Molecular dynamics simulations at constant pressure and/or temperature[a)]

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In the molecular dynamics simulation method for fluids, the equations of motion for a collection of particles in a fixed volume are solved numerically. The energy, volume, and number of particles are constant for a particular simulation, and it is assumed that time averages of properties of the simulated fluid are equal to microcanonical ensemble averages of the same properties. In some situations, it is desirable to perform simulations of a fluid for particular values of temperature and/or pressure or under conditions in which the energy and volume of the fluid can fluctuate. This paper proposes and discusses three methods for performing molecular dynamics simulations under conditions of constant temperature and/or pressure, rather than constant energy and volume. For these three methods, it is shown that time averages of properties of the simulated fluid are equal to averages over the isoenthalpic–isobaric, canonical, and isothermal–isobaric ensembles. Each method is a way of describing the dynamics of a certain number of particles in a volume element of a fluid while taking into account the influence of surrounding particles in changing the energy and/or density of the simulated volume element. The influence of the surroundings is taken into account without introducing unwanted surface effects. Examples of situations where these methods may be useful are discussed.

I. INTRODUCTION

Molecular dynamics and Monte Carlo methods have become important tools for the study of fluids.[1,2] They have been used to study the equilibrium and transport properties of model atomic liquids, such as the hard-sphere fluid,[3] the Lennard-Jones fluid,[4] and models for molecular liquids.[5]

The Monte Carlo method, as developed by Metropolis *et al.*[6] and extended in various ways,[1(a),(b)] is a procedure for evaluating configuration space equilibrium averages for constant temperature ensembles, such as the canonical ensemble and the isothermal–isobaric ensemble. In the canonical ensemble, the temperature T, volume V; and number of particles N are specified in advance, and an algorithm is used to generate a sequence of configurations. The average of any property over this sequence is an approximation to the measured value of that property for the thermodynamic state with the specified values of N, V, and T. Similarly, for the isothermal–isobaric ensemble, N, the pressure P, and T are specified in advance, and properties are averaged over a sequence of generated configurations.

In the molecular dynamics method, the Newtonian equations of motion of a set of N particles in volume V are solved numerically. The total energy E of the system is conserved as the system moves along its trajectory. The average of any property over the trajectory is an approximation to the measured value of that property for the thermodynamic state with the specified values of N, V, and E. Such an average is equivalent to an average over a microcanonical ensemble if the trajectory passes through all parts of phase space that have the specified energy.

In some situations it is desirable to perform simulations at constant temperature and/or pressure. For example, in studying dilute solutions, it is worthwhile to simulate both the pure solvent and the dilute solution at the same temperature and pressure. This corresponds to the usual experimental situation in which partial molar quantities of the solute are measured, and the comparison of calculated results with experiment is facilitated.[5(b)] Also, in studies of the glass transition in atomic fluids, it is helpful to be able to manipulate the pressure and temperature of the surroundings of the fluid being simulated.[4(d)] To achieve isothermal and/or isobaric conditions, with the appropriate energy and/or volume fluctuations, it has been necessary to use Monte Carlo methods, rather than molecular dynamics. An advantage of the molecular dynamics method, over the Monte Carlo method, is that molecular dynamics gives information about the time dependence and magnitude of fluctuations of position and momentum variables away from their equilibrium values, while Monte Carlo deals only with position variables and gives no information about the time dependence of fluctuations. Thus, in order to be able to specify the temperature and/or pressure of a simulation, it has been necessary to use the Monte Carlo method and thereby forgo the possibility of obtaining dynamical information from the same simulation.

The object of this paper is to present and discuss molecular dynamics methods for simulating a fluid subject to a constant pressure, constant temperature, or constant temperature and pressure. The trajectory averages for these three types of simulations correspond to averages over the isoenthalpic–isobaric, canonical, and isothermal–isobaric ensembles, respectively. These methods have the advantages of isothermal and/or isobaric simulation without sacrificing a dynamical description of the fluid.

A molecular dynamics calculation can simulate the motion of only a small number of particles (typically,

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between 50 and 1000). A physical system with this number of particles is more like a droplet than a bulk fluid, and its properties would be strongly affected by its surface. In order to eliminate the surface and obtain results for a bulk liquid, periodic boundary conditions[6] are ordinarily used. These conditions make all points in the simulated fluid equivalent to all other points. It is generally assumed that a molecular dynamics calculation with periodic boundary conditions gives results equivalent to the properties of a small volume embedded in a bulk sample of the material, provided that the length of the sample being simulated in several multiples of the correlation length of the bulk fluid.

However, a small group of 50 to 1000 particles in a volume element in a fluid is constantly subjected to energy and volume fluctuations due to the surrounding fluid. These fluctuations are responsible for equilibrating the volume element to the temperature and pressure of the surrounding fluid. The usual molecular dynamics method in effect suppresses these fluctuations and keeps the volume and energy for the N particles fixed. The methods discussed in this paper allow these fluctuations to be simulated, without introduction of an unwanted surface, by distributing the effect of the fluctuations throughout the volume of the simulated fluid.

These methods will be discussed for the special case of an atomic fluid. In Sec. II, the fluid of interest is discussed. Sections III–V discuss molecular dynamics simulations at constant pressure, constant temperature, and constant temperature and pressure, respectively. Section VI discusses potential applications of these techniques.

II. SYSTEM OF INTEREST

We imagine that the system of interest to be simulated is an atomic fluid. (All the methods and results are easily generalized to the case of molecular fluids.) In this section we will discuss the classical equations of motion for a fluid and define several types of ensemble averages.

The fluid of interest is N atoms, with coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ in a cubic volume V with periodic boundary conditions. Each component of each coordinate is a number between 0 and $V^{1/3}$. In using periodic boundary conditions, we imagine that if particle i is at $\mathbf{r}_i$, there is a set of image particles at positions $\mathbf{r}_i + \mathbf{n}V^{1/3}$, where $\mathbf{n}$ is a vector with integer components. The potential energy of the atoms is

$$U(\mathbf{r}^N) = \sum_{i<j} u(r_{ij}) \ . \tag{2.1}$$

In this sum, r_{ij} is to be interpreted as the distance between $\mathbf{r}_i$ and either $\mathbf{r}_j$ or the nearest image of particle j, whichever is closer. Thus,

$$r_{ij} = |\mathbf{r}_{ij}| \equiv \min_{\mathbf{n}} |\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}V^{1/3}| \ . \tag{2.2}$$

This is the minimum image convention. In all summations over particles, the lower and upper limits are 1 and N, respectively.

The Lagrangian for the fluid is

$$\mathfrak{L}_1(\mathbf{r}^N, \dot{\mathbf{r}}^N) = \frac{m}{2} \sum_i \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i - \sum_{i<j} u(r_{ij}) \ , \tag{2.3}$$

where m is the mass of an atom. The momenta are defined as

$$\mathbf{p}_i \equiv \frac{\partial \mathfrak{L}_1(\mathbf{r}^N, \dot{\mathbf{r}}^N)}{\partial \dot{\mathbf{r}}_i} = m\dot{\mathbf{r}}_i \ . \tag{2.4}$$

The Hamiltonian is

$$\begin{aligned} \mathfrak{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) &= \sum_i \dot{\mathbf{r}}_i \cdot \mathbf{p}_i - \mathfrak{L}_1 \\ &= (2m)^{-1} \sum_i \mathbf{p}_i \cdot \mathbf{p}_i + \sum_{i<j} u(r_{ij}) \ . \end{aligned} \tag{2.5}$$

The Hamiltonian equations of motion are

$$\frac{d\mathbf{r}_i}{dt} = \frac{\partial \mathfrak{H}_1}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m} \ , \tag{2.6a}$$

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial \mathfrak{H}_1}{\partial \mathbf{r}_i} = -\sum_{j(\neq i)} \hat{\mathbf{r}}_{ij} u'(r_{ij}) \ , \tag{2.6b}$$

where u' denotes the derivative of u and $\hat{\mathbf{r}}_{ij}$ denotes a unit vector in the direction of $\mathbf{r}_i - \mathbf{r}_j$, using the minimum image convention.

A measurable structural or thermodynamic property F of the system is associated with a function $F(\mathbf{r}^N, \mathbf{p}^N; V)$ of the mechanical state of the system. The usual assumption of statistical thermodynamics is that the measured F is equal to the ensemble average of the function F over a suitably chosen ensemble of states. In this paper we are concerned with four ensembles: the microcanonical (NVE) ensemble, the canonical (NVT) ensemble, the isothermal–isobaric (NPT) ensemble, and the isoenthalpic–isobaric (NPH) ensemble.

The microcanonical ensemble average of the function F will be denoted $F_{NVE}(N, V, E)$, where the subscript denotes the nature of the ensemble and the arguments denote the numerical values of N, V, and E. It is defined as

$$\begin{aligned} F_{NVE}(N, V, E) \equiv [N!\,\Omega(N, V, E)]^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \\ \times \delta[\mathfrak{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) - E] F(\mathbf{r}^N, \mathbf{p}^N; V) \ , \end{aligned} \tag{2.7}$$

where

$$\Omega(N, V, E) \equiv (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \, \delta[\mathfrak{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) - E] \tag{2.8}$$

is the microcanonical ensemble partition function. Here $\delta[x]$ denotes the Dirac δ function. The $\mathbf{r}_i$ integrations extend over the volume V and the $\mathbf{p}_i$ integrations extend over all values from $-\infty$ to $+\infty$ for all components. The canonical average is

$$\begin{aligned} F_{NVT}(N, V, T) \equiv [N!\,Q(N, V, T)]^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \\ \times \exp\left(-\frac{\mathfrak{H}_1(\mathbf{r}^N, \mathbf{p}^N; V)}{kT}\right) F(\mathbf{r}^N, \mathbf{p}^N; V) \ , \end{aligned} \tag{2.9}$$

where

$$Q(N, V, T) \equiv (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \exp\left(-\frac{\mathfrak{H}_1(\mathbf{r}^N, \mathbf{p}^N; V)}{kT}\right) \tag{2.10}$$

and k is Boltzmann's constant. The isothermal–isobaric ensemble average is

$$F_{NPT}(N,P,T) = [N!\,\Delta(N,P,T)]^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \times \exp\left(-\frac{[PV + \mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V)]}{kT}\right) F(\mathbf{r}^N, \mathbf{p}^N; V) , \quad (2.11)$$

where

$$\Delta(N,P,T) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \times \exp\left(-\frac{[PV + \mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V]}{kT}\right) . \quad (2.12)$$

Finally, the isoenthalpic–isobaric ensemble average is

$$F_{NPH}(N,P,H) = [N!\,\Gamma(N,P,H)]^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \times \delta[\mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) + PV - H] F(\mathbf{r}^N, \mathbf{p}^N; V) , \quad (2.13)$$

where

$$\Gamma(N,P,H) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \times \delta[\mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) + PV - H] . \quad (2.14)$$

This ensemble is not as commonly used as the others. It is related to the NPT ensemble in the same way as the microcanonical ensemble is related to the canonical ensemble. Thus $\Delta(N,P,T)$ is the Laplace transform of $\Gamma(N,P,H)$ with respect to H, just as $Q(N;V,T)$ is the Laplace transform of $\Omega(N,V,E)$ with respect to E, with $(kT)^{-1}$ being the Laplace transform variable in both cases.

These ensembles are equivalent for the calculation of thermodynamic quantities.[7,8] Thus, for example, if T in the NVT ensemble is chosen so that the average value of the energy is E, then the NVE ensemble with these same values for N, V, and E will give the same value for any thermodynamic property for large values of N. More precisely, if F is an intensive property, then F_{NVE}, F_{NVT}, F_{NPT}, and F_{NPH} are equal except for differences of order N^{-1}, if the parameters of each ensemble are chosen so that all ensembles have the same average value of N, V, and E. (If F is extensive, the differences are of order N^0.) Because of these differences, the fluctuations of thermodynamic quantities about their average values are different. In this sense, the various ensembles are not equivalent.

Next we define a trajectory average or time average. Suppose $\mathbf{r}^N(t)$, $\mathbf{p}^N(t)$, and $V(t)$ are specified in some way for $t \geq 0$. Then the trajectory average of a function $F(\mathbf{r}^N, \mathbf{p}^N; V)$ is defined as

$$\overline{F} = \lim_{T\to\infty} T^{-1} \int_0^T dt\, F(\mathbf{r}^N(t), \mathbf{p}^N(t); V(t)) , \quad (2.15)$$

provided the limit exists.

In the usual molecular dynamics method, N and V are fixed, an initial choice of $\mathbf{r}^N(0)$ and $\mathbf{p}^N(0)$ is made, and Hamilton's equations of the form of (2.6) or their equivalent are solved numerically. Then trajectory averages are calculated for thermodynamic properties. The energy $\mathcal{H}_1$ is conserved along the trajectory, and the hypothesis is made that the trajectory spends equal times in all equal volumes with that same value of energy. It follows that

$$\overline{F} = F_{NVE}(N,V,E) , \quad (2.16)$$

provided $\overline{F}$ is calculated from (2.15) using the solution of (2.6) and the values of N, V, and E on the right are those that correspond to the calculated trajectory. In other words, the trajectory average is equal to the microcanonical ensemble average, and hence the latter can be calculated from the molecular dynamics trajectory.[9]

In Secs. III–V, we show that there are ways of generating trajectories so that the trajectory average of any function is equal to the ensemble average of that function over the NPH, NVT, or NPT ensembles. These ways are modifications of the usual molecular dynamics, and thus they permit the use of molecular dynamics for the calculation of averages over these other ensembles.

III. MOLECULAR DYNAMICS AT CONSTANT PRESSURE

At constant pressure, the volume of a system of N particles fluctuates. To describe such fluctuations, we devise a molecular dynamics method in which the volume is a dynamical variable rather than a fixed quantity. The result will be a way of calculating trajectories so that the trajectory average of any property is equal to the NPH ensemble average of that property.

In the constant-pressure molecular dynamics method we replace the coordinates $\mathbf{r}_i$, $i = 1, \ldots, N$, of the atoms by scaled coordinates, ρ_i, $i = 1, \ldots, N$, defined in the following way

$$\rho_i = \mathbf{r}_i / V^{1/3}, \quad i = 1, 2, \ldots, N . \quad (3.1)$$

For $\mathbf{r}_i$ in the box of volume V, each component of ρ_i is a dimensionless number between zero and one. Consider the following Lagrangian, in which a new variable Q appears.

$$\mathcal{L}_2(\rho^N, \dot{\rho}^N, Q, \dot{Q}) = \tfrac{1}{2} m Q^{2/3} \sum_{i=1}^N \dot{\rho}_i \cdot \dot{\rho}_i - \sum_{i<j=1}^N u(Q^{1/3}\rho_{ij}) + \tfrac{1}{2} M \dot{Q}^2 - \alpha Q . \quad (3.2)$$

(In evaluating the potential energy term, we use the minimum image convention for the ρ vectors in the cube of unit volume.) If we interpret Q as the volume V, then the first two terms on the right are just the Lagrangian of Eq. (2.3) expressed in terms of the new variables. The third term is a kinetic energy for the motion of Q, and the fourth represents a potential energy, $+\alpha Q$, associated with Q. Here α and M are constants.

This Lagrangian can be given a physical interpretation. Suppose the fluid to be simulated is in a container of variable volume. The fluid can be compressed by a piston. Thus, Q, whose value is the volume, is the coordinate of the piston, αV is a pV potential derived from an external pressure α acting on the piston, and

M is the mass of the piston. The piston is not of the usual cylindrical type that expands or contracts the system along only one direction; instead, a change in Q causes an isotropic expansion or contraction. This interpretation is not entirely consistent with Eq. (3.2). If Eq. (3.1) holds with $V = Q$, then

$$\dot{\mathbf{r}}_i = Q^{1/3}\dot{\boldsymbol{\rho}}_i + \tfrac{1}{3}Q^{-2/3}\dot{Q}\boldsymbol{\rho}_i \ , \tag{3.3}$$

and the kinetic energy of the atoms should contain terms with factors of $\dot{Q}$ arising from the second term on the right. Such terms do not appear in Eq. (3.2).

Despite the absence of a consistent physical interpretation, Eq. (3.2) gives a well-defined Lagrangian, and we now analyze the dynamics it generates. We will call this system "the scaled system" to distinguish it from "the original system" whose Lagrangian is $\mathcal{L}_1$. The momentum conjugate to $\boldsymbol{\rho}_i$ will be denoted $\boldsymbol{\pi}_i$.

$$\boldsymbol{\pi}_i = \frac{\partial \mathcal{L}_2}{\partial \dot{\boldsymbol{\rho}}_i} = mQ^{2/3}\dot{\boldsymbol{\rho}}_i \ . \tag{3.4}$$

The momentum conjugate to Q will be denoted Π.

$$\Pi = \frac{\partial \mathcal{L}_2}{\partial \dot{Q}} = M\dot{Q} \ . \tag{3.5}$$

The Hamiltonian is

$$\begin{aligned}\mathcal{H}_2(\boldsymbol{\rho}^N, \boldsymbol{\pi}^N, Q, \Pi) &= \sum_{i=1}^{N} \dot{\boldsymbol{\rho}}_i \cdot \boldsymbol{\pi}_i + \dot{Q}\Pi - \mathcal{L}_2(\boldsymbol{\rho}^N, \dot{\boldsymbol{\rho}}^N, Q, \dot{Q}) \\ &= (2mQ^{2/3})^{-1}\sum_{i=1}^{N} \boldsymbol{\pi}_i \cdot \boldsymbol{\pi}_i + \sum_{i<j=1}^{N} u(Q^{1/3}\rho_{ij}) + (2M)^{-1}\Pi^2 + \alpha Q \ .\end{aligned} \tag{3.6}$$

The Hamiltonian equations of motion are:

$$\frac{d\mathbf{p}_i}{dt} = \frac{\partial \mathcal{H}_2}{\partial \boldsymbol{\pi}_i} = \frac{\boldsymbol{\pi}_i}{mQ^{2/3}} \tag{3.7a}$$

$$\frac{d\boldsymbol{\pi}_i}{dt} = -\frac{\partial \mathcal{H}_2}{\partial \boldsymbol{\rho}_i} = -Q^{1/3}\sum_{j(\neq i)=1}^{N} \frac{\boldsymbol{\rho}_{ij}u'(Q^{1/3}|\boldsymbol{\rho}_{ij}|)}{|\boldsymbol{\rho}_{ij}|} \tag{3.7b}$$

$$\frac{dQ}{dt} = \frac{\partial \mathcal{H}_2}{\partial \Pi} = \frac{\Pi}{M} \tag{3.7c}$$

$$\begin{aligned}\frac{d\Pi}{dt} = -\frac{\partial \mathcal{H}_2}{\partial Q} = -(3Q)^{-1}\Bigg(&-2(2mQ^{2/3})^{-1}\sum_{i=1}^{N} \boldsymbol{\pi}_i \cdot \boldsymbol{\pi}_i \\ &+ Q^{1/3}\sum_{i<j} \rho_{ij}u'(Q^{1/3}\rho_{ij}) + 3\alpha Q\Bigg) \ .\end{aligned} \tag{3.7d}$$

These equations of motion for the scaled system can be solved numerically to give the coordinates and momenta as a function of time. Such molecular dynamics calculations give trajectory for the scaled system: $\boldsymbol{\rho}^N(t)$, $\boldsymbol{\pi}^N(t)$, $Q(t)$, and $\Pi(t)$.

The trajectory average of any function, $G(\boldsymbol{\rho}^N, \boldsymbol{\pi}^N, Q, \Pi)$, of the coordinates and momenta of the scaled system is defined as in Eq. (2.15).

$$\bar{G} \equiv \lim_{T\to\infty} T^{-1}\int_0^T dt\, G(\boldsymbol{\rho}^N(t), \boldsymbol{\pi}^N(t), Q(t), \Pi(t)) \ . \tag{3.8}$$

We assume that this time average is equal to an ensemble average of G over an NE ensemble, i.e., an ensemble with fixed energy and fixed number of particles. (This can be regarded as a microcanonical, NVE, ensemble for the scaled system, in which V is unity since the coordinates $\boldsymbol{\rho}_i$ are constrained to lie within a dimensionless unit volume.) It follows that

$$\bar{G} = G_{NE}(N, E) \tag{3.9}$$

where

$$\begin{aligned}G_{NE}(N, E) = [N!\,\Omega_2(N, E)]^{-1}\int_1 d\boldsymbol{\rho}^N \int d\boldsymbol{\pi}^N \int_0^\infty dQ \int_{-\infty}^{\infty} d\Pi \\ \times \delta[\mathcal{H}_2(\boldsymbol{\rho}^N, \boldsymbol{\pi}^N, Q, \Pi) - E]G(\boldsymbol{\rho}^N, \boldsymbol{\pi}^N, Q, \Pi)\end{aligned} \tag{3.10}$$

and

$$\begin{aligned}\Omega_2(N, E) \equiv (N!)^{-1}\int_1 d\boldsymbol{\rho}^N \int d\boldsymbol{\pi}^N \int_0^\infty dQ \int_{-\infty}^{\infty} d\Pi \\ \times \delta[\mathcal{H}_2(\boldsymbol{\rho}^N, \boldsymbol{\pi}^N, Q, \Pi) - E] \ .\end{aligned} \tag{3.11}$$

In these two integrals, each $\boldsymbol{\rho}_i$ is integrated over the unit cube. The value of E to choose on the right-hand side of (3.9) is the constant energy of the trajectory used to calculate the left-hand side.

We now define a correspondence between the scaled system and the original system. This correspondence is given by

$$V = Q \ , \tag{3.12a}$$

$$\mathbf{r}_i = Q^{1/3}\boldsymbol{\rho}_i \ , \tag{3.12b}$$

$$\mathbf{p}_i = \boldsymbol{\pi}_i/Q^{1/3} \ . \tag{3.12c}$$

Every state of the scaled system corresponds to a unique value of V and a unique point in the phase space of the original system for that volume V. (Note that Π does not appear in these equations, so each V and phase-space point in the original system corresponds to a manifold of states of the scaled system.)

Using this correspondence, the calculated trajectory for the scaled system can be used to generate a trajectory for the original system. Along this latter trajectory, the volume varies with time.

$$V(t) = Q(t) \ , \tag{3.13a}$$

$$\mathbf{r}_i(t) = Q(t)^{1/3}\boldsymbol{\rho}_i(t) \ , \tag{3.13b}$$

$$\mathbf{p}_i(t) = \boldsymbol{\pi}_i(t)/Q(t)^{1/3} \ . \tag{3.13c}$$

The equations of motion for this trajectory can be derived from (3.13) and (3.7).

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m} + \tfrac{1}{3}\mathbf{r}_i\frac{d\ln V}{dt} \ , \tag{3.14a}$$

$$\frac{d\mathbf{p}_i}{dt} = -\sum_{j(\neq i)=1}^{N} \hat{r}_{ij}u'(\mathbf{r}_{ij}) - \tfrac{1}{3}\mathbf{p}_i\frac{d\ln V}{dt} \ , \tag{3.14b}$$

$$\frac{Md^2V}{dt^2} = -\alpha + \left(\frac{2}{3}\sum_{i=1}^{N}\frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} - \frac{1}{3}\sum_{i<j=1}^{N} r_{ij}u'(r_{ij})\right)\Big/ V \ . \tag{3.14c}$$

These equations are not the same as Hamilton's equations for the original system. Compare Eqs. (2.6). In the limit, however, that the mass of the piston, M, becomes infinitely large and $dV/dt = 0$ initially, these equations become equivalent to the dynamical equations for the original system.

The trajectory defined by Eq. (3.14) can be used to calculate time averages of any function $F(\mathbf{r}^N, \mathbf{p}^N; V)$ according to Eq. (2.15). The most important result of

this section is that *the time average of any F calculated from this trajectory is equal to the ensemble average of F for an isoenthalpic-isobaric ensemble in which the pressure is* α; i.e.,

$$\overline{F} = F_{NPH}(N, \alpha, H) , \tag{3.15}$$

for some appropriate value of H, except for negligible errors.

The proof is straightforward. For any function $F(\mathbf{r}^N, \mathbf{p}^N; V)$, we can define a corresponding $G(\rho^N, \pi^N, Q, \Pi)$ by

$$G(\rho^N, \pi^N, Q, \Pi) = F(Q^{1/3}\rho^N, \pi^N/Q^{1/3}; Q) . \tag{3.16}$$

Then it is clear that

$$\overline{G} = \overline{F} , \tag{3.17}$$

where the left-hand side is defined in Eq. (3.8) and the right-hand side in Eq. (2.15). Combining (3.17), (3.9), and (3.10), we find

$$\overline{F} = [N!\,\Omega_2(N, E)]^{-1} \int_1 d\rho^N \int d\pi^N \int_0^\infty dQ \int_{-\infty}^\infty d\Pi \times \delta[\mathcal{H}_2(\rho^N, \pi^N, Q, \Pi) - E] F(Q^{1/3}\rho^N, \pi^N/Q^{1/3}; Q). \tag{3.18}$$

The variables of integration are converted to V, $\mathbf{r}^N$, and ρ^N to obtain

$$\overline{F} = \frac{\int_{-\infty}^{\infty} d\Pi \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) + \alpha V + (2M)^{-2}\Pi^2 - E] F(\mathbf{r}^N, \mathbf{p}^N; V)}{\int_{-\infty}^{\infty} d\Pi \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V) + \alpha V + (2M)^{-1}\Pi^2 - E]} , \tag{3.19}$$

which looks very much like an ensemble average of F, except for the Π integration, which plays no role in any ensemble for the original system. In both the numerator and denominator, however, the integrand for fixed Π is closely related to the isoenthalpic-isobaric ensemble. Using (2.13) and (2.14), we find

$$\overline{F} = \frac{\int_{-\infty}^{\infty} d\Pi\, \Gamma(N, \alpha, E - \Pi^2/2M) F_{NPH}(N, \alpha, E - \Pi^2/2M)}{\int_{-\infty}^{\infty} d\Pi\, \Gamma(N, \alpha, E - \Pi^2/2M)} \tag{3.20}$$

The ensemble average in the numerator can be expanded in a power series in $\Pi^2/2M$.

$$F_{NPH}(N, \alpha, E - \Pi^2/2M) = F_{NPH}(N, \alpha, E) - \frac{\Pi^2}{2M} \frac{\partial F_{NPH}(N, \alpha, E)}{\partial H} + O(N^{-2}) . \tag{3.21}$$

The correction term is proportional to $\partial^2 F_{NPH}/\partial H^2$. We have assumed that F represents an intensive property in estimating the order of magnitude of the correction term. (If F were extensive, the correction would be of order N^{-1}.) Thus

$$\overline{F} = F_{NPH}(N, \alpha, E) - \frac{\partial F_{NPH}(N, \alpha, E)}{\partial H} \times \frac{\int_{-\infty}^{\infty} d\Pi\, \Gamma(N, \alpha, E - \Pi^2/2M)(\Pi^2/2M)}{\int_{-\infty}^{\infty} d\Pi\, \Gamma(N, \alpha, E - \Pi^2/2M)} + O(N^{-2}) . \tag{3.22}$$

The ratio of the two integrals can easily be shown to be equal to $\overline{\Pi^2/2M}$. [To show this, use Eqs. (3.9) and (3.10) for $G = \Pi^2/2M$, and transform the resulting integrals to integrals over $\mathbf{r}^N$, $\mathbf{p}^N$, and V, as we did in going from (3.18) to (3.19).] Therefore,

$$\overline{F} = F_{NPH}(N, \alpha, E) - \overline{\Pi^2/2M}\, \partial F_{NPH}(N, \alpha, E)/\partial H + O(N^{-2}) = F_{NPH}(N, \alpha, E - \overline{\Pi^2/2M}) + O(N^{-2}) . \tag{3.23}$$

Q.E.D. Compare Eq. (3.15). (If F had represented an extensive quantity, the correction term would be of order N^{-1}.) In deriving this result, we have assumed that $\overline{\Pi^2/2M}$ is of order N^0. The variable Π is a momentum conjugate to a coordinate that is coupled to $6N$ other position and momentum variables. The momentum Π appears in the Hamiltonian only in a quadratic energy term, $\Pi^2/2M$. The average, $\overline{\Pi^2/2M}$, will therefore be $\frac{1}{2}kT$, where T is the temperature corresponding to the fixed N and E of the scaled system. It follows that $\overline{\Pi^2/2M}$ is intensive.

In other words, when the trajectory used to calculate time averages of the original system is obtained from a trajectory of the scaled system, the time average of any F is the NPH ensemble average of that F. The value of P for the ensemble is the value of α in the Lagrangian of the scaled system. The value of H for the ensemble is the energy of the trajectory of the scaled system minus the time average kinetic energy associated with the motion of Q.

Using the equivalence of the various ensembles, we can conclude from (3.23) that

$$\begin{aligned}\overline{F} &= F_{NVE}(N, \overline{V}, E - \overline{\Pi^2/2M} - \alpha\overline{V}) + O(N^{-1}) \\ &= F_{NVT}(N, \overline{V}, T) + O(N^{-1}) \\ &= F_{NPT}(N, \alpha, T) + O(N^{-1}) ,\end{aligned} \tag{3.24}$$

where $T = k^{-1}\overline{\Pi^2/2M}$. Here the N^{-1} errors arise from the slight lack of equivalence of the ensembles. Note, however, that the error term in (3.23) is of order N^{-2}. Thus, the mean-square fluctuations in the NPH are equal to those that occur along the trajectory.

The results of this section provide a basis for a molecular dynamics simulation method for constant pressure. To simulate a fluid with Lagrangian $\mathcal{L}_1$, we construct the analogous scaled system with Lagrangian $\mathcal{L}_2$. The trajectory of the scaled system is converted into a trajectory for the fluid with volume fluctuations. Time averages along this trajectory can then be calculated. These time averages are equal to ensemble averages corresponding to the thermodynamic state with the desired pressure. In constructing the scaled system, we have to decide on the values of the constants α, E, and M.

The quantity α, which is a parameter appearing in $\mathcal{L}_2$ and in the equations of motion, is chosen to be the value of the pressure of the fluid thermodynamic state to be simulated.

The quantity E, which is the energy of the trajectory of the scaled system, is equal to the enthalpy of the fluid thermodynamic state to be simulated, except for a small correction of $\frac{1}{2}kT$. Thus, if desired, the value of this enthalpy can be precisely chosen in advance.

The quantity M is a parameter appearing in $\mathcal{L}_2$ and in the equations of motion. It can be interpreted as the mass of a piston whose motion expands or compresses the fluid. The trajectory averages calculated from a simulation are independent of the value of M, as long as M is finite and positive. [This follows from Eq. (3.23) by the following argument. A particular value of E for the scaled system implies a particular temperature of the scaled system and, hence, a particular value of $\overline{\Pi^2/2M}$ that is independent of M. Hence, despite the appearance of M on the right-hand side of Eq. (3.23), the right-hand side is independent of M.] Hence, any finite positive value can be chosen, if the only goal of the simulation is to calculate equilibrium averages.

If the goal is also to simulate the dynamics of atoms in a small volume under constant pressure conditions, then it is important to choose an appropriate value of M. Equation (3.14c) can be interpreted as Newton's third law for the coordinate of a piston on which two forces act. The first is $-\alpha$ and the second is

$$\left(\frac{2}{3}\sum_{i=1}^{N}\frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2M}-\frac{1}{3}\sum_{i<j=1}^{N}r_{ij}u'(r_{ij})\right)\Big/V\ .$$

The first is the negative of the external applied pressure and the second is the internal pressure of the fluid. An imbalance between these two forces causes an acceleration of the piston. The coordinate of the piston will fluctuate as the motion of the atoms causes the internal pressure to fluctuate. The time scale for this volume fluctuation will be determined by the mass of the piston, M. For a small sample of fluid imbedded in a much larger sample of fluid, the volume of the small sample will also fluctuate in response to an imbalance between the internal and external pressure. The time scale for the fluctuation of the volume of a sample of fluid is approximately equal to the length of the sample divided by the speed of sound in the sample. Thus, it is desirable to choose the mass M so that the time scale for the fluctuations of Q in the scaled system is approximately equal to $Q^{1/3}$ divided by the speed of sound in the fluid.

IV. MOLECULAR DYNAMICS AT CONSTANT TEMPERATURE

At constant temperature, the energy of a system of N particles fluctuates. In order to simulate such a system, we need some mechanism for introducing energy fluctuations. It might be possible to do this by inventing one or more additional degrees of freedom, as we did in the constant pressure case. We have not been able to do this in a practical way. Instead, we resort to the use of stochastic forces that act on the atoms of the sample and change their kinetic energy. The result will be a way of calculating trajectories so that the trajectory average of any property is equal to the NVT ensemble average of this quantity.

In the constant temperature molecular dynamics method, the equations of motion of the N particles in volume V are the Hamiltonian equations, Eq. (2.6), supplemented by a stochastic collision term in the equation for $d\mathbf{p}_i/dt$. Each stochastic collision is an instantaneous event that affects the momentum of one particle. The collisions suffered by a particle occur in accord with a Poisson process,[10,11] and the times at which different particles suffer collisions are statistically uncorrelated. Between stochastic collisions, the state of the system evolves in accordance with Eq. (2.6).

To perform the simulation we must first choose the numerical values of two parameters: T and ν. The first, T, is the desired temperature of the sample. The second, ν, is the mean rate at which each particle suffers stochastic collisions. The probability that a particular particle suffers a stochastic collision in any small time interval Δt is $\nu\Delta t$.

The times at which each particle suffers a collision is decided before beginning the simulation. This can be done by using random numbers to generate the values for the time intervals between successive collisions of a particle, such intervals being distributed according to

$$P(t)=\nu e^{-\nu t}\ , \tag{4.1}$$

where $P(t)\Delta t$ is the probability that an interval between collisions is between t and $t+\Delta t$. (Alternatively, as the calculation proceeds, random numbers can be used to decide which particles are to suffer collisions in any small time interval.)

We pick an initial set of positions and momenta $\mathbf{r}^N(0)$ and $\mathbf{p}^N(0)$, and integrate the Hamiltonian equations of motion until the time of the first stochastic collision. Suppose the particle suffering the collision is i. The value of the momentum of particle i after the collision is chosen at random from a Boltzmann distribution at temperature T. The change in momentum takes place instantaneously. All other particles are unaffected by the collision. Then the Hamiltonian equations for the entire collection of particles are integrated until the time of the next stochastic collision. This process is then repeated.

The result of this constant temperature molecular dynamics procedure is a trajectory, specified by $\mathbf{r}^N(t)$ and $\mathbf{p}^N(t)$, for N particles in a volume V with periodic boundary conditions. This trajectory can be used to calculate time averages of any function $F(\mathbf{r}^N,\mathbf{p}^N;V)$ according to Eq. (2.15). The central result of this section is that *under certain conditions* (see below) *the time average of any F calculated from this trajectory is equal to the ensemble average of F for the canonical ensemble in which the temperature is T*, i.e.,

$$\bar{F}=F_{NVT}(N,V,T)\ . \tag{4.2}$$

The proof of this theorem is very similar to the proof of the theorem that is basic to the use of Monte Carlo simulations to perform canonical ensemble averages.[11] First we note that the constant temperature molecular dynamics procedure generates a Markov chain in phase space.[12] The states in phase space for a finite number of particles are not countable. However, in practice the calculations will be performed using a finite number

of significant figures, and so we assume that the number of states is countable. Thus we can apply the many powerful theorems about Markov chains with a countable number of states.

For certain Markov chains, the probability that the simulated system is in each state at time t approaches a limit as $t \to \infty$, and this limiting probability distribution is independent of the initial state of the system. Then the time average of F along the trajectory is equal to an ensemble average calculated with the unique limiting distribution. Sufficient conditions for this to be true are that the chain must have stationary transition probabilities, must be irreducible and aperiodic, and must have an invariant probability distribution.[13] The invariant probability distribution is the unique limiting distribution.

Let $a_j^{(n)}$ be the probability that the state of the system is j at the nth time. Then for a Markov chain with stationary transition probabilities,

$$a_j^{(n+1)} = \Sigma_k a_k^{(n)} p_{kj} , \tag{4.3}$$

where p_{kj}, the probability of making a transition from state k to state j is one time step, is independent of n. For the constant-temperature molecular dynamics procedure, the transitions are caused by Hamiltonian motion and stochastic collisions. This procedure is consistent with these equations and satisfies the definition of a Markov chain.[14]

An invariant probability distribution u_i is defined as one that satisfies the equations

$$u_j = \Sigma_k u_k p_{kj} \tag{4.4}$$

$$\Sigma_j u_j = 1 . \tag{4.5}$$

If

$$a_j^{(n)} = u_j , \tag{4.6}$$

it follows that

$$a_j^{(n+1)} = u_j , \tag{4.7}$$

and

$$a_j^{(m)} = u_j \tag{4.8}$$

for all $m \geq n$. An invariant distribution, hence, is one that, if it were the actual distribution at one time, would remain the distribution for all times. For the constant-temperature molecular dynamics procedure, the canonical distribution, which is

$$[N!Q(N, V, T)]^{-1} \exp[-\mathcal{H}_1(\mathbf{r}^N, \mathbf{p}^N; V)/kT]$$

is an invariant probability distribution if T in this formula is the same as the T that governs the stochastic collisions. This follows because, as a consequence of Liouville's theorem, the Hamiltonian motion leaves this distribution unchanged[15] and because stochastic collisions of the type discussed above obviously leave the distribution unchanged.

To prove that an irreducible chain is aperiodic,[16] it is sufficient[17] to prove that there is at least one state i with $p_{ii} > 0$. Consider a state in which the potential energy of the particles is a local or global minimum and in which all the momenta are zero. (Such a state must exist if the energy of the system has a lower bound.) This state has a nonzero value of p_{ii}.

The remaining condition is that the chain be irreducible, i.e., that every state can be reached from every other state in a finite amount of time. Since this is probably not true under all circumstances, we prefer to keep this as a condition in the statement of the theorem. Hence the theorem should be restated as: *if the Markov chain generated by the constant temperature molecular dynamics procedure is irreducible in phase space, the time average of any F calculated from a trajectory is equal to the ensemble average of F for the canonical ensemble in which the temperature is T*, i.e.,

$$\overline{F} = F_{NVT}(N, V, T) . \tag{4.2}$$

Q.E.D.

Next we must consider the conditions under which the Markov chain is irreducible. First let us consider the Markov chain that is generated by Hamiltonian motion without stochastic collisions. This is obviously not irreducible in phase space because Hamiltonian motion conserves energy and momentum. If the system is started in one state, only states on the same manifold of constant energy and momentum can be reached. Each stochastic collision in the modified molecular dynamics procedure can change both the energy and momentum of the system. One can easily devise a sequence of pairs of stochastic collisions that will change both the energy and momentum of the system in any desired way. Thus by stochastic collisions it is possible to make transitions from any energy–momentum manifold to any other such manifold. Suppose that the chain generated by Hamiltonian motion is irreducible on the manifold of states of constant energy and momentum; that is, suppose that a Hamiltonian trajectory starting on any state eventually passes through every state of the same energy and momentum. It follows that the chain for the modified molecular dynamics procedure is irreducible in all of phase space, and the theorem applies.

One of the ways of justifying the use of molecular dynamics trajectories to calculate microcanonical ensemble averages is to assume that the Hamiltonian motion is irreducible on a manifold of constant energy and momentum. The paragraph above shows that this same assumption for all energies and momenta justifies the use of the constant-temperature molecular dynamics method to calculate canonical ensemble averages.

Irreducibility of Hamiltonian motion on the constant energy–momentum manifolds is a sufficient but not necessary condition for irreducibility of the constant-temperature molecular dynamics motion in all phase space. It is easy to imagine that the stochastic collisions increase the freedom of motion in phase space to such an extent that the latter motion is irreducible, even though the former is not.

A major cause for concern about lack of irreducibility of the motion generated by the constant-temperature molecular dynamics procedure arises from the possibility that at high density the system may be trapped in

certain regions of configuration space from which it cannot depart either in an infinitely long time or in the finite time of an actual simulation. Stochastic collisions may be of little help in eliminating this possibility because they do not directly affect the coordinates of the particles. If this situation actually exists for a particular fluid of interest and if the region of configuration space in which the system is trapped is atypical of most of the available configuration space, then trajectory averages calculated by the constant-temperature molecular dynamics will not be accurate approximations to canonical ensemble averages. These are conditions under which the usual molecular dynamics method and Monte Carlo method should also be expected to fail.

To perform a constant-temperature molecular dynamics calculation, it is necessary to choose a value of ν, the stochastic collision frequency for a particle. Equation (4.2) assures us, however, that the calculated trajectory averages are independent of the choice of ν if the irreducibility condition holds. In particular, the mean-square fluctuation of the total energy from its average value is independent of ν. The time dependence of the fluctuations will be very sensitive to ν, however. It is reasonable to choose ν so that the time for the decay of energy fluctuations along the trajectory will be the same as the time for decay of energy fluctuations of a small volume of real liquid surrounded by a much larger volume. This optimum value of ν can be estimated by the following procedure.

Consider a small sample of matter with volume V surrounded by a much larger heat bath of similar matter at temperature T. Suppose there is a temperature fluctuation in the small sample so that its average temperature is $T+\Delta T$. The small sample will gain or lose energy at a rate proportional to the temperature difference ΔT and to the thermal conductivity κ. By dimensional analysis, the rate of heat gain (in energy per unit time) is easily shown to be $-a\kappa\Delta T V^{1/3}$, where a is a dimensionless constant that depends on the shape of the sample and upon the temperature distribution within the small sample. The dynamics of this sample can be simulated by the constant-temperature molecular dynamics technique. Each stochastic collision changes the energy of the system by $-\frac{3}{2}k\Delta T$, since the average kinetic energy of a particle before collision is $\frac{3}{2}k(T+\Delta T)$ and after collision is $\frac{3}{2}kT$. The total rate of occurrence of stochastic collisions is $N\nu$. Hence the rate of energy gain is $-\frac{3}{2}N\nu k\Delta T$. If we equate these two expressions for the rate of energy gain, we find

$$\nu = \tfrac{2}{3}a\kappa V^{1/3}/kN = \tfrac{2}{3}a\kappa/k\rho^{1/3}N^{2/3}\,, \tag{4.9}$$

where

$$\rho = N/V \tag{4.10}$$

is the number density of particles. If the stochastic collisions are to simulate the effects of the surroundings of a collection of N atoms in a fluid, the collision frequency should be that given in this formula. Note that ν is of order $N^{-2/3}$, and the total collision rate for a sample is of order $N^{1/3}$. If some estimate of κ is available, then the proper choice of ν can be estimated using (4.10).

A crude but instructive estimate of ν can be obtained by imagining that N is unity, i.e., that the small system being simulated contains only one particle. Then all the other molecules comprise the heat bath, and it is reasonable to suppose that the required stochastic collision frequency should be the actual collision frequency ν_c for a particle. Applying Eq. (4.9) then, we find

$$\nu_c = (2a/3)\kappa/k\rho^{1/3}\,. \tag{4.11}$$

Hence (4.9) can be rewritten as

$$\nu = \nu_c/N^{2/3}\,. \tag{4.12}$$

For large enough N, the stochastic collision frequency will be much smaller than the intermolecular collision frequency. Therefore, for most of the time, most of the molecules will be moving according to the conservative equations of motion for a closed system. The stochastic interruptions will be infrequent, but they will cause the energy of the system to relax to a value appropriate to the temperature T at a rate appropriate for a system of N particles and will cause the energy to fluctuate about its equilibrium value with the magnitude appropriate to a canonical ensemble.

V. MOLECULAR DYNAMICS AT CONSTANT TEMPERATURE AND PRESSURE

At constant temperature and pressure, the energy, pressure, and enthalpy of a system of N particles fluctuate. In order to simulate such a system, we need some method for simulating these fluctuations. This can be done by introducing stochastic collisions into the constant-pressure molecular dynamics method. The result is a way to calculate trajectories so that the time average of any function F is equal to the NPT ensemble average of this quantity.

In the constant-temperature constant pressure molecular dynamics method we start with the Hamiltonian equations (3.7) for the scaled system. In addition, we imagine instantaneous stochastic collisions that affect the momentum of one particle at a time. As in Sec. IV, the collisions suffered by a particle occur in accord with a Poisson process, and the times at which the different particles suffer collisions are statistically uncorrelated. The mean frequency for these collisions is chosen according to the considerations discussed at the end of Sec. IV. (We could also have stochastic collisions that change the momentum Π of the piston.) Between stochastic collisions, the state of the system evolves in accordance with Eqs. (3.7).

Each stochastic collision is instantaneous, and so it occurs at a particular value of Q, the volume coordinate. The Boltzmann distribution for particle momentum π_i for a particular value of Q is proportional to

$$\exp[-\pi_i\cdot\pi_i/2mQ^{2/3}kT]\,.$$

The effect of each stochastic collision is to replace the momentum of the affected particle by a new value chosen at random from this distribution. (Note that the mean-square value of π_i depends on the value of Q.)

The calculated trajectory of the scaled system can

then be converted into a trajectory of the original system using the correspondence in Eq. (3.13). This latter trajectory can be used to calculate time averages of any function $F(\mathbf{r}^N, \mathbf{p}^N; V)$ according to Eq. (2.15). The most important result of this section is that *the time average of any F calculated from this trajectory is equal to the ensemble average of F for an isothermal–isobaric ensemble in which the pressure is α and the temperature is T*; i.e.,

$$\bar{F} = F_{NPT}(N, \alpha, T) , \tag{5.1}$$

where α is the parameter in the scaled Lagrangian and T is the temperature governing the effect of the stochastic collisions.

The proof of this theorem will merely be outlined, since it is similar to those in Secs. III and IV. For the function $F(\mathbf{r}^N, \mathbf{p}^N; V)$, we define the function $G(\rho^N, \pi^N, Q, \Pi)$ by Eq. (3.16). It follows that

$$\bar{F} = \bar{G} , \tag{5.2}$$

where the left-hand side is defined in Eq. (2.15) and the right-hand side in (3.8). Then we assume that the Hamiltonian motion of the scaled system is irreducible on a manifold of constant energy and constant total particle momentum in the phase space of the scaled system. Stochastic collisions will change the energy and momentum. It follows, as in Sec. IV, that the Markov chain generated by the combination of Hamiltonian motion and stochastic collisions is irreducible in the entire phase space of the scaled system. If $\alpha > 0$, an aperiodic state can be found by minimizing the $\mathcal{H}_2$. The stationary distribution for this Markov chain is a Boltzmann distribution at temperature T. It follows that

$$\bar{G} = G_{NT}(N, T) \equiv [N! Q_2(N, T)]^{-1} \int_1 d\rho^N \int d\pi^N \int_0^\infty dQ \int_{-\infty}^\infty d\Pi \times \exp\left(-\frac{\mathcal{H}_2(\rho^N, \pi^N, Q, \Pi)}{kT}\right) G(\rho^N, \pi^N, Q, \Pi) \tag{5.3}$$

where

$$Q_2(N, T) \equiv (N!)^{-1} \int_1 d\rho^N \int d\pi^N \int_0^\infty dQ \int_{-\infty}^\infty d\Pi \times \exp\left(-\frac{\mathcal{H}_2(\rho^N, \pi^N, Q, \Pi)}{kT}\right) . \tag{5.4}$$

Because Π appears in $\mathcal{H}_2$ only in a quadratic term that contains no other coordinates or momenta and because G is independent of Π [see Eq. (3.16)], the Π integrals in the numerator and denominator of Eq. (5.3) cancel. When the integrations over ρ^N, π^N, and Q are converted to integrations over $\mathbf{r}^N, \mathbf{p}^N$, and V using Eq. (3.12), the result is

$$\bar{G} = F_{NPT}(N, \alpha, T) . \tag{5.5}$$

Eq. (5.1) follows from (5.2) and (5.5).

Q.E.D.

VI. COMMENTS AND POTENTIAL APPLICATIONS

The methods discussed in this paper allow the dynamics of a system of a small number of particles at constant temperature and/or pressure to be simulated by calculation of trajectories in various ways. They simulate the effect of surrounding particles without creating undesirable surfaces. Moreover, the methods simulate not only the forces that drive the system to equilibrium at a given value of the temperature and/or pressure, but also the forces that cause the energy and/or volume of the system to fluctuate about their equilibrium values. The main conclusions of this paper are a set of theorems relating time averages along the calculated trajectory to ensemble averages in various ensembles.

The emphasis of the discussion has been on the calculation of ensemble averages of functions $F(\mathbf{r}^N, \mathbf{p}^N; V)$. An interesting, but still open, question is whether time correlation functions calculated along these trajectories are related to transport coefficients. For example, consider the momentum autocorrelation function, $C_{pp}(t)$. As a time integral along a trajectory it would be defined as

$$C_{pp}^{(t)}(t) \equiv N^{-1} \Sigma_i \lim_{T\to\infty} T^{-1} \int_0^T d\tau\, \mathbf{p}_i(t+\tau) \cdot \mathbf{p}_i(t) .$$

As an ensemble average, it would be defined as

$$C_{pp}^{(e)}(t) \equiv \langle N^{-1} \Sigma_i \mathbf{p}_i \cdot \mathbf{P}_i(t; \mathbf{r}^N, \mathbf{p}^N, V) \rangle$$

where $\mathbf{P}_i(t; \mathbf{r}^N, \mathbf{p}^N, V)$ is the momentum at time t of particle i, given that the state of the system at time 0 is $(\mathbf{r}^N, \mathbf{p}^N)$ in volume V, and the angular brackets denote an average over the ensemble of interest. In the calculation of $\mathbf{P}_i(t; \mathbf{r}^N, \mathbf{p}^N, V)$, the volume V is fixed and the motion should follow purely Hamiltonian dynamics. $C_{pp}^{(e)}(t)$ is related to the self-diffusion coefficient. Is it true that $C_{pp}^{(e)}(t) = C_{pp}^{(t)}(t)$, when the trajectory used on the right corresponds to the ensemble on the left in the sense of Secs. III–V of this paper?

More generally, it is true that the time evolution of any property of an N particle system simulated using the methods of Secs. III–V is the same as that of a real system of N particles surrounded by a much larger amount of similar matter at constant temperature and/or pressure? It is plausible that this is true for the constant-temperature–constant-pressure simulation if the parameters M and ν are chosen to make the time scales for the decay of volume and energy fluctuations in the simulation equal to values appropriate to the real system. It is even more plausible that properties calculated in simulations at constant pressure and temperature for small N are more similar to real properties than the usual constant energy constant volume simulations for the same small N. However, we have not been able to prove these conjectures.

These simulation methods are likely to be useful in a number of situations. (1) When a system is to be simulated for only a small number of thermodynamic states, these methods can be used to insure that desired values of temperature and/or pressure are achieved in each simulation. (2) The methods allow energy and density fluctuations to take place, thus perhaps facilitating the study of such processes as nucleation and phase separation which involve large fluctuations. (3) The meth-

ods allow the investigation of how a system responds to finite rates of heating, cooling, compression, and expansion. This may be useful for the study of the glass transition that takes place when a liquid is cooled and for the study of bubble formation that takes place when a liquid is heated and decompressed. (4) The methods allow the simulation of nonequilibrium processes such as chemical reactions and phase changes that release a large amount of energy. If such a process is simulated with the usual molecular dynamics method using a small system that has a small heat capacity, the temperature will rise to an unrealistic extent. In the case of chemical reactions, the rise in temperature may increase the rate of the reverse reaction in an unrealistic way. In the case of a phase transition to a phase of lower energy, the rise in temperature may destroy the newly formed nuclei of the emerging phase. The constant temperature simulations would eliminate these problems by allowing the extra energy to be released to the surroundings at a physically reasonable rate.

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[5]See, for example: (a) F. H. Stillinger and A. Rahman, J. Chem. Phys. 60, 1545 (1974); (b) J. Owicki and H. A. Scheraga, J. Am. Chem. Soc. 99, 7413 (1977); (c) H. Popkie, H. Kistenmacher, and E. Clementi, J. Chem. Phys. 59, 1323 (1973); (d) P. J. Rossky and M. Karplus, J. Am. Chem. Soc. 101, 1913 (1979); (e) W. B. Streett and D. J. Tildesley, Proc. R. Soc. London A 348, 485 (1976).

[6]N. Metropolis, A. W. Metropolis, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).

[7]T. L. Hill, *An Introduction to Statistical Thermodynamics* (Addison-Wesley, Reading, 1960), p. 38.

[8]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 110.

[9]In the dynamics calculation, the momentum of the system is also conserved. Thus, it would be more accurate to say that the trajectory average is equal to an ensemble average in which the total momentum is specified in addition to N, V, and E.

[10]W. Feller, *An Introduction to Probability Theory and Its Applications*, 3rd ed. (Wiley, New York, 1950), Vol. I, pp. 446–448.

[11]E. Parzen, *Stochastic Processes* (Holden-Day, San Francisco, 1962), pp. 117–123.

[12]Strictly speaking, it generates a Markov process rather than a Markov chain, since the time is a continuous rather than discrete variable. The dynamical equations describing the process will in practice be solved by using a discrete grid of times, and we assume that it is correct to regard the process as a chain and apply theorems that have been proven for chains.

[13]Reference 10, p. 394.

[14]Reference 10, p. 374.

[15]Any distribution function that expresses the probability density at a point in phase space as a function of only the value of the Hamiltonian at that point is invariant with respect to the motion generated by that Hamiltonian.

[16]An aperiodic chain is a chain all of whose states are aperiodic. See Ref. 10, p. 387, for the definition of an aperiodic state.

[17]If such a state exists, it is aperiodic (Ref. 10, p. 387), and hence the chain is aperiodic if it is irreducible (Ref. 10, p. 391).