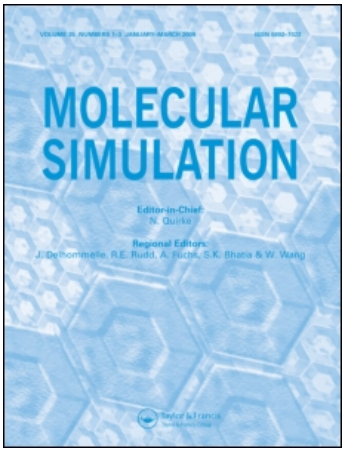

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Grand Molecular Dynamics: A Method for Open Systems

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GRAND MOLECULAR DYNAMICS: A METHOD FOR OPEN SYSTEMS

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We present a new molecular dynamics method for studying the dynamics of open systems. The method couples a classical system to a chemical potential reservior. In the formulation, following the extended system dynamics approach, we introduce a variable, ν to represent the coupling to the chemical potential reservoir. The new variable governs the dynamics of the variation of number of particles in the system. The number of particles is determined by taking the integer part of ν. The fractional part of the new variable is used to scale the potential energy and the kinetic energy of an additional particle; i.e., we introduce a *fractional particle*. We give the ansatz Lagrangians and equations of motion for both the isothermal and the adiabatic forms of grand molecular dynamics. The averages calculated over the trajectories generated by these equations of motion represent the classical grand canonical ensemble (μVT) and the constant chemical potential adiabatic ensemble (μVL) averages, respectively. The microcanonical phase space densities of the adiabatic and isothermal forms the molecular dynamics method are shown to be equivalent to adiabatic constant chemical potential ensemble, and grand canonical ensemble partition functions. We also discuss the extension to multi-component systems, molecular fluids, ionic solutions and the problems and solutions associated with the implementation of the method. The statistical expressions for thermodynamic functions such as specific heat; adiabatic bulk modulus, Grüneissen parameter and number fluctuations are derived. These expressions are used to analyse trajectories of constant chemical potential systems.

KEY WORDS: Molecular dynamics, number fluctuations, chemical potential, extended system dynamics, thermodynamic response functions, open systems

I. INTRODUCTION

Since its introduction by Alder and Wainwright [1], molecular dynamics has been an important technique for studying condensed matter systems ranging from simple monatomic liquids to biological macromolecules. The traditional form of molecular dynamics simulation represents the microcanonical (NVE) ensemble. Starting with Andersen's paper [2] on constant pressure molecular dynamics, new forms of the molecular dynamics method have emerged to simulate different equilibrium ensembles, for example the constant stress molecular dynamics of Parrinello and Rahman [3] and the constant temperature molecular dynamics of Nosé [4] have both followed the extended system approach of Reference [2]. Whether adiabatic or isothermal, all these forms of the molecular dynamics method represent the same category of statistical mechanical ensembles, namely the ensembles corresponding to closed physical systems. However, most physical phenomena occur under conditions where energy and matter exchange take place between the system and its physical surroundings. The methodology of Monte Carlo was extended to treating open systems in the 1970's through the development of the grand canonical Monte Carlo method [5, 6].

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As yet, equilibrium molecular dynamics methods have been restricted to studying only closed physical systems. This leaves a powerful simulation method deficient in studying a large segment of classical many body problems in statistical mechanics.

One possibility, in extending molecular dynamics methods to treat open systems, is to use a stochastic procedure to introduce particles into the system from a chemical potential reservoir, by analogy to what is suggested for generating the isothermal ensemble in Reference [2]. This approach could possibly give rise to a hybrid molecular dynamics method where one would have particle number fluctuations. However, like all hybrid (stochastic-deterministic) techniques, this would not be a truly dynamical method. Achieving a dynamical process to simulate open systems is possible by including additional dynamical variables to couple the system to chemical potential and temperature reservoirs. In the following, with dynamical couplings, we obtain an extended system Lagrangian (and Hamiltonian) describing the actual system at a constant chemical potential. In order to obtain this Hamiltonian, we introduce two conditions. First, the phase space dimensionality of the system should be a variable. Second, the time average of a dynamical variable along the trajectory generated by this Hamiltonian should be equivalent to the grand ensemble average of the same variable, or in other words, the partition function corresponding to this extended ensemble expressed only in real phase space variables should yield the equilibrium grand ensemble partition function.

These conditions are met in the following way. In order to couple the system under consideration to the chemical potential reservoir, we introduce a continuous real variable, ν, whose integer part is taken as the number of particles, N, in the system. Also introduced is an additional particle whose kinetic energy and potential energy are scaled by $\xi = \nu - N$. Such a scaling has a long history in statistical mechanics from Born [7] Onsager [8] and Kirkwood [9] to more modern work in the area of scaled particle theory [10].

If we only use the above prescription without introducing the coupling to a heat bath, the equations of motion of this extended system will generate number fluctuations at constant volume V, constant chemical potential μ, and constant *Hill energy*, $L = E - \mu N$ [11]. The corresponding system is a semi-open system, where only matter exchange is allowed but energy exchange with the surroundings is not allowed, i.e. *adiabatic but porous walls enclose the system*. We have called L, Hill energy, since this semi-open system has been mentioned in Hill's book on statistical mechanics [11]. This ensemble was discussed in the literature by Ray *et al* [12], where they derived the statistical expression for number fluctuations in this ensemble. We present more on the statistical mechanics of the (μVL) ensemble and derive the statistical expressions for the specific heat, Grüneissen parameter and adiabatic bulk modulus using Laplace transform methods [13, 14].

The coupling to a temperature bath is achieved by introducing the Nosé thermostat [4]. The resulting equations of motion then are shown to generate an open system at constant temperature, constant chemical potential and constant volume, i.e. the classical grand canonical ensemble. In the following section, we present the adiabatic and isothermal forms of the new method and obtain equations of motion for the *extended* system variables. Section III contains the explicit connections to the Grand canonical partition function. The fourth section covers the extension to multicomponent systems and the derivation of the formulas to analyse the system are given in the fifth section. The implementation of the method for a simple fluid is presented in the sixth section. The seventh section presents comparisons of both spatial and time

correlation functions from GMD with the corresponding quantities from a microcanonical trajectory. In the last section, we conclude with a discussion of the implications for future work.

II. GRAND MOLECULAR DYNAMICS METHOD

A. Statistical Ensembles and Extended System Dynamics

In statistical descriptions of classical systems six classic statistical mechanical ensembles arise corresponding to different physical conditions. These are:

i. the microcanonical, (*NVE*), ensemble;
ii. the canonical, (*NVT*), ensemble;
iii. the isoenthalpic-isobaric, (*NPH*), ensemble;
iv. the isothermal-isobaric, (*NPT*) ensemble;
v. the adiabatic constant chemical potential, (μVL), ensemble;
vi. the grand canonical, (μVT), ensemble.

If the description of the system is restricted to the conventional phase space $\Gamma(\{\mathbf{p},\mathbf{x}\})$, only the first two of these ensembles, the microcanonical and canonical ensembles can fully be described through their respective partition functions depending only on the phase space variables, $\{\mathbf{p},\mathbf{x}\}$. The density of states and the partition function are given by

$$\omega(NVE) = \frac{1}{C_N}\int \delta(\mathscr{H} - E)\, d\tau \tag{1}$$

and

$$Z(NVT) = \frac{1}{C_N}\int e^{-\mathscr{H}/k_B T} d\tau \tag{2}$$

where $d\tau$ is the volume element in $6N$ dimensional phase space, $\mathscr{H}$ is the N-body Hamiltonian and C_N is a constant. The other ensembles can only be described in an augmented phase space, obtained from the "mechanical" phase space by adding additional quantities as dynamical variables. For instance, the constant pressure ensembles partition functions are expressed with the addition of volume as the augmentation variable.

$$\omega(NPH) = \frac{1}{C_N}\int \delta(\mathscr{H} + PV - H)\, d\tau\, dV \tag{3}$$

$$Z(NPT) = \frac{1}{C_N}\int e^{-(\mathscr{H} + PV)/k_B T} d\tau\, dV \tag{4}$$

Similarly, for the constant chemical potential ensembles, we have

$$\omega(\mu VL) = \sum_{N=0}^{\infty} \frac{1}{C_N}\int \delta(\mathscr{H} - \mu N - L)\, d\tau \tag{5}$$

$$Z(\mu VT) = \sum_{N=0}^{\infty} \frac{1}{C_N}\int e^{-(\mathscr{H} - \mu N)/k_B T} d\tau \tag{6}$$

The number of particles can be thought of as the augmentation variable or we can interpret the phase space of constant chemical potential ensembles as a collection of conventional phase spaces.

Since the conventional form of molecular dynamics is based on Hamiltonian mechanics, it generates trajectories corresponding to the microcanonical ensemble. As mentioned above, Anderson, by using the volume of the system as an additional augmentation variable, obtained the isoenthalpic-isobaric form of molecular dynamics [2]. In a similiar fashion, Nosé introduced the extension variables, s and p_s into a Hamiltonian description and succeeded in extending the method to simulate systems under constant temperature conditions [4]. With the augmentation and extension variables, extended system Hamiltonians are still constants of motion, and they are still energy-like quantities. Essentially, the trajectories in the extended phase space variables correspond to microcanonical ensembles. However, their projection onto physical system phase spaces represent ensembles other than the microcanonical ensemble.

Following Nosé's notation, in the rest of this paper we use the primed coordinates and moments $\{\mathbf{x}',\mathbf{p}'\}$ for the canonical variables of the physical system, and the unprimed variables $\{\mathbf{x},\mathbf{p}\}$ for the virtual coordinates and momenta of the particles. The former set corresponds to the physical system, whereas the latter set represents the virtual system. After including the additional variables, we obtain the *extended system*. Thus, in new forms of molecular dynamics there are four different systems under consideration: *the physical system, the virtual system, the extended physical system* and *the extended virtual system*. A detailed account of the extended system dynamics has been given recently by Jellinek [15] in the context of generalizations of Nosé's isothermal molecular dynamics [4].

B. Number as a Dynamical Variable and Fractional Particles

Following the extended system dynamics formalism, we introduce an augmentation variable, v, related to the time evolution of the number of particles. To obtain a dynamical equation for v, a kinetic energy, $K_v = \frac{1}{2}W\dot{v}^2$, and a potential energy term $U_v = \mu v$ are added to the system's Lagrangian, where W is a "mass" associated with the new dynamical variable v and μ is the chemical potential. This is like having a phantom particle in the system with its own couplings to the extended virtual system. Coupling with the particle reservoir is then obtained by the following method, which has been used in different contexts as early as the 1920's [7–10]. Assume that the potential energy of the $(N + 1)$–particle system, U_{N+1}, is composed of terms $\varphi(r_{ab})$ representing the pairwise interaction of particles a and b,

$$U_{N+1} = \sum_{a=1}^{N} \sum_{b>a}^{N+1} \varphi(r_{ab}). \tag{7}$$

We assign the parameter ξ to the $(N + 1)$-st particle, such that each pairwise term involving the $(N + 1)$-st particle is to be multiplied by ξ. We can then write Equation (7) as

$$U_{N+1} = \sum_{a=1}^{N-1} \sum_{b>a}^{N} \varphi(r_{ab}) + \xi \sum_{b=1}^{N} \varphi(r_{b,N+1}) \tag{8}$$

which separates the interaction potential into two terms, one of which does not

contain the $(N + 1)$-st particle, and the other which contains the $(N + 1)$-st particle. We define N, the number of particles, as the integer part of v, and ξ as the fractional part of v.

$$\xi = v - N \tag{9}$$

According to our convention, ξ can only take on values in between 0 and 1. If ξ goes to 1 we recover Equation (7), whereas $\xi = 0$, leads to N-particle potential energy and N and $N + 1$ are redefined accordingly. Similiar relations hold for the kinetic energy of the N- and $(N + 1)$-particle systems. Thus, by allowing ξ to vary from 0 to 1, we formally add a particle to a system of N-particles. We shall call the $(N + 1)$-st particle throughout this paper the *fractional* particle. Together with the variables corresponding to actual particles the extra variables, $(v, p_v, \mathbf{x}_f, \mathbf{p}_f)$, constitute the *virtual extended system* corresponding to the adiabatic form of the grand molecular dynamics method.

C. *Adiabatic Form of the Method*

For the sake of simplicity, first we present the case where only the coupling to the chemical potential reservoir is considered. As we pointed out in the introduction, this form corresponds to the classical adiabatic constant chemical potential, (μVL), ensemble. Using the above arguments, we write an ansatz Lagrangian for the adiabatic form as follows

$$\begin{aligned}\mathscr{L}_1(\mathbf{x}_a,\dot{\mathbf{x}}_a,\ \mathbf{x}_f,\ \dot{\mathbf{x}}_f,\ v,\dot{v}) &= \sum_{a=1}^{N} \frac{1}{2} m\dot{\mathbf{x}}_a^2 + \frac{(v - N)}{2} m\dot{\mathbf{x}}_f^2 + \frac{1}{2} W\dot{v}^2 \\ &\quad - \sum_{a=1}^{N-1} \sum_{b>a}^{N} \varphi(r_{ab}) - (v - N) \sum_{a=1}^{N} \varphi(r_{fa}) + \mu v. \end{aligned} \tag{10}$$

We used $(v - N)$ in Equation (10), instead of the scaling parameter ξ, since v is the continuous dynamical variable appearing in the equations of motion. The variables $(\mathbf{x}_a, \dot{\mathbf{x}}_a;\ a = 1,...,N)$, are the virtual coordinates and velocities of N full particles (for the adiabatic case, the virtual and physical variables for full particles are identical) and $(\mathbf{x}_f, \dot{\mathbf{x}}_f)$, are the coordinates and velocities of the *fractional* particle. v is the additional continuous variable which represents the variation of the number of particles in the physical system and $\dot{v}$ is the velocity of this additional variable. The first three terms on the right hand side of Equation (10) are the kinetic energies associated with N full particles, the fractional particle and the additional variable or phantom particle. The next two terms are the potential energy terms representing interactions between full particles only, and between full particles and the fractional particle, respectively. The last term is the chemical potential energy associated with the system.

The equations of motion corresponding to the Lagrangian above are

$$m\ddot{x}_{ai} = -\sum_{b=1}^{N} \frac{\partial\varphi(r_{ab})}{\partial r_{ab}} \frac{x_{abi}}{r_{ab}} - (v - N) \frac{\partial\varphi(r_{af})}{\partial r_{af}} \frac{x_{afi}}{r_{af}}, \tag{11}$$

$$(v - N)m\ddot{x}_{fi} = -(v - N) \sum_{a=1}^{N} \frac{\partial\varphi(r_{fa})}{\partial r_{fa}} \frac{x_{fai}}{r_{fa}} - m\dot{v}\dot{x}_{fi}, \tag{12}$$

$$W\ddot{v} = \frac{1}{2} m\dot{x}_f^2 + \mu - \sum_{a=1}^{N} \varphi(r_{fa}). \tag{13}$$

Where the subscripts a,b denote the particle indices, and the subscript $i = 1,2,3$ denotes the x,y,z components of the vector joining the particles. In the course of a grand molecular dynamics simulation these coupled equations are solved simultaneously. When the value of $\xi = v - N$ becomes equal to 1, a new full particle is added into the system or when it becomes equal to 0 the current fractional particle is deleted from the system. In either case, a new fractional particle subsequently takes the role of the earlier one. The details of insertion or deletion of particles are covered below.

We have given the Equation (11–13) in terms of pairwise additive potential energy functions, but the extension to more general types of interactions containing many-body forces is straightforward.

The Hamiltonian for the *virtual extended system*

$$\mathscr{H}_1(\mathbf{x}_a, \mathbf{p}_a, \mathbf{x}_f, \mathbf{p}_f, v, p_v) = \sum_{a=1}^{N} \frac{\mathbf{p}_a^2}{2m} + \frac{\mathbf{p}_f^2}{2(v-N)m} + \frac{p_v^2}{2W} + U(r_{ab}) + (v-N)U(r_{fa}) - \mu v \tag{14}$$

generates a constant energy, $\mathscr{H}_1 = \mathscr{E}_1$, constant volume ensemble in the extended phase space with varying dimensions, $6N(t) + 8$. In addition to the Hamiltonian, $\mathscr{H}_1$, theoretically, the conserved quantities for the virtual extended system are the total linear momentum, $\mathscr{P} = \sum \mathbf{p}$, including the linear momentum of the fractional particle, and total angular momentum of the extended system, $\mathscr{M} = \sum \mathbf{x} \times \mathbf{p}$. But the conservation of total linear momentum is not strictly realized during the insertion and deletion of particles. Instead, it can only be made to fluctuate about zero. Similarly, the conservation of total angular momentum can not be realized mainly due to periodic boundary conditions as well as the insertion and deletion processes. In fact, this is the case in the traditional form of molecular dynamics unless one is simulating a cluster with free boundaries. Again for liquid state simulations this quantity fluctuates about a preset value; conventionally this preset value is chosen as zero.

D. *Isothermal Form of the Method*

As we mentioned in the introduction, Nosé, [4] by introducing an additional variable has managed to couple the system to an external heat bath, and thereby obtained the isothermal form of molecular dynamics. Using the same form of coupling to a heat bath at temperature T, we obtain the following extended system Lagrangian and Hamiltonian for the isothermal form of grand molecular dynamics from Equations (10) and (14).

$$\mathscr{L}_2(\mathbf{x}_a, \dot{\mathbf{x}}_a, \dot{\mathbf{x}}_f, \mathbf{x}_f, v, \dot{v}, s, \dot{s}) = \sum_{a=1}^{N} \frac{1}{2} m s^2 \dot{\mathbf{x}}_a^2 + \frac{(v-N)}{2} m s^2 \dot{\mathbf{x}}_f^2 + \frac{1}{2} W \dot{v}^2 + \frac{1}{2} Q \dot{s}^2 - \sum_{a=1}^{N-1} \sum_{b>a}^{N} \varphi(r_{ab}) - (v-N) \sum_{a=1}^{N} \varphi(r_{fa}) + \mu v - g k_B T \ln s \tag{15}$$

and

$$\mathscr{H}_2(\mathbf{x}_a, \mathbf{p}_a, \mathbf{x}_f, \mathbf{p}_f, v, p_v, s, p_s) = \sum_{a=1}^{N} \frac{\mathbf{p}_a^2}{2ms^2} + \frac{\mathbf{p}_f^2}{2(v-N)ms^2} + \frac{p_v^2}{2W}$$

$$+ \frac{p_s^2}{2Q} + \sum_{a=1}^{N-1} \sum_{b>a}^{N} \varphi(r_{ab}) + (v - N) \sum_{a=1}^{N} \varphi(r_{fa})$$
$$- \mu v + g k_B T \ln s \tag{16}$$

The extension variable s is the parameter coupling the system to a heat bath, p_s is the corresponding momentum and Q is the mass associated with s. Nosé interpreted this variable s as the time scaling factor, it may as well be interpreted as mass scaling [16], $m' = ms^2$. If one assumes the original interpretation of s and uses scaled time then g should be taken as $3(N + 1) + 1$, but if the unscaled time is used then g must be taken as $3(N + 1)$ [17]. In either case when the conservation of total linear momentum constraint is imposed, it was shown that g must be replaced by $g - 3$ [18]. We chose the form of the potential energy corresponding to the heat bath variable as in the original formulation of Nosé [4]. The remaining terms in Equations (15–16) are defined the same way as in the adiabatic form.

The equations of motion can easily be obtained from Equation (15).

$$ms^2 \ddot{x}_{ai} = - \sum_{b=1}^{N} \frac{\partial \varphi(r_{ab})}{\partial r_{ab}} \frac{x_{abi}}{r_{ab}} - (v - N) \frac{\partial \varphi(r_{af})}{\partial r_{af}} \frac{x_{afi}}{r_{af}} - 2ms\dot{s}\dot{x}_{ai}, \tag{17}$$

$$(v - N)ms^2 \ddot{x}_{fi} = - (v - N) \sum_{a=1}^{N} \frac{\partial \varphi(r_{fa})}{\partial r_{fa}} \frac{x_{fai}}{r_{fa}} - ms^2 \dot{v}\dot{x}_{fi} - 2(v - N)ms\dot{s}\dot{x}_{fi}, \tag{18}$$

$$W\ddot{v} = \mu + \frac{1}{2}ms^2 \dot{x}_f^2 - \sum_{a=1}^{N} \varphi(r_{fa}) \tag{19}$$

and

$$Q\ddot{s} = \left(\sum_a \frac{1}{2}ms^2 \dot{x}_a^2 + \frac{1}{2}(v - N)ms^2 \dot{x}_f^2 - g k_B T \right) / s. \tag{20}$$

The virtual extended system variables in Equation (16) are related to the extended physical system variables as follows:

$$\begin{aligned} \mathbf{x}'_a &= \mathbf{x}_a, & \mathbf{p}'_a &= \mathbf{p}_a / s \\ \mathbf{x}'_f &= \mathbf{x}_f, & \mathbf{p}'_f &= \mathbf{p}_f / s(v - N) \\ v' &= v, & p'_v &= p_v \\ s' &= s, & p'_s &= p_s. \end{aligned} \tag{21}$$

The Hamiltonian given by Equation (16), $\mathcal{H}_2 = \mathcal{E}_2$, also represents a constant energy, constant volume ensemble in the extended phase space, like the Hamiltonian describing the adiabatic form, but the extended phase space in this case contains two more additional degrees of freedom corresponding to the Nosé extension variables, s and p_s.

Using the same procedure introduced in Reference [4] we can demonstrate that the partition function of this constant energy, constant volume and constant chemical potential ensemble can be reduced to the grand canonical partition function when it is expressed in terms of the real system variables. We give the explicit connection in the following section.

III. CONNECTION TO CLASSICAL CONSTANT CHEMICAL POTENTIAL ENSEMBLES

A. Equivalence to Grand Canonical Ensemble Partition Function

The extended system Hamiltonian, $\mathscr{H}_2$, given by Equation (16), defines a constant energy surface in a $6N(t) + 10$ dimensional phase space. Since, there are no restrictions on the number of particles, the density of states for this *extended* system is then given by

$$\omega_{ext}(\mathscr{E}_2, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N!} \int dr_{ext}\, \delta(\mathscr{H}_2(\mathbf{p}_a, \mathbf{x}_a, \mathbf{p}_f, \mathbf{x}_f, p_\xi, \xi, p_s, s; N) - \mathscr{E}_2) \quad (22)$$

where dr_{ext} is the volume element of the extended phase space

$$dr_{ext} = ds dp_s\, d\xi\, dp_\xi\, d\mathbf{x}_f\, d\mathbf{p}_f\, d\tau$$

and $d\tau$ is given by

$$d\tau = \prod_{a=1}^{N} d\mathbf{x}_a\, d\mathbf{p}_a$$

After performing the change of variables according to Equation (21), we can integrate out the s dependence using a property of Dirac δ-functions:

$$\delta(F(s)) = \frac{\delta(s - s_0)}{F'(s)},$$

where s_0 is the root of $F(s) = 0$, and $F'(s)$ is the derivative of the function $F(s)$ with respect to s. Performing the integration of momentum variables, p'_ξ, p'_s and $\mathbf{p}'_f$, we obtain

$$\omega_{ext}(\mathscr{E}_2, V, \mu) = C(T) \sum \frac{1}{N!(3N+4)} \int d\tau'\, d\mathbf{x}'_f d\xi'\, \xi'^{3/2} e^{-\xi(U(x_{fa})-\mu)/k_B T}\, e^{-(\mathscr{H}-\mu N)/k_B T}$$

where $\mathscr{H}$ is the N-particle physical system Hamiltonian

$$\mathscr{H}(\mathbf{p}'_a, \mathbf{x}'_a) = \sum_{a=1}^{N} \frac{\mathbf{p}'^2_a}{2m} + U(\mathbf{x}'_1, \ldots, \mathbf{x}'_N)$$

and $C(T)$ is a constant deBroglie wavelength-like factor obtained after integration

$$C(T) = 2\pi e^{\delta_2/k_B T} (QW)^{1/2} (2\pi m k_B T)^{3/2}$$

After translating the origin to $\mathbf{x}'_f$, we can perform the $\mathbf{x}'_f$ integration to yield V, the constant volume occupied by the system. Then, ω_{ext} reduces to

$$\omega_{ext}(\mathscr{E}_2, V, \mu) = VC(T) \sum \frac{1}{N!(3N+4)} \int d\tau'\, d\xi'\, \xi'^{3/2} e^{-(\mathscr{H}(x'_a, p'_a)-\mu N)/k_B T}\, e^{-\xi'(U_f-\mu)/k_B T}$$

Here U_f is the potential energy of a fictitious particle placed at the origin due to the rest of the real particles. If we replace it by its average, $\langle U_f \rangle$, a constant, the ξ integration can also be performed. In fact, the average of U_f can be determined from the long time average of the equation of motion for v, Equation (11), as $\langle U_f \rangle = \mu + \frac{3}{2} k_B T$. The integration over ξ subsequently yields another constant term. The final expression for the ω_{ext} is

$$\omega_{ext}(\mathscr{E}_2, V, \mu) = \tilde{C}(T, V) \sum \frac{1}{N!(3N+4)} \int d\tau' exp\left(-\frac{(\mathscr{H}(\mathbf{p}'_a, \mathbf{x}'_a) - \mu N)}{k_B T}\right) \quad (23)$$

where $\tilde{C}(T, V)$ is a new constant. In the equivalence proof sketched above, no constraints on the total linear momentum and total angular momentum are imposed. The proof can also be obtained by imposing $\mathscr{P} = const.$ condition, and following the same procedure as in the reference 18, provided $3N + 4$ is replaced by $3N + 1$. Inspecting Equation (23), we see that the probability density is proportional to $exp(-\mathscr{H}(p'_a, x'_a) - \mu N/k_B T)$. Except for the factor $(1/(3N + 4)$, the final expression is the same as the classical grand canonical ensemble partition function. The appearance of the factor $(1/(3N + 4))$ is plausible. In some sense, it introduces the correct counting for the method. At any moment during the simulation, even though one of the particles is a *fractional* particle, the actual number of particles will always be $N + 1$. If we write $3N + 4 \simeq 3(N + 1)$, we obtain $(N + 1)!$ in place of $N!$.

B. *Equivalence of Time Averages to Adiabatic Constant Chemical Potential Ensemble Averages*

Using the trajectories generated by Equations (11–13), one can calculate the time averages of a dynamical function $D(\mathbf{x}'_a, \mathbf{p}'_a, N; N = 0,..., \infty, a = 1,...,N)$. The time average of any dynamical function calculated over this trajectory is appoximately equivalent to the ensemble average of the same dynamical function for the adiabatic constant chemical potential (μVL) ensemble, for an appropriate value of L. This can be shown by following the same procedure as in Reference [2] where the time average of a dynamical quantity is shown to be equal to the isoenthalpic-isobaric ensemble average of the same quantity.

For a dynamical function $A(\mathbf{x}'^N, \mathbf{p}'^N; N)$ given in terms of the coordinates and momenta of the physical system, we can define the corresponding approximately equivalent dynamical function in the virtual extended system variables as $B(\mathbf{x}^N, \mathbf{p}^N, \mathbf{x}_f, \mathbf{p}_f, \xi, p_\xi; N)$ such that

$$\bar{B}(\mathbf{x}^N, \mathbf{p}^N, \mathbf{x}_f, \mathbf{p}_f, \xi, p_\xi; N) \simeq \bar{A}(\mathbf{x}'^N, \mathbf{p}'^N; N) \quad (24)$$

The $\bar{A}$ and $\bar{B}$ in Equation (24) represents the time averages of A and B over the trajectories generated by the Hamiltonian, $\mathscr{H}_1$, and defined as

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt\, A(\mathbf{x}'^N(t), \dot{\mathbf{p}}^N(t); N)$$

$$\bar{B} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt\, B(\mathbf{x}^N(t), \mathbf{p}^N(t), \mathbf{x}_f(t), \mathbf{p}_f(t), \xi(t), p_\xi(t); N(t)).$$

Then, by assuming ergodicity we write

$$\bar{A} \simeq < A >_{\mu VL}. \quad (25)$$

The right hand side of Equation (25) is the (μVL) ensemble average of A. We define the ensemble average of A in the ensemble corresponding to the extended system as

$$< A >_{\mu V \mathscr{E}_1} = \frac{1}{\omega} \sum_0^\infty \frac{1}{N!} \int_0^l d\xi \int dp_\xi \int d\mathbf{x}_f \int d\mathbf{p}_f \int d\tau\, \delta(\mathscr{H}_1 - \mathscr{E}_1) A(\mathbf{x}'^N, \mathbf{p}'^N; N) \quad (26)$$

where $d\tau = d\mathbf{p}^N d\mathbf{x}^N$ and

$$\omega = \sum_0^\infty \frac{1}{N!} \int_0^l d\xi \int dp_\xi \int d\mathbf{x}_f \int d\mathbf{p}_f \int d\tau\, \delta(\mathscr{H}_1 - \mathscr{E}_1). \tag{27}$$

After replacing the canonical variables of the extended system Hamiltonian by the physical system variables, we obtain

$$< A >_{\mu V \mathscr{E}_1} = \frac{1}{\omega} \sum_0^\infty \frac{1}{N!} \int_0^l d\xi \int dp_\xi \int d\mathbf{x}'_f \int d\mathbf{p}'_f \int d\tau\, \delta(\mathscr{H}_1 - \mathscr{E}_1)\, A(\mathbf{x}'^N, \mathbf{p}'^N; N). \tag{28}$$

The last expression is very much like a (μVL) ensemble average of A except for the p_ξ integration and the appearance of an additional fractional particle. For a fixed value of $p_\xi^2/2W$ and a fixed contribution from the fractional particle, say E_f, this is indeed closely related to the adiabatic constant chemical potential ensemble average. The corresponding value for L is therefore $\mathscr{E}_1 - E_f - p_\xi^2/2W + \mu\xi$. In fact this was obvious from the outset. Since, the Hamiltonian for the adiabatic form already contained the terms corresponding to the internal energy of the N-body system, $\mathscr{H}(\mathbf{x}, \mathbf{p}; N)$ and the chemical potential energy contribution for the N-body system, $(-\mu N)$, which gives a sum, $L = E - \mu N$. The additional energy terms corresponding to the fractional particle and the phantom variable are apparently small compared to the N-body system energy and they constitute a negligible error. The statistical expressions for the thermodynamic functions in the (μVL) ensemble to be utilized in the adiabatic form of the new method are given in section VI.

IV. EXTENSION TO MULTI-COMPONENT SYSTEMS

The constant chemical potential molecular dynamics will ultimately find its most important uses in multi-component and molecular systems. One example of obvious importance would be ionic solutions and their osmotic equilibria. In this section, we will present the extension of the method to multi-component systems.

In order to extend the method to n-component systems, we introduce n-phantom variables v_α where $\alpha = 1, \ldots, n$. Their relation to the number of particles will be the same as above; i.e. the integer part of v_α will be N_α. Then we will have n-scaling factors, $\xi_\alpha = v_\alpha - N_\alpha$ to scale the additional particles from each species. The corresponding system will have a total of $N_1 + \ldots + N_n$ full particles and n-additional scaled particles. For each v_α, we introduce a similiar kinetic energy term, $K(\dot{v}_\alpha) = \frac{1}{2} W_\alpha \dot{v}_\alpha^2$ and a potential energy term, $U(v_\alpha) = \mu_\alpha v_\alpha$. In addition to interactions only between full particles, the interactions between full particles and fractional particles, and the interactions among fractional particles of different species are also allowed. Thus, the Lagrangian for the adiabatic dynamics of the multi-components system can be written as

$$\begin{aligned}\mathscr{L}(\mathbf{x}_{\alpha a}, \dot{\mathbf{x}}_{\alpha a}, \mathbf{x}_{\alpha f}, \dot{\mathbf{x}}_{\alpha f}, v_\alpha, \dot{v}_\alpha) &= \sum_{\alpha=1}^{n} \sum_{a=1}^{N_\alpha} \frac{1}{2} m_\alpha \dot{\mathbf{x}}_{\alpha a}^2 + \sum_{\alpha=1}^{n} \frac{v_\alpha - N_\alpha}{2} m_\alpha \dot{\mathbf{x}}_{\alpha f}^2 \\ &+ \sum_{\alpha=1}^{n} \frac{1}{2} W_\alpha \dot{v}_\alpha^2 - \sum_{\alpha=1}^{n} \sum_{a=1}^{N_\alpha - 1} \sum_{b>a}^{N_\alpha} \varphi_{\alpha\alpha}(r_{ab}) - \sum_{\alpha=1}^{n-1} \sum_{\beta>\alpha}^{n} \sum_{a=1}^{N_\alpha} \\ &\times \sum_{b=1}^{N_\beta} \varphi_{\alpha\beta}(r_{ab}) - \sum_{\alpha=1}^{n} (v_\alpha - N_\alpha) \sum_{a=1}^{N_\alpha} \varphi_{\alpha\alpha}(r_{af}) - \sum_{\alpha=1}^{n-1} \sum_{\beta>\alpha}^{n}\end{aligned}$$

$$\times (v_\alpha - N_\alpha)(v_\beta - N_\beta)\, \varphi_{\alpha\beta}(r_{ff'}) + \sum_{\alpha=1}^{n} \mu_\alpha v_\alpha \tag{29}$$

The first three terms are the kinetic energy terms associated with the full particles, *fractional* particles and the additional *phantom* variables, respectively. The following two potential energy terms are the potential energy contribution due to interactions between the full particles. The first one represents the interaction between the same kind of full particles, whereas the second one is the interaction between different kinds of full particles. These two type of interactions are distinguished by the use of the same Greek subscripts ($\alpha\alpha$) and different Greek subscripts ($\alpha\beta$) for the pair potential term. We used the same convention to denote the interactions between full and fractional, and between only the fractional particles. The equations of motion generated by this Lagrangian will be similiar to what we have obtained for single-component system for the actual full particles. Hence, we only give the equations of motion for the fractional particles and the variables v_α.

$$\begin{aligned} m_\alpha \ddot{x}_{\alpha fi} &= -\frac{\dot{v}_\alpha}{v_\alpha - N_\alpha} m_\alpha \dot{x}_{\alpha fi} - \sum_{a=1}^{N_\alpha} \frac{\partial \varphi_{\alpha\alpha}(r_{fa})}{\partial r_{fa}} \frac{x_{fai}}{r_{fa}} \\ &\quad - \sum_{\beta=1}^{n} (v_\beta - N_\beta) \frac{\partial \varphi_{\alpha\beta}(r_{ff'})}{\partial r_{ff'}} \frac{x_{ff'i}}{r_{ff'}}, \end{aligned} \tag{30}$$

where f and f' stand for different fractional particles. For the additional coordinates we have

$$W_\alpha \ddot{v}_\alpha = \mu_\alpha + \frac{1}{2} m_\alpha \dot{x}_{\alpha f}^2 - \sum_{a=1}^{N_\alpha} \varphi_{\alpha\alpha}(r_{fa}) - \sum_{\beta}^{n} (v_\beta - N_\beta)\varphi_{\alpha\beta} \tag{31}$$

The multi-component case described above is straightforward for simple or molecular fluids with neutral atoms or molecules. By constraint, this may be used to introduce a multi-site molecule even if it includes internal degrees of freedom. If the system under consideration is an ionic solution, we need to introduce the additional constraint of electroneutrality of the system at any moment. The extension to ionic systems must take this condition into account. This condition could be satisfied, for instance, in the case of salt solutions by introducing a single v variable (or two which are constrained) to monitor the number of positive and negative ions in the solvent, and other v's for the solvent molecules. This prescription leads to simultaneous addition or deletion of pairs of ions. This sort of constraint is also required for the atoms in molecules to avoid fractional species. However, with some care in the choice of the constraint and the model potential surface it would be possible to simulate a dissociative equilibrium.

V. (μ, V, L) RESPONSE FUNCTIONS FOR ANALYSIS

The main objective of this section of the paper is to give some details of the statistical mechanics of the adiabatic constant chemical potential (μVL) ensemble. In mathematical terms, the partition functions of the two grand ensembles are related to each other by a Laplace-Stieltjes transformation,

$$\Xi(\mu, V, T) = \int d\beta e^{-\beta L}\, \omega(\mu, V, L) \tag{32}$$

where $\Xi(\mu, V, T)$ is the grand canonical partition function and $\omega(\mu, V, L)$ is the partition function of the (μVL) ensemble and $\beta = (1/k_B T)$. The explicit form of $\omega(\mu, V, L)$ is given by

$$\omega(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int \delta(L + \mu N - \mathscr{H}) d\tau \tag{33}$$

and $\mathscr{H}$ is the Hamiltonian of the system,

$$\mathscr{H}(\mathbf{p}, \mathbf{x}, N) = \sum \frac{\mathbf{p}_a^2}{2m} + \mathscr{U}(\mathbf{x}_1, ..., \mathbf{x}_N) \tag{34}$$

Conceptually, the difference between these two ensembles amounts to converting the diathermal partition between a (μVT) system and surrounding reservoirs into an adiabatic one. Some aspects of the statistical mechanics of this ensemble were discussed earlier by Ray *et al.*[12] in the context of a complete pairing between classical adiabatic and isothermal ensembles, where they named this ensemble as the *dernier*, or last ensemble. In addition, the expression for the number fluctuations in this ensemble has been obtained by an adiabatic differentiation methods [13].

The Laplace transform method, which enormously simplifies the statistical treatment of adiabatic ensembles, has been applied to the microcanonical ensemble [21] isoenthalpic-isobaric ensemble [13] and molecular dynamics ensembles [14]. Here, it is applied to the (μVL) ensemble, in order to yield formulas for analysis of the trajectories.

The adiabatic ensembles are characterized by the extent to which the coordinates $\{\mathbf{x}\}$ and momenta $\{\mathbf{p}\}$ of the system are restricted, within the phase space defined by the Hamiltonian, $\mathscr{H}$, of the system. In the (μVL) ensemble this manifold is defined by constant Hill energy, $L = E - \mu N$. We first give the phase space volume, the density of states and the definition of the probability density [11,12]. The phase space volume of the (μVL) ensemble, $\Phi(\mu, V, L)$ is defined after reference [12] as

$$\Phi(\mu, V, L) = \sum_{N=0}^{\infty} \frac{1}{C_N} \int \Theta(L + \mu N - \mathscr{H}) d\tau \tag{35}$$

where Θ is the unit step function, $d\tau$ is a 6N-dimensional volume element in phase space

$$d\tau = \prod_a d\mathbf{p}_a d\mathbf{x}_a$$

and $C_N = N! h^{3N}$. The fundamental thermodynamic potential is the entropy, and is defined through the Boltzmann relation

$$S(\mu, V, L) = k_B \ln \Phi(\mu, V, L) \tag{36}$$

It is used as the connection formula between statistical mechanics and thermodynamics for this ensemble. The density of states,

$$\omega = \left(\frac{\partial \Phi}{\partial L}\right)$$

is defined above in Equation (5). Thus, following the convention of reference [12] the probability density for the (μVL) ensemble is given by

$$W(\mathbf{p}, \mathbf{q}, N) = \frac{\delta(L + \mu N - \mathscr{H})}{\omega C_N} \tag{37}$$

which is normalized such that

$$\sum_{N=0}^{\infty} \int W(\mathbf{p}, \mathbf{x}, N)\, d\tau = 1. \tag{38}$$

Given the above, the ensemble average of a dynamical variable, $A(\mathbf{p}, \mathbf{x})$, is defined as

$$< A > = \sum_N \int A(\mathbf{p}, \mathbf{x}, N)\, W d\tau \tag{39}$$

It is widely appreciated that the thermodynamic averages calculated for intensive properties in different ensembles differ by only of the order $(1/N)$ [12, 20]. But, the properties which depend on the fluctuations differ by unity. Hence, these characteristic fluctuations or related properties need to be described within the ensemble of interest.

In addition to obtaining statistical expressions for the temperature, average kinetic energy and pressure, we shall also need the fluctuation expressions for the related thermodynamic quantities such as the specific heat at constant volume and constant chemical potential, a Grüneissen-like parameter and the adiabatic bulk modulus in the (μVL) ensemble. The Laplace transform method is based on expressing the phase space volume, density of states and the ensemble averages in a form where the integrands depend only on the configuration space variables. We illustrate the reduction procedure for the phase space volume, Φ. We start by taking the Laplace transform of Equation (35)

$$\hat{\mathscr{L}}\Phi = \sum_N \frac{1}{C_N} \int e^{-sL} \Theta(L + \mu N - \mathscr{H})\, d\tau dL \tag{40}$$

to obtain

$$\hat{\mathscr{L}}\Phi = \sum_N \frac{1}{C_N} \int \frac{1}{s} e^{-s(\mathscr{H} - \mu N)} d\tau \tag{41}$$

Integrating over momentum variables, we get

$$\hat{\mathscr{L}}\Phi = \sum_N \frac{(2\pi m)^{3N/2}}{C_N} \int \frac{e^{-s(\mathscr{U} - \mu N)}}{s^{(3N/2+1)}} d^N\mathbf{x} \tag{42}$$

where $\mathscr{U}$ is the interaction potential which is a function of the configuration space variables only. After taking the inverse Laplace transform of the result the following expression is obtained for the phase space volume of the (μVL) ensemble:

$$\Phi = \sum_N \frac{(2\pi m)^{3N/2}}{C_N \Gamma(3N/2 + 1)} \int (L + \mu N - \mathscr{U})^{3N/2}\, \Theta(L + \mu N - \mathscr{U})\, d^N\mathbf{x} \tag{43}$$

Note that the term $(L + \mu N - \mathscr{U})$ is equal to the kinetic energy of the system, and it only depends on configuration space variables and number of particles. We exploit this fact to obtain the average kinetic energy of the system.

Obviously, a similiar result can be obtained for $\omega(\mu, V, L)$

$$\omega = \sum_N \frac{(2\pi m)^{3N/2}}{C_N \Gamma(3N/2)} \int (L + \mu N - \mathcal{U})^{(3N/2)-1} \Theta(L + \mu N - \mathcal{U})\, d^N \mathbf{x} \quad (44)$$

The corresponding expression for the ensemble average of a dynamical variable, $A(\mathbf{x}; N)$ is now seen to be

$$< A > = \frac{1}{\omega} \sum_N \frac{(2\pi m)^{3N/2}}{C_N \Gamma(3N/2)} \int A(\mathbf{x}; N)(L + \mu N - \mathcal{U})^{(3N/2)-1} \Theta(L + \mu N - \mathcal{U})\, d^N \mathbf{x} \quad (45)$$

Using the thermodynamic law, $TdS = dL + PdV + Nd\mu$, we can write the following thermodynamic definitions for temperature, pressure and average number of particles in the (μVL) ensemble

$$\frac{1}{T} = \left(\frac{\partial S}{\partial L}\right)_{V\mu} \quad (46.a)$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{L\mu} \quad (46.b)$$

$$\frac{N}{T} = \left(\frac{\partial S}{\partial \mu}\right)_{VL} \quad (46.c)$$

The corresponding statistical expressions, in terms of phase volume and phase density for these thermodynamic functions, can be obtained easily by using the Boltzmann relation for entropy. For instance, the statistical definition of temperature is

$$k_B T = \frac{\Phi}{\omega} \quad (47)$$

Using the above expression for the temperature and the definition of statistical average, given by Equation (45), we find the correlated average of the kinetic energy per particle as

$$\left\langle \frac{K}{N} \right\rangle = \frac{3}{2} k_B T \quad (48)$$

Note that, in this ensemble, the relation between temperature and kinetic energy differs from that of constant particle number ensembles, i.e. closed ensembles. Here, both the kinetic energy and number of particles are fluctuating variables, and they are correlated. Yet, this expression also differs from that of the grand canonical ensemble where one has

$$\frac{\langle K \rangle}{\langle N \rangle} = \frac{3}{2} k_B T \quad (49)$$

where correlation between K and N is broken. In order to obtain the pressure expression, we use the scaling transformtion $x = V^{1/3} q$ in taking the volume derivatives, then the result is

$$P = \frac{2\langle K \rangle}{3V} - \left\langle \frac{\partial \mathcal{U}}{\partial V} \right\rangle \quad (50)$$

A trivial result for the average number of particles follows from Equation (15.c),

where we have

$$N_{\text{th}} = \langle N \rangle. \tag{51}$$

The subscript *th* is used to denote the thermodynamic or *measured* value, whereas angular brackets represent the statistical averages. We use the statistical expressions for temperature, pressure and average number of particles, Equations (47), (50) and (51), below in order to obtain the expressions for the specific heat, Grüneissen parameter, adiabatic bulk modulus and the number fluctuations.

A. Specific heat

Isochoric specific heat is defined for this ensemble as

$$C_{V\mu} = \left(\frac{\partial L}{\partial T}\right)_{V\mu} \tag{52}$$

Using the statistical expression for temperature, Equation (47), we obtain the following expression

$$\frac{k_B}{C_{V\mu}} = \frac{\partial}{\partial L}\left(\frac{\Phi}{\omega}\right) = 1 - \frac{\Phi}{\omega}\frac{1}{\omega}\left(\frac{\partial \omega}{\partial L}\right) \tag{53}$$

After evaluating the partial derivative of ω with respect to L, this expression reduces to

$$\frac{k_B}{C_{V\mu}} = 1 - \left\langle \frac{K}{N} \right\rangle \left(\left\langle \frac{N}{K} \right\rangle - \frac{2}{3} \left\langle \frac{1}{K} \right\rangle \right). \tag{54}$$

This expression is naturally different from the expression in microcanonical ensemble [21], due to the correlation between N and K. The corresponding grand canonical expression can be obtained by taking the temperature derivative of $\langle \mathcal{H} - \mu N \rangle$.

$$\frac{C_{V\mu}}{k_B} = \frac{1}{(k_B T)^2}\left(\langle (\mathcal{H} - \mu N)^2 \rangle - \langle \mathcal{H} - \mu N \rangle^2 \right)$$

$$\frac{C_{V\mu}}{k_B} = \frac{1}{(k_B T)^2}\left[\delta(\mathcal{H}^2) - 2\mu\delta(\mathcal{H}N) + \mu^2 \delta(N^2) \right] \tag{55}$$

where $\delta(AB)$ is introduced to represent the square fluctuations and defined as usual

$$\delta(AB) = \langle AB \rangle - \langle A \rangle \langle B \rangle. \tag{56}$$

B. Grüneissen Parameter

The Grüneissen parameter is the counterpart of the temperature derivative of pressure which is obtained in isothermal ensembles. Customarily, it is defined in the microcanonical ensemble as

$$\gamma_V = V\left(\frac{\partial P}{\partial E}\right)_V \tag{57}$$

where also the particle number is constant, which is implicit in the above defintion.

In the (μVL) ensemble we define the Grüneissen parameter as

$$\gamma_{V_\mu} = V\left(\frac{\partial P}{\partial L}\right)_{V_\mu}. \tag{58}$$

By taking the derivative of the statistical expression for pressure, Equation (15.b), with respect to L we obtain the following

$$\gamma_{V_\mu} = -V\left(\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)\left(\frac{3/2N-1}{K}\right)\right\rangle - \left\langle\frac{\partial \mathcal{U}}{\partial V}\right\rangle\left\langle\frac{3/2N-1}{K}\right\rangle\right) + \langle N\rangle - \langle K\rangle\left(\left\langle\frac{N}{K}\right\rangle - \frac{2}{3}\left\langle\frac{1}{K}\right\rangle\right) \tag{59}$$

The form of Equation (58) is similiar to the microcanonical expression [5], but in the microcanonical ensemble the last two terms could be replaced by Nk_B/C_V exactly; here the same can be done only when the fluctuations in N and the correlation between K and N are negligibly small.

C. *Adiabatic bulk modulus*

Thermodynamic definition of the adiabatic bulk modulus is

$$B_S = -V\left(\frac{\partial P}{\partial V}\right)_S. \tag{60}$$

In evaluating the bulk modulus we use the following definition, which is obtained by using the thermodynamic identities and properties of partial differentials of multivariable functions

$$B_S = -V\left(\frac{\partial P}{\partial V}\right)_L - V\left(\frac{\partial P}{\partial L}\right)_V\left(\frac{\partial L}{\partial V}\right)_S \tag{61}$$

or

$$B_S = B_L + \gamma_V P \tag{62}$$

where B_L is introduced as a shorthand for the first term in Equation (61), the bulk modulus at constant L. Since we have already calculated γ_V and P, we only give the expression for B_L. Starting with Equation (50), after we evaluate the derivatives with respect to volume we obtain

$$B_L = V\left\langle\left(\frac{\partial^2 \mathcal{U}}{\partial V^2}\right)\right\rangle - V\left[\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)^2\left(\frac{3/2N-1}{K}\right)\right\rangle - \left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)\frac{3/2N-1}{K}\right\rangle\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)\right\rangle\right] + 2\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)N\right\rangle - \left\langle\frac{\partial \mathcal{U}}{\partial V}\right\rangle\langle N\rangle - \frac{2}{3V}(\langle NK\rangle - \langle N\rangle\langle K\rangle) - \left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)\frac{N}{K}\right\rangle\langle K\rangle + \frac{2}{3V}\langle K\rangle + \frac{2}{3}\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)\frac{1}{K}\right\rangle\langle K\rangle \tag{63}$$

The corresponding expression in microcanonical ensemble, B_E has essentially the same terms except for the fact that the N dependence can be trivially factored out. In the case of the microcanonical ensemble, the full adiabatic bulk modulus expression

is simplified by adding the explicit forms of P and γ_V, and by reorganizing the terms. The result of which has the following form:

$$B_S = -V\left(\frac{3N}{2} - 1\right)\left(\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)^2 K^{-1}\right\rangle - 2\left\langle\left(\frac{\partial \mathcal{U}}{\partial V}\right)K^{-1}\right\rangle\left\langle\frac{\partial \mathcal{U}}{\partial V}\right\rangle + \left\langle\frac{\partial \mathcal{U}}{\partial V}\right\rangle^2 \langle K^{-1}\rangle\right) + \frac{Nk_BT}{V}\left(1 + 2\gamma_V - \frac{Nk_B}{C_V}\right) + \left\langle\frac{\partial^2 \mathcal{U}}{\partial V^2}\right\rangle \tag{64}$$

In contrast, here the explicit full expression for the adiabatic bulk modulus is merely more cumbersome.

D. Number fluctuations

The statistical expression for number fluctuations can be obtained by taking the derivative of Equation (51) with respect to chemical potential μ,

$$\left(\frac{\partial < N >}{\partial \mu}\right) = \left\langle\left(\frac{\frac{3N}{2} - 1}{K}\right)N^2\right\rangle - \left\langle\left(\frac{\frac{3N}{2} - 1}{K}\right)N\right\rangle\langle N\rangle \tag{65}$$

If we only retain second order fluctuations, and approximate $(3N/2) - 1)/K$ as $1/k_BT$, we can write above expression as

$$\left(\frac{\partial\langle N\rangle}{\partial \mu}\right) = \frac{1}{k_BT}\left(\langle N^2\rangle - \langle N\rangle^2\right) \tag{66}$$

which is the same expression obtained in References [12]. Indeed one obtains the same expression in grand canonical ensemble, but in that case the derivative is evaluated at constant temperature. The thermodynamic expression corresponding to the number fluctuations contains the entropy explicitly. This is given by Equation (25) in reference [12].

$$\frac{\delta(N^2)}{k_BT\langle N\rangle^2} = \frac{1}{VB_S(1 + D)}$$

where

$$D = \left(\frac{TS}{C_P}\right)\left(\frac{S}{VB_T} - 2\alpha\right).$$

In the expression for D, α is the thermal expansivity, B_T the isothermal bulk modulus, and C_P the isobaric heat capacity. Thus, the calculations of number fluctuations from atomistic simulations will enable us to obtain an estimate of entropy and free energy of the system.

VI. ADDITIONAL ASPECTS AND IMPLEMENTATION

The molecular dynamics for open systems is formulated by employing the extended system dynamics approach used earlier [2] in developing the constant pressure and/or constant temperature [4] forms of molecular dynamics methods. Still, there are some

crucial differences, both practical and formal, between the present method and earlier constant pressure and constant temperature forms of extended system dynamics formulations. The phantom variable, v, monitors creation or annihilation of a particle in the system; *i.e.* it changes the *dimension* of the phase space in the new method. Whereas in the earlier constant pressure and constant temperature methods, the extra variable modifies only the trajectory of the system in a fixed dimensional phase space. Even though the variable v is continuous, the changes in the number of real particles occur in discrete jumps, N to $N + 1$ or N to $N - 1$, as in the physical processes. In order to preserve the continuity, a new concept, the *fractional particle*, is introduced into the extended system dynamics formalism.

The new features in the molecular dynamics method for open systems require additional elaboration. The equations of motion are solved exactly the same way as in closed system molecular dynamics methods in between two successive integer values v, $\{v(t) \mid (N, N + 1), N = 0, ..., \infty\}$, during the simulation. When the value of v becomes an integer in the course of simulation, N, or $N + 1$ a deletion or addition step is taken, depending on the value of v. The addition and deletion steps are executed by a search process based on local density and the continuity of the phase space trajectories. For instance, at n-th iteration v becomes equal to N, the fractional particle of n-th iteration is deleted, and one of the existing N-full particles is converted into a fractional particle for the succeding iterations. In choosing this new fractional particle the search is biased by the requirement of the continuity and the smoothness of the phase space trajectories of the number variable v, i.e. the proper time development of v is preserved. Thus, the kinetic energy and the potential energy of each of the current N particles tested against the kinetic energy and potential energy content of the deleted fractional particle, since the generalized force for the number variable is mainly determined by the difference, $K_f - U_f$, Equation (13),(18). With this test, the full particle which has the closest value is chosen as the new fractional particle. In the case where $v = N + 1$, the addition step is executed as follows: First, the current fractional particle is converted into a full particle. Then, the next fractional particle is created by using a local density biased search. In order to keep tract of the local density for the system under consideration, the simulation cell is divided into smaller equal volume $M_x \times M_y \times M_z$ cubic subcells, from the positions of the full particles and fractional particle the occupation number for each of these subcells is obtained. As first step of the search the minimum occupation number and the identities of the subcells with the minimum occupation number are determined. With a proper grid choice, the minimum occupation number can always be made to be 0, i.e. an empty subcell. Next, by placing a preconstructured $N \times N \times N$ grid on these minimum occupation number subcells, potential energy contents for each of the test positions are obtained. Using the same continuity and smoothness requirement, the new fractional particle is determined. But, now the comparison is made in between the potential energy contents of test points and potential energy content of the old fractional particle, and the unscaled kinetic energy of the new fractional particle is chosen the same as the unscaled kinetic energy of the old fractional particle.

VII. RESULTS AND DISCUSSION

For these demonstration calculations we have chosen a periodic box of a simple fluid, liquid argon, at a temperature of 110°K. The mass parameter W was set to unity. For

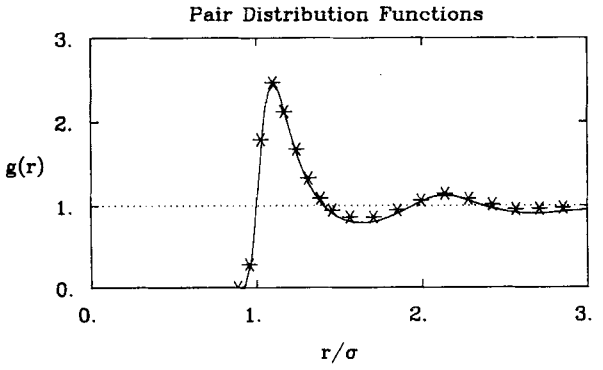

Figure 1 The radial pair distribution function. The solid line corresponds to the results of the GMD calculation; the stars are for an NVE run.

the calculation presented, a fifth order predictor-corrector algorithm was used to integrate the equations of motion with a time step of 1.52 fs for 400,000 steps after equilibrating for 100,000 steps. We have chosen a system in equilibrium with the chemical potential appropriate for a system averaging 289 particles at a reduced density of 0.45. The results of a comparison of the equilibrium pair distribution function with an appropriate microcanonical simulation are presented in Figure 1. where we have chosen

$$N_{NVE} = <N>_{\mu VL}$$

In addition, as a test of the truely dynamical nature of the simulation, we show a comparison of the velocity autocorrelation and its corresponding power spectrum in Figure 2. Both the spatial and time-like correlations appear to be faithfully represented in this simulation approach.

The number of particles exhibits stable fluctuations after equilibrium is achieved. A number of thermodynamic properties depended sensitively on the number fluctua-

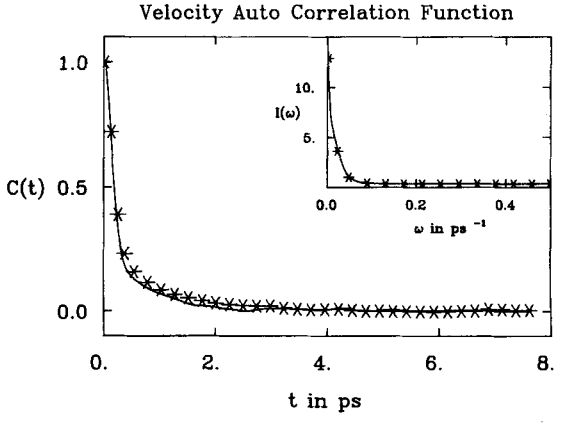

Figure 2 The velocity autocorrelation function and its power spectrum. The solid line corresponds to the results of the GMD calculation; the stars are for an NVE run.

tions. Convergence properties of all the thermodynamic variables also depend on these fluctuations. As a test, the specific heat at constant volume and constant chemical potential was evaluated over different segments of the run using the fluctuations formula, equation (51). The calculation was performed by using 20,000 data points over 200,000 steps. The result was

$$\frac{C_{V\mu}}{<N>k_B} = 5.62$$

$$<N> = 288.3$$

The calculation was repeated over an independent segement of 200,000 time steps using 20,000 data points and the result obtained was

$$\frac{C_{V\mu}}{<N>k_B} = 5.58$$

$$<N> = 289.9$$

As can be seen from the final two values the second order moments for K.E. have converged. The values for the two segments are within 1% of each other and the total result for the the run was

$$\frac{C_{V\mu}}{<N>k_B} = 5.60 \pm 0.02$$

$$<N> = 289.0 \pm 1.0$$

Other response functions, Grüneissen parameter and bulk modulus are also represented by second order formulas, equations (59) and (63). The convergence for γ was not as good over the two segments. The values obtained for the first of these equal segments:

$$\gamma_{V\mu} = 0.29$$

and for the second segment of the same length

$$\gamma_{V\mu} = 0.35$$

The convergence of sensitive properties such as γ and B_S may be dependent on the fictitious mass, W, as it determines the rate at which particles are introduced of destroyed. In a sense, for a Gibbs like picture, W controls the porosity of the "walls" around our representative member of the ensemble. With this in mind it may be possible to increase the rate of convergence with a smaller value for W. Clearly, since W is in the equations of motion a very small value of W would require a reduced time step. We are currently pursuing calculations to test these conjectures.

VIII. CONCLUDING REMARKS AND SUMMARY

We have presented a molecular dynamics method which simulates equilibrium grand ensembles. In formulating the method, the extended system dynamics approach introduced by Andersen [2] has been used as the starting point. A feature of the new method is the introduction of the fractional particle concept into the formalism of

extended systems. The concept is essentially the same one used by researchers in liquid state theory as a formal or computational concept [7–9]. Later, it was exploited to develop scaled particle theory [10]. We have shown the same concept can be used to generate number fluctuations in molecular dynamics computer simulations. We derived equations of motion for the extended systems corresponding to the adiabatic and isothermal forms of the new method. An equivalence proof was given for the isothermal case. Also the extension to multi-component systems has been illustrated.

This particular formulation of grand ensemble molecular dynamics method is not unique, at least for the isothermal case. Recently, Jellinek [15] and Jellinek and Berry [22] in their generalization of isothermal molecular dynamics, have shown that there are several possible choices for coupling to a heat bath. In addition to different couplings to a heat bath, one may also introduce other forms of scaling for the fractional particle.

As in earlier forms of extended system dynamics, the mass parameter, W, associated with the additional variable is an adjustable parameter. By changing the value of mass parameter, the period of number fluctuations can be tuned. The grand dynamics method like Grand Canonical Monte Carlo can be exploited to determine the entropies and/or free energies of systems of concern. In addition to free energy calculations, the new method has many potential applications. They range from calculations involving simple fluids, mixtures, molecular fluids, ionic solutions, to problems in material sciences such as super-lattices, interfaces, liquid metal alloys and problems involving biological macromolecules. Recently a great deal of attention has been given to the calculation of free energy or chemical potential differences in complicated biomolecular systems [23]. A common problem is how to scale the interactions with respect to simulated time. In an application of the methods developed herein, the actual particle or interaction scaling would be dictated by a dynamical variable in a process coupled to all the equations of motion in the system. Other difficult examples in free energy calculations could be approached as well. For instance, in a non-Boltzmann sampling scheme to acquire a particular cut in the potential of mean force between two complicated species, this scheme would allow for an easier choice of an optimal bias, for strongly adsorbed species, like counterions, would "disappear" when the chemical potential became unfavourable. Work along these lines is currently underway.

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