\mathbf{h}}]} \sum_{l=1}^d h_{\beta l} \frac{\partial \log[Q(\vec{\mathbf{h}})]}{\partial h_{\alpha l}} \right. \\ &\quad \left. - P_{\text{ext}} \delta_{\alpha\beta} \right\rangle = 0 \end{aligned} \quad (2.16)$$

is satisfied and, hence, this indicates that Eq. (2.15) is the appropriately generalized isothermal–isobaric partition function. Equation (2.15) is slightly different from the ensemble that has been used most commonly in simulations, namely,

$$\Delta = \int d\vec{\mathbf{h}} \exp[-\beta P_{\text{ext}} \det(\vec{\mathbf{h}})] Q(\vec{\mathbf{h}}). \quad (2.17)$$

The tensorial virial theorem satisfied by Eq. (2.17),

$$\left\langle P_{\alpha\beta} - \left[P_{\text{ext}} - \frac{(d-1)kT}{\det(\vec{h})} \right] \delta_{\alpha\beta} \right\rangle = 0, \quad (2.18)$$

is inconsistent with the isothermal-isobaric ensemble. Note that Eq. (2.15) is only valid for isotropic pressure. The fully nonlinear formulation of the constant tension ensemble which satisfies an appropriate tensorial virial theorem different from Eq. (2.16), and introduces a fixed reference lattice, has been discussed elsewhere.⁸ Here, the generalized isothermal-isobaric ensemble, Eq. (2.15) will be used. This is a fully nonlinear treatment of the case that isotropic tension is applied along the instantaneous lattice vectors.¹⁵

The equations of motion necessary to produce the desired ensemble, Eq. (2.15), are

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{\vec{\mathbf{p}}_g}{W_g} \mathbf{r}_i, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{\vec{\mathbf{p}}_g}{W_g} \mathbf{p}_i - \left(\frac{1}{N_f} \right) \frac{\text{Tr}[\vec{\mathbf{p}}_g]}{W_g} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i, \\ \dot{\vec{\mathbf{h}}} &= \frac{\vec{\mathbf{p}}_g \vec{\mathbf{h}}}{W_g}, \quad \dot{\vec{\mathbf{p}}}_g = V(\vec{\mathbf{P}}_{\text{int}} - \vec{\mathbf{I}} P_{\text{ext}}) + \left[\frac{1}{N_f} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} \right] \vec{\mathbf{I}} - \frac{p_\xi}{Q} \vec{\mathbf{p}}_g, \end{aligned} \quad (2.19)$$

$$\dot{\xi} = \frac{p_\xi}{Q}, \quad \dot{p}_\xi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{1}{W_g} \text{Tr}[\vec{\mathbf{p}}_g \vec{\mathbf{p}}_g] - (N_f + d^2)kT,$$

where $V = \det[\vec{\mathbf{h}}]$, $\vec{\mathbf{I}}$ is the identity matrix, $\text{Tr}[\vec{\mathbf{p}}_g \vec{\mathbf{p}}_g]$ is the sum of the squares of all the elements of the matrix, $\vec{\mathbf{p}}_g$, and

$$(P_{\text{int}})_{\alpha\beta} = \frac{1}{V} \left[\sum_{i=1}^N \frac{(\mathbf{p}_i)_\alpha (\mathbf{p}_i)_\beta}{m_i} + (\mathbf{F}_i)_\alpha (\mathbf{r}_i)_\beta - (\vec{\phi}' \vec{\mathbf{h}}')_{\alpha\beta} \right], \quad (2.20)$$

$$(\phi')_{\alpha\beta} = \frac{\partial \phi(\mathbf{r}, \vec{\mathbf{h}})}{\partial (h)_{\alpha\beta}} \quad (2.21)$$

defines the pressure tensor. The modularly invariant form of the box momenta $\vec{\mathbf{p}}_g$ are taken from earlier work.^{6,7,16} These equations of motion have conserved quantity:

$$\begin{aligned} H' &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2W_g} \text{Tr}[\vec{\mathbf{p}}_g \vec{\mathbf{p}}_g] + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, \vec{\mathbf{h}}) \\ &+ P_{\text{ext}} \det[\vec{\mathbf{h}}] + (N_f + d^2)kT\xi \end{aligned} \quad (2.22)$$

and Jacobian, $J = \det[\vec{\mathbf{h}}]^{1-d} \exp[(N_f + d^2)\xi]$. This leads to the partition function

$$\begin{aligned} \Delta &= \frac{\exp[E/kT]}{(N_f + d^2)kT} \int d p_\xi d \vec{\mathbf{h}} d \vec{\mathbf{p}}_g \int_{D(\vec{\mathbf{h}})} d \mathbf{p} d \mathbf{r} \det[\vec{\mathbf{h}}]^{1-d} \\ &\times \exp \left[-\frac{H'}{kT} \right], \end{aligned} \quad (2.23)$$

where

$$\begin{aligned} H'' &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2W_g} \text{Tr}[\vec{\mathbf{p}}_g \vec{\mathbf{p}}_g] + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, \vec{\mathbf{h}}) \\ &+ P_{\text{ext}} \det[\vec{\mathbf{h}}]. \end{aligned} \quad (2.24)$$

The equations of motion reduce to the uniform scaling case when $d=1$ and are modularly invariant. They also au-

tomatically and naturally satisfy the constraint that the volume $\det[\vec{\mathbf{h}}]$ be greater than or equal to zero, $\text{Tr}[\vec{\mathbf{p}}_g] = W_g \sum_{ij} \dot{h}_{ij} h_{ji}^{-1} = (W_g / \det[\vec{\mathbf{h}}]) \sum_{ij} \dot{h}_{ij} (d \det[\vec{\mathbf{h}}] / dh_{ij}) = W_g \log(\det[\vec{\mathbf{h}}])$. In addition, if the thermostat is decoupled, the isenthalpic-isobaric ensemble is recovered.

As stated above, the quantity $\text{Tr}[\vec{\mathbf{p}}_g]$ is equal to $W_g \log(V)$ and is therefore related to p_ξ of the previous section. In analogy with \dot{p}_ξ , the average of $d \text{Tr}[\vec{\mathbf{p}}_g] / dt$ obeys the virial theorem (see Appendix B)

$$\left\langle \frac{d \text{Tr}[\vec{\mathbf{p}}_g]}{dt} \right\rangle = dkT + d \langle V(P_{\text{int}} - P_{\text{ext}}) \rangle = 0 \quad (2.25)$$

and each of the individual $\vec{\mathbf{p}}_g$ satisfy the tensorial virial theorem

$$\langle (\dot{p}_g)_{\alpha\beta} \rangle = \langle VP_{\alpha\beta} - [VP_{\text{ext}} - kT] \delta_{\alpha\beta} \rangle = 0. \quad (2.26)$$

C. Hybrid method

It is possible to separate out the isotropic volume fluctuations from other changes in the simulation cell. Such a separation allows different time scales to be associated with the two types of motion (isotropic and anisotropic) through introduction of different masses for the independent momenta. This separation also makes it easy to change from a fully flexible cell to an isotropically flexible cell within the same computational framework. Such an approach is only useful for $d > 1$.

In order to separate out the isotropic fluctuations, the following equations of motion are proposed:

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{\vec{\mathbf{p}}_{g_0}}{W_{g_0}} \mathbf{r}_i + \frac{p_\epsilon}{W} \mathbf{r}_i, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{\vec{\mathbf{p}}_{g_0}}{W_{g_0}} \mathbf{p}_i - \left(1 + \frac{d}{N_f} \right) \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i, \\ \dot{V} &= \frac{dV p_\epsilon}{W}, \\ \dot{p}_\epsilon &= dV(P_{\text{int}} - P_{\text{ext}}) + \frac{d}{N_f} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon, \\ \dot{\vec{\mathbf{h}}}_0 &= \frac{\vec{\mathbf{p}}_{g_0} \vec{\mathbf{h}}_0}{W_{g_0}}, \\ \dot{\vec{\mathbf{p}}}_{g_0} &= V(\vec{\mathbf{P}}_{\text{int}} - \vec{\mathbf{I}} P_{\text{ext}}) - \frac{V}{d} \text{Tr}[\vec{\mathbf{P}}_{\text{int}} - \vec{\mathbf{I}} P_{\text{ext}}] \vec{\mathbf{I}} - \frac{p_\xi}{Q} \vec{\mathbf{p}}_{g_0}, \end{aligned} \quad (2.27)$$

$$\dot{\xi} = \frac{p_\xi}{Q},$$

$$\dot{p}_\xi = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \frac{p_\epsilon^2}{W} + \frac{1}{W_{g_0}} \text{Tr}[\vec{\mathbf{p}}_{g_0} \vec{\mathbf{p}}_{g_0}] - (N_f + d^2)kT,$$

where $V^{1/d} \vec{\mathbf{h}}_0 = \vec{\mathbf{h}}$, the instantaneous pressure P_{int} is given by Eq. (2.4), and the pressure tensor is given by Eq. (2.20). The necessary condition that the $\det[\vec{\mathbf{h}}_0]$ remain equal to one is

automatically satisfied provided $\text{Tr}[\vec{\mathbf{p}}_{g_0}]$ is initially zero as $\log(\det[\vec{\mathbf{h}}_0]) = \text{Tr}[\vec{\mathbf{p}}_{g_0}]$. Therefore, the $\vec{\mathbf{h}}_0$ have no dynamics for $d < 2$.

The conserved quantity for the equations of motion, Eqs. (2.27), is

$$H' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2W_{g_0}} \text{Tr}[\vec{\mathbf{p}}_{g_0} \vec{\mathbf{p}}_{g_0}] + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V, \vec{\mathbf{h}}_0) + P_{\text{ext}}V + (N_f + d^2)kT\xi \quad (2.28)$$

and the Jacobian is $J = \exp[(N_f + d^2)\xi]$. The new dynamical equations lead to the partition function

$$\Delta = \frac{\exp[E/kT]}{(N_f + d^2)kT} \int d\mathbf{p}_\xi d\mathbf{p}_\epsilon dV d\vec{\mathbf{h}}_0 d\vec{\mathbf{p}}_{g_0} \times \int_{D(\vec{\mathbf{h}}_0, V)} d\mathbf{p} d\mathbf{r} \exp\left[-\frac{H''}{kT}\right] \delta(\det[\vec{\mathbf{h}}_0] - 1) \times \delta(\text{Tr}[\vec{\mathbf{p}}_{g_0}]), \quad (2.29)$$

where

$$H'' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2W_{g_0}} \text{Tr}[\vec{\mathbf{p}}_{g_0} \vec{\mathbf{p}}_{g_0}] + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + \phi(\mathbf{r}, V, \vec{\mathbf{h}}_0) + P_{\text{ext}}V. \quad (2.30)$$

If the thermostat is decoupled, the isoenthalpic–isobaric ensemble is recovered. Also, virial theorems are satisfied by $\langle \dot{p}_\epsilon \rangle$ and $\langle \dot{\mathbf{p}}_{g_0} \rangle$. Note, that both the dynamics and the ensemble produced by the hybrid method are equivalent to the preceding formulation. However, the hybrid method can be a computationally convenient scheme.

D. Elimination of cell rotations

The equations of motion for the case of a flexible simulation cell were derived using the full matrix of Cartesian cell parameters $\vec{\mathbf{h}}$ or equivalently $\vec{\mathbf{h}}_0$. The cell can therefore, in general, rotate in space.⁵ This motion can make data analysis difficult and should be eliminated.

The origin of the rotational motion of the cell lies in pressure tensor, $P_{\alpha\beta}$ [see Eq. (2.20)]. If the instantaneous value of the components of the pressure tensor are asymmetric, $P_{\alpha\beta} \neq P_{\beta\alpha}$, then there will be a torque on the cell that will cause it to rotate. This suggests that there are two options that can be used to eliminate the rotations. The first is to work with the symmetrized tensor $\bar{P}_{\alpha\beta} = (P_{\alpha\beta} + P_{\beta\alpha})/2$. Here, if the total angular momentum of the cell is initially zero, the cell should not rotate. A second option is to work with a restricted set of cell parameters that only respond to the upper/lower triangle of the tensor. This freezes the rotations out.

It is possible to implement either of these two options within both of the sets of equations of motion derived for fully flexible cells, i.e., the normal method, Eqs. (2.19), and the hybrid method, Eqs. (2.27). The application to the symmetrized tensor will be considered first. Here, the constraint $\vec{\mathbf{g}} = \vec{\mathbf{g}}^T$ in the normal method or $\vec{\mathbf{g}}_0 = \vec{\mathbf{g}}_0^T$ in the hybrid method

must be introduced to the dynamics through the use of Lagrange multipliers. (Note, $\vec{\mathbf{g}}$ and $\vec{\mathbf{g}}_0$ are defined by the time integrals of $W_{\vec{\mathbf{g}}} \dot{\vec{\mathbf{g}}} = \vec{\mathbf{p}}_{\vec{\mathbf{g}}}$ and $W_{g_0} \dot{\vec{\mathbf{g}}}_0 = \vec{\mathbf{p}}_{g_0}$, respectively.) Eliminating the multipliers results in the replacement of $P_{\alpha\beta}$ by $\bar{P}_{\alpha\beta}$ in Eqs. (2.19) and (2.27). In the normal method, the constraint imposes the conservation laws

$$\frac{d[\vec{\mathbf{p}}_{\vec{\mathbf{g}}} - \vec{\mathbf{p}}_{\vec{\mathbf{g}}}^T]}{dt} = 0 \rightarrow W_{\vec{\mathbf{g}}} \frac{dJ_{\text{tot}}}{dt} = 0 \quad (2.31)$$

in two dimensions and

$$\frac{d[\vec{\mathbf{p}}_{\vec{\mathbf{g}}} - \vec{\mathbf{p}}_{\vec{\mathbf{g}}}^T]}{dt} = 0 \rightarrow W_{\vec{\mathbf{g}}} \frac{d[\vec{\mathbf{h}}\mathbf{J}_{\text{tot}}]}{dt} = 0 \quad (2.32)$$

in three dimensions where the \mathbf{J}_{tot} are the components of the total angular momentum of the cell and the identity $\vec{\mathbf{p}}_{\vec{\mathbf{g}}} = W_{\vec{\mathbf{g}}} \vec{\mathbf{h}} \vec{\mathbf{h}}^{-1}$ has been used. In the hybrid method, the imposed conservation laws are

$$\frac{d[\vec{\mathbf{p}}_{g_0} - \vec{\mathbf{p}}_{g_0}^T]}{dt} = 0 \rightarrow W_{g_0} \frac{d[V^{-1}J_{\text{tot}}]}{dt} = 0 \quad (2.33)$$

in two dimensions and

$$\frac{d[\vec{\mathbf{p}}_{g_0} - \vec{\mathbf{p}}_{g_0}^T]}{dt} = 0 \rightarrow W_{g_0} \frac{d[V^{-1}\vec{\mathbf{h}}\mathbf{J}_{\text{tot}}]}{dt} = 0 \quad (2.34)$$

in three dimensions. The only solution consistent with initial condition $\vec{\mathbf{p}}_{\vec{\mathbf{g}}} = \vec{\mathbf{p}}_{\vec{\mathbf{g}}}^T$ or $\vec{\mathbf{p}}_{g_0} = \vec{\mathbf{p}}_{g_0}^T$ is $\mathbf{J}_{\text{tot}} = 0$. The conservation laws guarantee that \mathbf{J}_{tot} will remain zero and the cell will not rotate (i.e., a fixed point of the dynamics is utilized).

The application to the case of an upper triangular cell is also simple. Here, the constraint that $h_{ij} = 0$, $i > j$ or $(h_0)_{ij} = 0$, $i > j$ must be enforced. Introduction and elimination of the Lagrange multipliers reveals that only the upper triangle of the equations of motion need to be considered. This is obvious since upper triangular matrices form a closed algebra. It should be noted that the dynamics produces the ensemble

$$\Delta = \int dV d\vec{\mathbf{h}}_0 \exp[-\beta P_{\text{ext}}V] Q(V, \vec{\mathbf{h}}_0) \delta(\det[\vec{\mathbf{h}}_0] - 1) \times \prod_{l=1}^d (h_0)_{ll}^{l-1}, \quad (2.35)$$

$$\Delta = \int d\vec{\mathbf{h}} \exp[-\beta P_{\text{ext}} \det(\vec{\mathbf{h}})] Q(\vec{\mathbf{h}}) \times \prod_{l=1}^d (h)_{ll}^{l-1} \det[\vec{\mathbf{h}}]^{1-d},$$

where the space of the $\vec{\mathbf{h}}_0, \vec{\mathbf{h}}$ has been weighted to account for the unequal *a priori* sampling of the upper triangular form. In this space, the tensorial virial theorem

$$\left\langle P_{\alpha\beta} - P_{\text{ext}} \delta_{\alpha\beta} \right\rangle = \left\langle \frac{kT}{\det[\vec{h}]} \sum_{l=\beta}^d \frac{\partial \log[Q(\vec{h})]}{\partial h_{\alpha l}} h_{\beta l} - P_{\text{ext}} \delta_{\alpha\beta} \right\rangle = 0 \quad (2.36)$$

is obeyed where $\beta \geq \alpha$. Using the form of the canonical partition function, it can be shown $P_{\alpha\beta}$ is still given by Eq. (2.20). However, if the matrix of cell parameters is constrained to be symmetric, the pressure tensor that satisfies the virial theorem is no longer given by Eq. (2.20). This third option is therefore to be avoided.

The two methods outlined above will eliminate rotations of the simulation cell. In both methods, however, some information about the behavior of the off-diagonal components of the pressure tensor has also been eliminated. Therefore, the average of all the off-diagonal components of the pressure tensor should be monitored to ensure that each is independently equal to zero. This is more physically meaningful when the method based on the symmetrized tensor is used because the weight associated with the space of the \vec{h}_0 remains uniform. The symmetrized method must therefore be considered a somewhat better way to eliminate rotations of the simulations cell. [On a technical note, the quantity $N_f + d^2$ that appears in the equations of motion for \mathbf{p}_ξ must be changed to $N_f + d(d+1)/2$ in the upper triangular case.]

E. Temperature control

In the equations of motion written above, a single thermostat was coupled to the particles and volume/cell variables. While this scheme is usually effective it does not always perform well. For example, large periodic oscillations in the total kinetic energy were found to develop in protein simulations.¹⁷ Also, the equations of motion are not always ergodic.⁴ The Nosé-Hoover chain method has been developed to overcome these difficulties.¹⁴ In this method, the thermostats themselves are thermostatted to form a chain:

$$\dot{\xi}_i = \frac{p_{\xi_i}}{Q_i}, \quad \dot{p}_{\xi_i} = \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - N_f kT \right] - p_{\xi_i} \frac{p_{\xi_2}}{Q_2}, \quad (2.37)$$

$$\dot{p}_{\xi_j} = \left[\frac{p_{\xi_{j-1}}^2}{Q_{j-1}} - kT \right] - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q_{j+1}}, \quad \dot{p}_{\xi_M} = \left[\frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - kT \right],$$

where M is the chain length. Therefore, in actual simulations, it is useful to thermostat the particles using a Nosé-Hoover chain. It is also useful to use an independent chain to thermostat the volume/box variables to ensure these stiff variables properly sample the phase space. These additions are completely consistent with the results presented above. However, if constraints on the particle degrees of freedom are introduced, the volume/box variables and all degrees of freedom involved in the constraints, must share the same thermostat (see Appendix D).

F. Mass choice of the extended variables

It has been shown elsewhere^{3,14} that the masses of the particle thermostats should be taken to be $Q_{p_1} = N_f kT/\omega_p^2$, $Q_{p_i} = kT/\omega_p^2$, where ω_p is the frequency at which the particle thermostats fluctuate. Similarly, the masses of the barostat/cell parameter thermostats should be taken to be $Q_{b_1} = d(d+1)kT/2\omega_b^2$ for the upper triangle case, $Q_{b_1} = d^2 kT/\omega_b^2$ for the symmetric case, and $Q_{b_i} = kT/\omega_b^2$ in general. (It has been assumed that the particles and the barostats are independently thermostatted.) The masses of the barostat/cell parameters themselves^{3,6} should be taken to be $W = (N_f + d)kT/\omega_b^2$, $W_g = W_{g_0} = (N_f + d)kT/d\omega_b^2$.

III. VELOCITY VERLET BASED INTEGRATORS

A treatment of the integration of the similar equations of motion under Verlet integration has been developed elsewhere.⁶ Here, a closely related treatment of velocity Verlet integration is briefly presented. In velocity Verlet,¹⁸ the relationships

$$x(\Delta t) = x(0) + \dot{x}(0)\Delta t + \frac{\ddot{x}(0)}{2} \Delta t^2 + O(\Delta t^3),$$

$$\dot{x}(\Delta t) = \dot{x}(0) + [\ddot{x}(0) + \ddot{x}(\Delta t)] \frac{\Delta t}{2} + O(\Delta t^3) \quad (3.1)$$

are used. In cases where the second time derivative depends on the first, the $\dot{x}(\Delta t)$ can be determined iteratively though this, in practice, sacrifices reversibility. Appendix D reviews the velocity Verlet integration of the equations of motion presented in Sec. II F.

As discussed in Appendix D, the advantage of the hybrid method is apparent under Verlet-type integration. Basically, if a calculation constrained to permit only isotropic fluctuations of the simulations cell, Eqs. (2.9), is changed to permit the full fluctuations of the cell, Eqs. (2.27), the numerical integration of the volume is performed in exactly the same way. However, if the normal method, Eqs. (2.19), is used to generate the full fluctuations then the volume will be determined differently even if the anisotropic forces and velocities are zero. Note, this is a product of the Verlet-type integration scheme and not of the equations of motion themselves (see Sec. III C).

IV. RESULTS

Two model problems were used to test the new methods proposed herein: a particle in a one-dimensional periodic potential and C_{60} molecules in the bulk solid/fluid phases.

A. Particle in a 1D periodic potential

In this pedagogical example, a particle is assumed to move in the potential

$$\phi(x, V) = \frac{m\omega^2 V^2}{4\pi^2} \left[1 - \cos\left(\frac{2\pi x}{V}\right) \right] \quad (4.1)$$

with $m=1$, $\omega=1$, $Q_p=1$, $Q_b=9$, $W=18$, $kT=1$, $P_{\text{ext}}=1$, $M_b=1$, $M_p=2$. In the calculations, the barostat and the particle are each given an independent Nosé-Hoover chain of

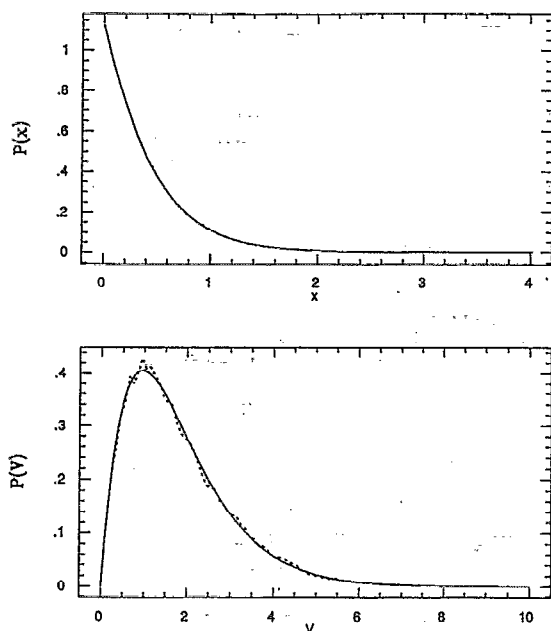


FIG. 2. (a) Position distribution function of the Model problem (dotted line). The solid line is the exact result. (b) Volume distribution function of the Model problem (dotted line). The solid line is the exact result.

thermostats¹⁴ to ensure ergodicity (M indicates the chain length). The probability distribution functions obtained from the calculation are compared to the exact results in Fig. 2. The agreement is good. The average energy and volume were also found to be in good agreement with the exact results.

B. Solid and fluid phase C_{60}

In high-temperature solid and fluid C_{60} , the roughly spherical C_{60} molecules are essentially rotating freely. It is therefore possible to model the true molecule-molecule interaction with a simple spherical pair potential. Such an effective pair potential can be obtained by assuming that the surfaces of two spheres (i.e., the molecules) have a uniform density of carbon atoms which interact via a Lennard-Jones potential. Integration over the surfaces of the two spheres yields¹⁹

$$\phi_{C_{60}-C_{60}}(r) = 4\epsilon_C(60)^2 \times \left\{ \frac{\sigma_C^{12}}{r^{12}} \left[\frac{(1+s)^9 + (1-s)^9 - 2(1-s^2)^9}{90s^2(1-s^2)^9} \right] - \frac{\sigma_C^6}{r^6} \left[\frac{1-s^2/2 + s^4/6}{(1-s^2)^3} \right] \right\}, \quad (4.2)$$

where r is the center of mass distance between the molecules/spheres, $s = \sigma_{C_{60}}/r$, and the parameters ϵ_C , σ_C , and $\sigma_{C_{60}}$ are given in Table I.

A system consisting of $N=864$ C_{60} molecules (corresponding to a $6 \times 6 \times 6$ bcc lattice with four molecules/unit cell) was studied at two different temperatures, $T=2600$ K, the superheated solid, and $T=2700$ K, the gas, at a pressure of 500 atm (for a complete phase diagram see Ref. 19) using both the isotropic and the hybrid methods. Similarly, a transition between the two phases (solid to gas at 2700 K) was also studied using the two methods. The equations of motion were integrated by using the iterative Verlet based algorithm with a time step of 5 fs. The particle and volume/cell variables were independently thermostatted with Nosé-Hoover chains ($M_b = M_p = 5$) and the thermostat and barostat/cell

TABLE I. Structure and thermodynamics data: neat C_{60} solid and gas. ($\epsilon_C=33$ K, $\sigma_{C_{60}}=7.1$ Å, $\sigma_C=3.469$ Å).

Quantity	T=2600 K (solid)		T=2700 K (gas)	
	Isotropic ^a	Hybrid ^a	Isotropic ^b	Hybrid ^b
E_{cons}^c	3.11×10^{-5}	3.71×10^{-5}	2.27×10^{-5}	3.02×10^{-5}
$\langle V \rangle$ (Å ³)	7.34×10^5	7.36×10^5	1.09×10^6	1.09×10^6
$\langle a \rangle$ (Å)	90.2	90.3	103	111
$\langle b \rangle$ (Å)	90.2	90.3	103	92.3
$\langle c \rangle$ (Å)	90.2	90.3	103	109
$\langle \alpha \rangle$ (deg)	90.0	90.0	90.0	91.1
$\langle \beta \rangle$ (deg)	90.0	90.0	90.0	97.2
$\langle \gamma \rangle$ (deg)	90.0	90.0	90.0	93.2
$\langle P \rangle$ (atm)	500	500	500	500
$\langle P_{11} \rangle$ (atm)	507	498	500	500
$\langle P_{22} \rangle$ (atm)	495	501	501	500
$\langle P_{33} \rangle$ (atm)	498	501	499	499
$\langle P_{12} \rangle$ (atm)	-1	1	2	-2
$\langle P_{13} \rangle$ (atm)	6	-2	-1	1
$\langle P_{23} \rangle$ (atm)	-7	-1	-1	0
$-\langle \phi/N \rangle$ (K)	1.42×10^4	1.41×10^4	7.85×10^3	7.85×10^3

^aAverages over 100 ps.

^bAverages over 250 ps.

^c $E_{\text{cons}} = 1/N_i \sum_{k=1}^{N_i} [H'_{(k)} - H'_{(0)}]/H'(0)$, where $H'(k)$ is the value of the conserved quantity at the k th time step and N_i is the number of time steps.

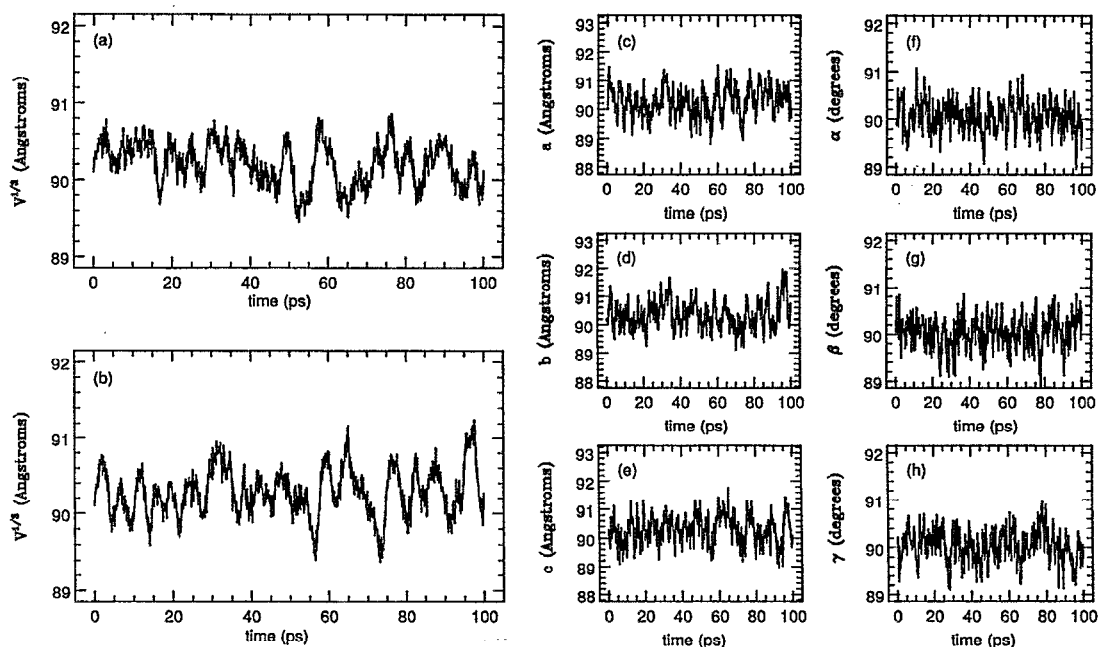


FIG. 3. Time histories of simulation cell parameters during equilibrium constant NPT simulations of solid C_{60} at $T=2600$ K, $P_{\text{ext}}=500$ atm: (a) isotropic algorithm; (b)–(h) hybrid algorithm.

mass parameters chosen according to the prescription given in Sec. II F ($\omega_b=2$ ps $^{-1}$ and $\omega_p=1$ ps $^{-1}$). The potential was truncated at 40 Å and long-range corrections to the potential energy (and the pressure through the virial) included to account for the neglected long-range attractive interactions.

Equilibrium simulations of the fluid and solid phases are considered first. In Figs. 3 and 4, the behavior of the volumes and individual cell parameters from isotropic and hybrid simulations of the two state points are compared. In both phases, the fluctuations of the volume are similar for two

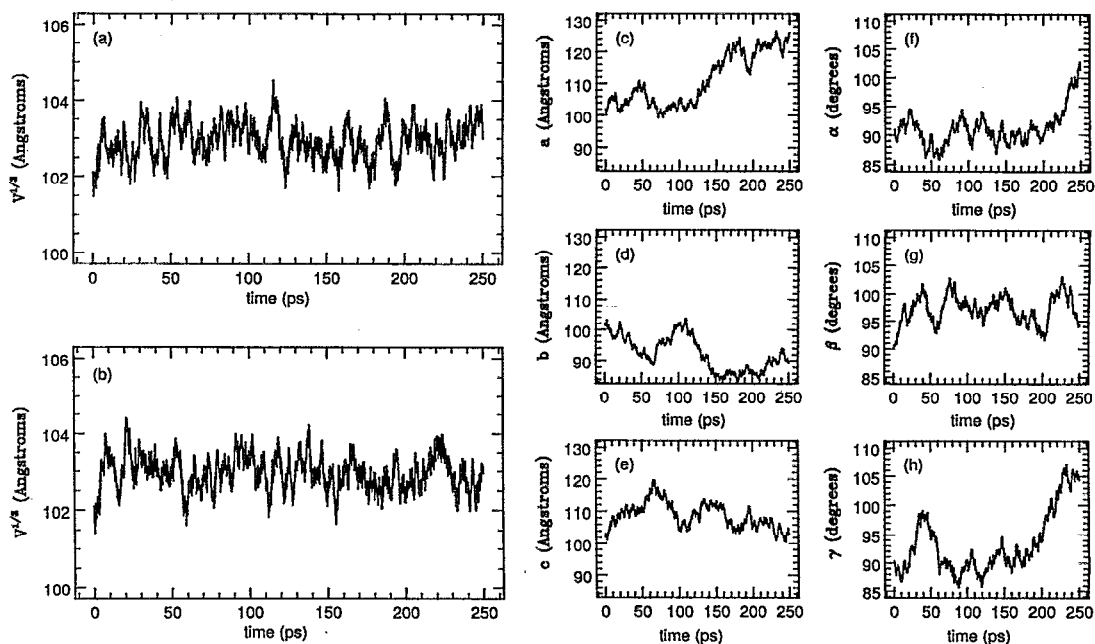


FIG. 4. Time histories of simulation cell parameters during equilibrium constant NPT simulations of gaseous C_{60} at $T=2700$ K, $P_{\text{ext}}=500$ atm: (a) isotropic algorithm; (b)–(h) hybrid algorithm.

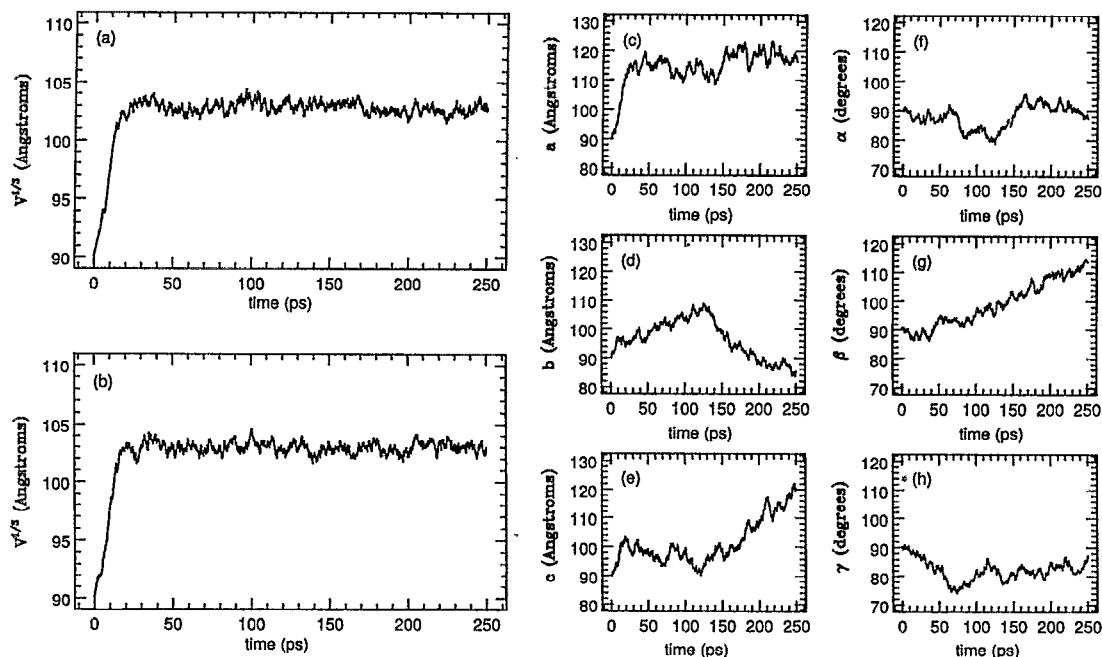


FIG. 5. Time histories of simulation cell parameters during constant NPT simulations of a structural transition from solid to gaseous states of C_{60} at $T=2700$ K, $P_{ext}=500$ atm: (a) isotropic algorithm; (b)–(h) hybrid algorithm.

methods and in the fully flexible studies (the hybrid calculations) the cell remains essentially cubic on the time scale of the simulations. This second point is by no means guaranteed in the gas phase study where the partition function is independent of cell shape. In fact, cells with large sides (a, b, c) and small/large angles are a non-negligible part of the free shape phase space $\int d\mathbf{h}_0 \delta(\det[\mathbf{h}_0] - 1)$ and will eventually appear. However, the metastability of the roughly cubic cells is a useful result. With the exception of the individual cell lengths and angles in the hybrid gas simulation, the corresponding average structural and thermodynamic properties of the two phases computed using the isotropic and hybrid methods are identical within statistical errors (Table I) and agree with previous work at constant volume.²⁰

The transition from the solid to gas phase was also studied using the two methods (see Fig. 5). Again, the behavior of the volume is similar for the two methods. The transition occurs in roughly 15 ps and the final volumes are the same. In the hybrid study, the cell appears to be distorting slowly, but significantly, from its initially cubic shape. Nonetheless, the transition was not affected and the results are in good agreement with the isotropic calculation.

V. CONCLUSIONS

New constant pressure methodologies have been developed and tested on model and more realistic problems. The methods were found to perform well under equilibrium conditions and during structural transitions such as an evaporation of a solid to form a gas. The methods outlined above

should find wide application in modeling condensed phase behavior of complex molecules.

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APPENDIX A

In this appendix, it is shown the conservation law, $\mathbf{F}_{c.m.}=0$, can effect the volume distribution function generated by the modified equations of motion, Eqs. (2.7). Basically, satisfying the Liouville equation for the entire distribution is insufficient to guarantee that the individual pieces are properly generated.

In order to demonstrate this important result, consider a system of free particles in a periodic box. The modified equations of motion for the particle positions, the \mathbf{r}_i , are auxiliary variables, i.e., the dynamics of the \mathbf{r}_i depend on all the other dynamical variables but not vice versa. Therefore, the time average of any position independent quantity will not depend on the particle positions. The distribution function of the reduced phase space (no positions) is, thus, all important. The reduced phase space (V, \mathbf{p} only) generated by the modified equations of motion, Eqs. (2.7), is

$$\Delta = \frac{\exp[E/kT]}{(N_f+1)kT} \int dp_\xi dp_\epsilon \mathbf{p} dV V^{N_f-1} \exp\left[-\frac{H''}{kT}\right], \quad (\text{A1})$$

$$H'' = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{p_\epsilon^2}{2W} + \frac{p_\xi^2}{2Q} + P_{\text{ext}}V.$$

The new equations, Eqs. (2.9), however, generate

$$\Delta = \frac{\exp[E/kT]}{(N_f+1)kT} \int dp_\xi dp_\epsilon \mathbf{p} dV V^{N_f} \exp\left[-\frac{H''}{kT}\right], \quad (\text{A2})$$

the isothermal–isobaric/correct result. Basically, the phase space associated with the particle positions serves to mask the fact that the volume distribution produced by Eqs. (2.7) is incorrect.

$$\langle P_{\text{int}} - P_{\text{ext}} \rangle = \frac{\int dV \exp[-\beta P_{\text{ext}}V] Q(V) [kT \{ \partial \log[Q(V)] / \partial V \} - P_{\text{ext}}]}{\int dV \exp[-\beta P_{\text{ext}}V] Q(V)} = 0,$$

$$\langle P_{\text{int}} \rangle = P_{\text{ext}},$$

while the second and less familiar theorem relates the internal and external work,

$$\langle (P_{\text{int}} - P_{\text{ext}})V \rangle = \frac{\int dV \exp[-\beta P_{\text{ext}}V] Q(V) V [kT \{ \partial \log[Q(V)] / \partial V \} - P_{\text{ext}}]}{\int dV \exp[-\beta P_{\text{ext}}V] Q(V)} = -kT,$$

$$\langle P_{\text{int}}V \rangle = P_{\text{ext}}\langle V \rangle - kT. \quad (\text{B2})$$

Both theorems are invariant properties of the isothermal–isobaric ensemble and as such are (both) always satisfied, independent of system, boundary condition, etc. (the only input to the derivations is the statistical mechanical definition of the ensemble and the pressure). Incorrect/different ensembles possess incorrect/different virial theorems. For example, the ensemble generated by Hoover dynamics [Eq. (2.1)] has the two theorems

$$\langle P_{\text{int}} \rangle = P_{\text{ext}} + kT \langle V^{-1} \rangle, \quad (\text{B3})$$

$$\langle P_{\text{int}}V \rangle = P_{\text{ext}}\langle V \rangle, \quad (\text{B4})$$

where the averages are over Eq. (2.5).

APPENDIX C

It has been shown elsewhere that for systems with no external forces ($\sum_{i=1}^N \mathbf{F}_i = 0$), the Nosé–Hoover canonical dynamics method^{4,5} only gives rise to the canonical distribution if the total linear momentum is taken to be zero.¹³ In this appendix, it will be demonstrated that this constraint can be eliminated under Nosé–Hoover chain dynamics,²¹ a simple extension of the Nosé–Hoover scheme. In addition, the other “problem” with Nosé–Hoover-type methods under these conditions ($\sum_{i=1}^N \mathbf{F}_i = 0$), that the total linear momentum cannot change sign or direction is addressed.

The Nosé–Hoover chain method employs the equations of motion

In the general case, $\mathbf{F}_{\text{c.m.}} = 0$ and $\tilde{P}_{\text{int}} = P_{\text{int}} + \mathbf{r}_{\text{c.m.}} \cdot \mathbf{F}_{\text{c.m.}}$,⁶ the modified equations of motion, Eqs. (2.7), retain the same pathology. In an appropriate set of normal modes, the $\mathbf{r}_{\text{c.m.}}$ can be seen to be auxiliary variables. This leads to the realization that the volume distribution produced by the dynamics is, in error, by the, now, familiar factor of V , the volume.

APPENDIX B

There are two important pressure virial theorems associated with isothermal–isobaric ensemble that are used in the analysis presented in text. The first and more familiar theorem relates the internal and external pressure

$$\langle P_{\text{int}} - P_{\text{ext}} \rangle = \frac{1}{\Delta} \int dV \exp[-\beta P_{\text{ext}}V] \int_{D(V)} d\mathbf{p} d\mathbf{r} \times \exp[-\beta H(\mathbf{p}, \mathbf{r})] (P_{\text{int}} - P_{\text{ext}}),$$

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, \quad \dot{\mathbf{p}}_i = -\nabla_i V(\mathbf{r}) - \mathbf{p}_i \frac{p_{\xi_1}}{Q_1}, \\ \dot{s}_1 &= \frac{dNs_1 p_{\xi_1}}{Q_1}, \quad \dot{s}_i = \frac{s_i p_{\xi_i}}{Q_i}, \\ \dot{p}_{\xi_1} &= \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - dNkT \right] - p_{\xi_1} \frac{p_{\xi_2}}{Q_2}, \end{aligned} \quad (\text{C1})$$

$$\dot{p}_{\xi_j} = \left[\frac{p_{\xi_{j-1}}^2}{Q_{j-1}} - kT \right] - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q_{j+1}}, \quad \dot{p}_{\xi_M} = \left[\frac{p_{\xi_{M-1}}^2}{Q_{M-1}} - kT \right],$$

where each thermostat variable (s_i) is in turn thermostatted to form a chain. The dynamics conserves

$$\begin{aligned} H'(\mathbf{p}, \mathbf{r}, \mathbf{s}, \mathbf{p}_\xi) &= V(\mathbf{r}) + \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i=1}^M \frac{p_{\xi_i}^2}{2Q_i} + kT \ln(s_1) \\ &\quad + \sum_{i=2}^M kT \ln(s_i). \end{aligned} \quad (\text{C2})$$

However, if $\sum_{i=1}^N \nabla_i V(\mathbf{r}) = 0$ 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 of $s_1^{1/dN}$ appears in this conservation law due to the nonstandard but convenient definition of \dot{s}_1 . In general, Nosé–Hoover dynamics is recovered for $M=1$.

First, it will be demonstrated that the Nosé–Hoover chain dynamics ($M > 1$), indeed, generates the canonical distribution for the case $\sum_{i=1}^N \mathbf{F}_i = 0$. The partition function generated by the said dynamics for an ergodic system with the desired constraint $\sum_{i=1}^N \mathbf{F}_i = 0$ is

$$Q = \int \prod_{i=1}^N d\mathbf{r}_i \prod_{i=1}^{N-1} d\mathbf{p}'_i \prod_{i=1}^M p_{\xi_i} \prod_{i=1}^M ds_i d\mathbf{P} \delta^3[s_1^{1/dN} \mathbf{P} - \mathbf{P}'] \times \delta \left[V(\mathbf{r}) + \sum_{i=1}^{N-1} \frac{\mathbf{p}'_i{}^2}{2m_i} + \frac{\mathbf{P}^2}{2M} + \sum_{i=1}^M \frac{p_{\xi_i}^2}{2Q_i} + kT \ln(s_1) + kT \sum_{i=2}^M \ln(s_i) - E \right], \quad (\text{C3})$$

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

where a set of normal modes that separates the total linear momentum $\{\mathbf{p}', \mathbf{P}\}$ but diagonalizes the kinetic energy has been introduced.¹³ The integrals over the thermostat variables (the s) range from zero to infinity. The canonical ensemble is therefore generated by the dynamics for the formerly pathological $\mathbf{P}(0) \neq 0$ ($M > 1$). (The momentum distribution of the canonical ensemble, by definition, includes the full fluctuations of the center of mass momentum.)

It should be noted that only the magnitude of the total linear momentum P appears in the partition function ($P^{d-1} \exp[-P^2/2MkT]$). This is consistent with the fact that only the magnitude of the total linear momentum P appears in the equations of motion. Indeed, the total linear momentum can change neither sign nor direction under these conditions due to the structure of the dynamics. Therefore, the center of mass of the system will move off to infinity. This explains why simulations are generally performed with $\mathbf{P} = 0$. Nonetheless, the canonical distribution is clearly generated provided Nosé–Hoover chains are used as shown above. The directional pathology can be overcome ($d > 1$) by introducing a matrix of Nosé–Hoover chains each coupled to one component of the kinetic energy tensor. (The off-diagonal terms are of course thermostatted to have average value zero not NkT .) Under these conditions, the full fluctuations of the \mathbf{P} will be generated.

For completeness, the zero linear momentum condition will be considered. Taking $\mathbf{P}'(0) = 0, s_1(0) \neq 0$ gives $\mathbf{P}(t) = 0$ for all time (the fixed point of the dynamics). This is equivalent changing the equation of motion for the particle velocities presented in Eq. (A1) to

$$\dot{\mathbf{p}}_i = -\nabla_i V(\mathbf{r}) - (\mathbf{p}_i - \mathbf{P}_{\text{c.m.}}) \frac{p_{\xi_1}}{Q_1} \quad (\text{C4})$$

which can be formally shown to generate canonical ensemble, with the zero linear momentum constraint, for all

values of M , provided the parameter N in Eq. (A1) is decreased by d . For a more complete treatment of the issues discussed here, see Ref. 24.

APPENDIX D

In this appendix, velocity Verlet integration of equations of motion that yield the microcanonical ensemble (*NVE*), the canonical ensemble (*NVT*) and the isothermal isobaric ensemble (*NPT*) are reviewed.

1. Constant energy (*NVE*)

At constant energy, the velocity Verlet integrator can be applied in a straightforward manner:

$$\mathbf{r}_i(\Delta t) = \mathbf{r}_i(0) + \mathbf{v}_i(0)\Delta t + \mathbf{F}_i(0) \frac{\Delta t^2}{2m_i}, \quad (\text{D1})$$

$$\mathbf{v}_i(\Delta t) = \mathbf{v}_i(0) + [\mathbf{F}_i(0) + \mathbf{F}_i(\Delta t)] \frac{\Delta t}{2m_i}.$$

An arbitrary set of constraints can be handled by the Shake/Rattle algorithm.^{22,23}

2. Constant temperature (*NVT*)

The velocity Verlet integrator for the equations of motion, Eqs. (2.37), is

$$\mathbf{r}_i(\Delta t) = \mathbf{r}_i(0) + \mathbf{v}_i(0)\Delta t + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0)\mathbf{v}_{\xi}(0) \right] \frac{\Delta t^2}{2},$$

$$\xi(\Delta t) = \xi(0) + \mathbf{v}_{\xi}(0)\Delta t + G_{\xi}(0) \frac{\Delta t^2}{2}, \quad (\text{D2})$$

$$\mathbf{v}_i(\Delta t) = \mathbf{v}_i(0) + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0)\mathbf{v}_{\xi}(0) \right] \frac{\Delta t}{2} + \left[\frac{\mathbf{F}_i(\Delta t)}{m_i} - \mathbf{v}_i(\Delta t)\mathbf{v}_{\xi}(\Delta t) \right] \frac{\Delta t}{2},$$

$$\mathbf{v}_{\xi}(\Delta t) = \mathbf{v}_{\xi}(0) + [G_{\xi}(0) + G_{\xi}(\Delta t)] \frac{\Delta t}{2},$$

where $G_{\xi} = (1/Q)[\sum_{i=1}^N m_i \mathbf{v}_i^2 - N_f kT]$. The velocities are in practice determined iteratively through

$$\mathbf{v}_i^k(\Delta t) = \frac{1}{[1 + (\Delta t/2)\mathbf{v}_{\xi}^{k-1}(\Delta t)]} \times \left\{ \mathbf{v}_i(0) + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0)\mathbf{v}_{\xi}(0) + \frac{\mathbf{F}_i(\Delta t)}{m_i} \right] \frac{\Delta t}{2} \right\}, \quad (\text{D3})$$

$$\mathbf{v}_{\xi}^k(\Delta t) = \mathbf{v}_{\xi}(0) + [G_{\xi}(0) + G_{\xi}^k(\Delta t)] \frac{\Delta t}{2}$$

with initial guess $\mathbf{v}_{\xi}^0(\Delta t) = \mathbf{v}_{\xi}(-\Delta t) + 2G_{\xi}(0)\Delta t$. Note, if constraints are present the iterative determination of the velocities is independent of Rattle. That is, $\mathbf{v}_i(0) + [(\mathbf{F}_i(0)/m_i) - \mathbf{v}_i(0)\mathbf{v}_{\xi}(0) + (\mathbf{F}_i(\Delta t)/m_i)]\Delta t/2$ is Rattled and the iterative process is permitted to scale these values. (Rattle enforces $\sum_i \mathbf{v}_i \cdot \nabla_{\mathbf{r}_i} \sigma_j = 0$ which is independent of a scaling factor on the \mathbf{v} .) This is possible because all par-

ticles involved in a common constraint must be coupled to the same thermostat within the present formalism.

3. Constant pressure (NPT): Isotropic

In order to integrate Eqs. (2.9), it is convenient to derive velocity Verlet expressions for $\{s_i(\Delta t) = \exp[-\epsilon(\Delta t)] \times \mathbf{r}_i(\Delta t), \dot{s}_i(\Delta t) = \exp[-\epsilon(\Delta t)] \mathbf{v}_i(\Delta t)\}$ and then convert them into desired quantities, $\{\mathbf{r}_i(\Delta t), \mathbf{v}_i(\Delta t)\}$. The result is

$$\begin{aligned} \mathbf{r}_i(\Delta t) &= e^{[\epsilon(\Delta t) - \epsilon(0)]} \left\{ \mathbf{r}_i(0) + \mathbf{v}_i(0) \Delta t + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0) \mathbf{v}_\xi(0) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(0) \mathbf{v}_\epsilon(0) \right] \frac{\Delta t^2}{2} \right\}, \\ \xi(\Delta t) &= \xi(0) + \mathbf{v}_\xi(0) \Delta t + G_\xi(0) \frac{\Delta t^2}{2}, \\ \epsilon(\Delta t) &= \epsilon(0) + \mathbf{v}_\epsilon(0) \Delta t + \left[\frac{F_\epsilon(0)}{W} - \mathbf{v}_\epsilon(0) \mathbf{v}_\xi(0) \right] \frac{\Delta t^2}{2}, \\ \mathbf{v}_i(\Delta t) &= e^{[\epsilon(\Delta t) - \epsilon(0)]} \left\{ \mathbf{v}_i(0) + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0) \mathbf{v}_\xi(0) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(0) \mathbf{v}_\epsilon(0) \right] \frac{\Delta t}{2} \right\} + \left[\frac{\mathbf{F}_i(\Delta t)}{m_i} - \mathbf{v}_i(\Delta t) \mathbf{v}_\xi(\Delta t) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(\Delta t) \mathbf{v}_\epsilon(\Delta t) \right] \frac{\Delta t}{2}, \\ \mathbf{v}_\xi(\Delta t) &= \mathbf{v}_\xi(0) + [G_\xi(0) + G_\xi(\Delta t)] \frac{\Delta t}{2}, \\ \mathbf{v}_\epsilon(\Delta t) &= \mathbf{v}_\epsilon(0) + \left[\frac{F_\epsilon(0)}{W} - \mathbf{v}_\epsilon(0) \mathbf{v}_\xi(0) \right] \frac{\Delta t}{2} + \left[\frac{F_\epsilon(\Delta t)}{W} - \mathbf{v}_\epsilon(\Delta t) \mathbf{v}_\xi(\Delta t) \right] \frac{\Delta t}{2}, \end{aligned} \quad (\text{D4})$$

where

$$\begin{aligned} G_\xi &= \frac{1}{Q} \left\{ \sum_{i=1}^N m_i \mathbf{v}_i^2 + W \mathbf{v}_\epsilon^2 - (N_f + 1) kT \right\}, \\ F_\epsilon &= dV(P_{\text{int}} - P_{\text{ext}}) + \frac{d}{N_f} \sum_{i=1}^N m_i \mathbf{v}_i^2. \end{aligned} \quad (\text{D5})$$

The velocities can be determined iteratively as in Sec. D 2 and an arbitrary set of constraints on the particle degrees of freedom can be handled using the Shake and Rattle algorithms. However, as the particle velocities are not the time derivatives of the particle positions, $\dot{\mathbf{r}} = \mathbf{v} + \mathbf{v}_\epsilon \mathbf{r}$, all the degrees of freedom involved in the constraints must be coupled to the same thermostat and this thermostat must, in turn, be coupled to the volume. The volume is part of the surface of constraint and links all the constraints in the problem. (The Lagrange multipliers for all the constraints appear in the volume equations of motion through the pressure tensor and independent sets of constraints can no longer be said to exist as in the NVT case. The restriction on the number of thermostats can be relaxed in the limit that the volume evolves

slowly, to provide better temperature control in the simulation.) In addition, Rattle must now be applied as part of the iterative procedure. Alternatively, only the center of mass degrees of freedom of partially rigid or rigid subunits may be barostatted (i.e., scaled by the volume).⁵ Note that this second procedure produces a slightly different ensemble in partially flexible molecules.

4. Constant pressure (NPT): Flexible

The equations of motion, Eqs. (2.27), the hybrid method, can be integrated by deriving expressions for

$$\begin{aligned} s_i(\Delta t) &= \exp[-\epsilon(\Delta t)] \tilde{\mathbf{h}}_0^{-1}(\Delta t) \mathbf{r}_i(\Delta t), \\ \dot{s}_i(\Delta t) &= \exp[-\epsilon(\Delta t)] \tilde{\mathbf{h}}_0^{-1}(\Delta t) \mathbf{v}_i(\Delta t), \\ \dot{\tilde{\mathbf{h}}}_0(\Delta t) &= \tilde{\mathbf{v}}_{g_0}(\Delta t) \tilde{\mathbf{h}}_0(\Delta t) \end{aligned} \quad (\text{D6})$$

from velocity Verlet and then convert them into desired quantities $\{\mathbf{r}_i(\Delta t), \mathbf{v}_i(\Delta t), \tilde{\mathbf{v}}_{g_0}(\Delta t)\}$. The result is

$$\begin{aligned} \mathbf{r}_i(\Delta t) &= e^{[\epsilon(\Delta t) - \epsilon(0)]} \tilde{\mathbf{h}}_0(\Delta t) \tilde{\mathbf{h}}_0^{-1}(0) \left\{ \mathbf{r}_i(0) + \mathbf{v}_i(0) \Delta t + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0) \mathbf{v}_\xi(0) - 2 \tilde{\mathbf{v}}_{g_0}(0) \mathbf{v}_i(0) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(0) \mathbf{v}_\epsilon(0) \right] \frac{\Delta t^2}{2} \right\}, \\ \xi(\Delta t) &= \xi(0) + \mathbf{v}_\xi(0) \Delta t + G_\xi(0) \frac{\Delta t^2}{2}, \\ \epsilon(\Delta t) &= \epsilon(0) + \mathbf{v}_\epsilon(0) \Delta t + \left[\frac{F_\epsilon(0)}{W} - \mathbf{v}_\epsilon(0) \mathbf{v}_\xi(0) \right] \frac{\Delta t^2}{2}, \\ \mathbf{h}_0(\Delta t) &= \left\{ \tilde{\mathbf{I}} + \tilde{\mathbf{v}}_{g_0}(0) \Delta t + \left[\frac{1}{W_{g_0}} \tilde{\mathbf{F}}_{g_0}(0) + \tilde{\mathbf{v}}_{g_0}^2(0) - \tilde{\mathbf{v}}_{g_0}(0) \mathbf{v}_\xi(0) \right] \frac{\Delta t^2}{2} \right\} \tilde{\mathbf{h}}_0(0), \\ \mathbf{v}_i(\Delta t) &= e^{[\epsilon(\Delta t) - \epsilon(0)]} \tilde{\mathbf{h}}_0(\Delta t) \tilde{\mathbf{h}}_0^{-1}(0) \left\{ \mathbf{v}_i(0) + \left[\frac{\mathbf{F}_i(0)}{m_i} - \mathbf{v}_i(0) \mathbf{v}_\xi(0) - 2 \tilde{\mathbf{v}}_{g_0}(0) \mathbf{v}_i(0) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(0) \mathbf{v}_\epsilon(0) \right] \frac{\Delta t}{2} \right\} + \left[\frac{\mathbf{F}_i(\Delta t)}{m_i} - \mathbf{v}_i(\Delta t) \mathbf{v}_\xi(\Delta t) - 2 \tilde{\mathbf{v}}_{g_0}(\Delta t) \mathbf{v}_i(\Delta t) - \left(2 + \frac{d}{N_f} \right) \mathbf{v}_i(\Delta t) \mathbf{v}_\epsilon(\Delta t) \right] \frac{\Delta t}{2}, \\ \mathbf{v}_\xi(\Delta t) &= \mathbf{v}_\xi(0) + [G_\xi(0) + G_\xi(\Delta t)] \frac{\Delta t}{2}, \end{aligned} \quad (\text{D7})$$

$$\mathbf{v}_\epsilon(\Delta t) = \mathbf{v}_\epsilon(0) + \left[\frac{F_\epsilon(0)}{W} - \mathbf{v}_\epsilon(0) \mathbf{v}_\xi(0) \right] \frac{\Delta t}{2} + \left[\frac{F_\epsilon(\Delta t)}{W} - \mathbf{v}_\epsilon(\Delta t) \mathbf{v}_\xi(\Delta t) \right] \frac{\Delta t}{2},$$

$$\vec{\mathbf{v}}_{g_0}(\Delta t) = \left\{ \vec{\mathbf{v}}_{g_0}(0) + \left[\frac{1}{W_{g_0}} \vec{\mathbf{F}}_{g_0}(0) + \vec{\mathbf{v}}_{g_0}^2(0) - \vec{\mathbf{v}}_{g_0}(0) \mathbf{v}_\xi(0) \frac{\Delta t}{2} \vec{\mathbf{h}}_0(0) \vec{\mathbf{h}}_0^{-1}(\Delta t) + \left[\frac{1}{W_{g_0}} \vec{\mathbf{F}}_{g_0}(\Delta t) + \vec{\mathbf{v}}_{g_0}^2(\Delta t) - \vec{\mathbf{v}}_{g_0}(\Delta t) \mathbf{v}_\xi(\Delta t) \right] \frac{\Delta t}{2} \right\} \vec{\mathbf{h}}_0^{-1}(\Delta t) \vec{\mathbf{h}}_0(0) \vec{\mathbf{v}}_{g_0}(0) \right. \\ \left. - \frac{\lambda^n \Delta t^2}{2 W_{g_0}} \frac{(\det[\vec{\mathbf{h}}_0(\Delta t)^{n-1}] - 1)}{\det[\vec{\mathbf{h}}_0(\Delta t)^{n-1}] \text{Tr}[\vec{\mathbf{h}}_0^{-1}(\Delta t)^{n-1} \vec{\mathbf{h}}_0(0)]} \right\} \vec{\mathbf{h}}_0^{-1}(\Delta t) \vec{\mathbf{h}}_0(0) \vec{\mathbf{v}}_{g_0}(0) \quad (\text{E2})$$

The iteration proceeds until $|\det[\vec{\mathbf{h}}_0] - 1| = 0$ within a desired tolerance. This portion of the algorithm is generally called Shake. The velocity part of the algorithm, Rattle, is trivial since we simply choose the multiplier λ so that

$$\vec{\mathbf{v}}_{g_0}(\Delta t) = \vec{\mathbf{v}}_{g_0}(\Delta t)^0 + \left(\frac{1}{1 + \mathbf{v}_\xi(\Delta t) \Delta t / 2} \right) \frac{\lambda \Delta t}{2 W_{g_0}} \vec{\mathbf{I}} \quad (\text{E3})$$

is traceless:

$$\left(\frac{1}{1 + \mathbf{v}_\xi(\Delta t) \Delta t / 2} \right) \frac{\lambda \Delta t}{2 W_{g_0}} = -\frac{1}{d} \text{Tr}[\vec{\mathbf{v}}_{g_0}(\Delta t)^0]. \quad (\text{E4})$$

It is important to note that the second time derivatives of all the variables in the problem are velocity dependent. Therefore, the velocities must be generated by repeatedly, (a) iterating velocity Verlet itself to convergence and (b) applying Rattle, until *all* the velocities are determined within a desired tolerance.

The outlined procedures, Shake and iteration plus Rattle, should converge rapidly because the "exact" value of the multiplier has already been substituted into the equations of motion ($d \text{Tr}[\vec{\mathbf{v}}_{g_0}]/dt = 0$). Thus, only small corrections, on the order of Δt^3 , necessary for the finite time step integrator to satisfy the constraint within the desired tolerance are generated by Shake and Rattle. We therefore find the CPU time taken by this part of the program to be negligible.

where

$$G_\xi = \frac{1}{Q} \left[\sum_{i=1}^N m_i \mathbf{v}_i^2 + W \mathbf{v}_\epsilon^2 + W_{g_0} \text{Tr}[\vec{\mathbf{v}}_{g_0} \vec{\mathbf{v}}_{g_0}^T] - (N_f + d^2) kT \right], \quad (\text{D8})$$

$$\vec{\mathbf{F}}_{g_0} = V(\vec{\mathbf{P}}_{\text{int}} - \vec{\mathbf{I}} \mathbf{P}_{\text{ext}}) - \left(\frac{V}{d} \right) \text{Tr}[\vec{\mathbf{P}}_{\text{int}} - \vec{\mathbf{I}} \mathbf{P}_{\text{ext}}] \vec{\mathbf{I}}.$$

The velocities can be determined iteratively as in the previous two subsections. The constraint that $\det[\vec{\mathbf{h}}_0] = 1$ must be enforced with a Shake/Rattle routine (see Appendix E). The advantage of the hybrid method over a method involving only $\vec{\mathbf{h}}$ is that the volume is integrated in exactly the same way as in the isotropic case. In addition, the constraint that $\vec{\mathbf{v}}_{g_0}$ remain symmetric is conserved exactly by the integrator (see Sec. II D) and the angular momenta of the cell remains zero.

APPENDIX E

In this appendix, it is shown how the Shake/Rattle algorithm can be used to constrain $\det[\vec{\mathbf{h}}_0] = 1$, in the integration of the hybrid method, Eqs. (2.27). Briefly, if the term $-\lambda(\det[\vec{\mathbf{h}}_0] - 1)$ is introduced to the conserved quantity of the hybrid method, Eq. (2.28), then the additional term $\lambda \vec{\mathbf{I}}$ must be added to the force on the $\vec{\mathbf{p}}_{g_0}$ in Eqs. (2.27). This results in the term $\lambda \vec{\mathbf{h}}_0 / W_{g_0}$ in the expression for $\vec{\mathbf{h}}_0$. In the Shake/Rattle algorithm^{22,23} the following iterative procedure is used to determine the cell positions at time Δt and the cell velocities at time $\Delta t/2$,

$$\vec{\mathbf{h}}_0(\Delta t)^n = \vec{\mathbf{h}}_0(\Delta t)^{n-1} + \frac{\lambda^n \Delta t^2}{2 W_{g_0}} \vec{\mathbf{h}}_0(0),$$

$$\vec{\mathbf{v}}_{g_0}(\Delta t/2)^n = \left\{ \vec{\mathbf{v}}_{g_0}(\Delta t/2)^{n-1} \vec{\mathbf{h}}_0(\Delta t)^{n-1} + \frac{\lambda^n \Delta t}{2 W_{g_0}} \vec{\mathbf{h}}_0(0) \right\} \vec{\mathbf{h}}_0^{-1}(\Delta t)^n, \quad (\text{E1})$$

where n labels the iteration number. The value of the n th increment to the total multiplier λ^n is determined by a first-order Taylor series expansion:

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