Towards a computational chemical potential for nonequilibrium steady-state systems

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We explore an approach to derive a computable chemical potential analog for thermostatted steady-state systems arbitrarily far from equilibrium. Although our method is not rigorous, it is based on theoretical and numerical evidence and exploits analogies with Widom's method widely used in computer simulations of equilibrium fluids. We obtain two formulas, one for steady states and one for the transient region. Despite being analogous to the equilibrium expression, the steady-state formula can only be used for approximate calculations. Possessing less obvious characteristics, we present representative calculations for the transient approach and discuss its numerical feasibility. [S1063-651X(99)04511-0]

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I. INTRODUCTION

There is an ongoing effort to establish statistical mechanics for nonequilibrium steady-state (NESS) fluids similar to the Gibbsian ensemble theory for equilibrium systems [1–3]. The need for such a theory is especially great in computer simulations when a system is modeled in atomic or molecular detail. These numerical models can provide insight into complex phenomena such as the phase separation of polymer blends under the impact of shear [4]. However, without a microscopic theory of thermodynamic character we are unable to mimic and understand the essence of phase coexistence in NESS. A mere extension of the rules of linear irreversible thermodynamics beyond the linear regime is not sufficient. These rules, based on minimization of the dissipation, are local [5], thus, are irrelevant as global potential functions indicating phase stability.

Simple arguments are sufficient to make it clear why minimal dissipationlike criteria cannot be candidates as markers for nonequilibrium phase transitions. If one has two coexisting fluid phases in equilibrium and at $t=0$ turns on a weak, time-independent dissipative field (for instance, charged particles in homogeneous electric field) the properties of the phase coexistence will not change considerably. *If the coexistence properties were determined by the minimum of the entropy production*, for instance, there should be a relationship between the zero field transport coefficients in the two phases and the corresponding chemical potentials, since the dissipation of each phase is proportional to its transport coefficient related to the dissipative field. Therefore the weighted sum of the relevant transport coefficients in phase balance should be a minimum with respect to the same sum in other states of the system at the given macroscopic constraints. This condition should hold for all types of possible transports and all types of phase transitions. Clearly, this cannot be the case.

Another objection against the application of exclusively dissipation-based extremum principles for phase coexistence applies also beyond the linear regime of one-component systems. The minimum of the entropy production (or any other analog of it) would require identical dissipation per particle in the coexisting phases. If the dissipation of the two phases were different the extremum condition would act to decrease the amount of the more dissipative phase. This would lead either to the annihilation of one of the phases or (if it were possible) to two phases with equal dissipation per particle. *If such extremum principles were applicable in a vapor-liquid coexistence*, for instance, any dissipative field, no matter how small, would annihilate the gas phase entirely.

It appears that returning to the concepts of equilibrium thermodynamics might yield a solution. The task is to find a generalized expression for the chemical potential which is valid under the usual circumstances of nonequilibrium molecular dynamics (NEMD) simulations, i.e., in homogeneous, steady state systems with acting external field and a synthetic thermostat [2]. Although these models are artificial due to the presence of the numerical feedback removing the dissipative heat instantaneously, they are well-defined and well-studied systems. Any advance in the theory of these models helps the understanding of real systems.

The chemical potential, being a derivative of the entropy, is expected to be less controversial than the entropy itself. (Even if the NESS entropy does not have a well-defined and unique value, its partial derivatives might have such properties [6].) Still, determination of such a quantity appears problematic because all the direct equilibrium methods, which might serve as analogies, directly sample the phase space of the system. Since the phase space distribution function of a NEMD model is a fractal quantity, one might face insurmountable barriers.

In Sec. II we derive a formally simple expression of a chemical potential analog (CPA). The derivation relies on the recently performed numerical experiments of Evans and Searles [7]. Then in Sec. III we discuss an alternative derivation which, at first glance, might seem more attractive. The latter approach is not entirely new. Several years ago we performed calculations based on similar ideas [8]. In those calculations, however, we used the equilibrium technique in

a NESS system of hardcore particles knowing that the result can only be an approximation to the actual value. Here, we perform a systematic derivation but present no representative calculations for the method, because we have no reference data to check the accuracy of the results. However, in Sec. IV, we present simulation results using the formula of Sec. II. Interestingly, this formula does not require stochastic sampling of the system but does rely on having good statistics and numerical integration. In Sec. V we present our conclusions.

II. CPA EXPRESSION FROM THE TRANSIENTS

We adopt an approach similar to the thermostatted non-linear response theory of Evans and Morriss developed for NEMD models [2,7]. These theories start with the formal solution of the Liouville equation. Before $t=0$ the system can be characterized by the canonical distribution function. This distribution is propagated forward in time taking into account the impact of the steady external field turned on at $t=0$ [2,7].

For $t \geq 0$ the equations of motion are

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m} + C_i \mathbf{F}_e$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + D_i \mathbf{F}_e - \alpha \mathbf{p}_i, \qquad (1)$$

where $\mathbf{q}_i$, $\mathbf{p}_i$ are the position and momentum of particle i, $\mathbf{F}_i$ is the Newtonian and $\mathbf{F}_e$ is the external force, and C_i, D_i are phase functions that describe the coupling of the external field to the system. The dissipative flux $\mathbf{J}(\Gamma)$ is defined in terms of the unthermostatted time derivative of the internal energy

$$\dot{H}(\Gamma) \equiv -J(\Gamma)\mathbf{F}_e \qquad (2)$$

where $\Gamma \equiv (\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N, \mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)$ is a point in phase space. If our thermostat is an ergostat, i.e., the feedback constrains the internal energy to a constant, the instantaneous value of α is

$$\alpha = \frac{-\mathbf{J} \cdot \mathbf{F}_e}{\Sigma(\mathbf{p}_i^2/m)}. \qquad (3)$$

It is well-established that in NESS the overwhelming majority of the observed trajectory segments are entropy increasing [9]. In such cases a phase-space volume element σ shrinks exponentially [7]:

$$\sigma(\Gamma(t)) = \sigma(\Gamma(0)) \exp\left\{ -\int_0^t 3N\alpha[\Gamma(s)]ds \right\}. \qquad (4)$$

It has been shown recently that the shrinkage of a phase-space volume element is correctly described by the dissipation integral in Eq. (4) at least for times shorter than the characteristic time-correlation length of the dissipative process [7].

NEMD models are well-defined NESS systems with well-defined means and fluctuations. Our present model obeys strict energy conservation. Due to the definition of the ergostat in Eq. (3) this condition is maintained not only in the

transition period but in the infinite time limit of the steady state as well. We have essentially zero probability—especially for strong external fields typical in simulations—to observe entropy decreasing trajectory segments [9]. If we want to estimate a microcanonical-type probability of finding our NESS system in a single point of phase space, we can take the product of the starting equilibrium distribution function and the rate of shrinkage of the phase space. Following Eq. (4), the shrinkage rate can be estimated as follows:

$$f_N(\Gamma(t)) = f_N(\Gamma(0)) \exp\left\{ -3N \int_0^t \alpha(s)ds \right\} \qquad (5)$$

where the subscript N refers to the number of particles in the system.

The exponential shrinkage of the phase-space volume element is a manifestation of the dimensional contraction of the distribution function [10]. This fractal behavior raised concerns regarding the nonanalytic nature of the distribution function [11]. In addition to the nonanalitic behavior the phase-space volume of the strange attractor in the infinite time limit is inaccurate because of the finite memory caused by Lyapunov instability. In addition to these difficulties, the norm of Eq. (5) is a function of time. After a short initial period this norm becomes essentially zero. However, in the present derivation we are interested only in *relative* probabilities. The compared functions possess very similar properties which may eventually cancel out their problematic character.

Using Eq. (5) as a probability distribution function we can obtain the NESS analog of the chemical potential by applying the so-called Widom test particle method [12] well-known in the computer simulation methodology of equilibrium systems [15]. The idea of this derivation is to define the position of particle $N+1$ as the origin of the system, then integrate out the three position variables from the canonical partition function.

$$-\beta\mu = \left(\frac{\partial \beta A}{\partial N} \right)_{V,\beta} = \beta A(N+1, V, \beta) - \beta A(N, V, \beta)$$

$$= -\ln\left[\left(\frac{h^{-3}}{N+1} \right) \frac{\int d\Gamma_{N+1} \exp(-\beta H_{N+1})}{\int d\Gamma_N \exp(-\beta H_N)} \right]$$

$$= \beta\mu^{id} - \ln\langle \exp(-\beta\phi) \rangle \qquad (6)$$

where A is the Helmholtz function, $H_{N+1} = H_N + \phi + 3/(2\beta)$. The first term on the right-hand side of Eq. (6) is the ideal gas part of the chemical potential, $\beta\mu^{id} = \ln(\rho\Lambda^3)$, where $\rho = N/V$ is the number density and $\Lambda = [(2\pi\beta\hbar^2)/m]^{1/2}$ is the de Broglie wavelength.

At this stage there are several ways to exploit the analogy with Eq. (6). One can estimate the CPA from sampling a NESS system represented by a NEMD simulation. (We will turn to this in the following section.) However, from a theoretical point of view the most straightforward is the picture described in Eqs. (1)–(5). In the latter case the result for the chemical potential analog μ^* can be given as follows:

$$\beta\mu*(t) = \beta\mu^{id}(0) - \ln\left\langle \exp\left\{ -\beta\phi(0) - 3\int_0^t [(N+1)\alpha_{N+1} - N\alpha_N]ds \right\} \right\rangle. \quad (7)$$

The only difference between Eqs. (6) and (7) is the extra integral in the exponent of Eq. (7). At equilibrium the random insertions sample states of the $(N+1)$-particle system from the N-particle system. In the case of simple fluids this estimate is accurate enough to exploit for numerical calculations. [Unfortunately, the reverse of this approach, sampling the N-particle phase space from the $(N+1)$-particle one, although correct in principle and more easily achieved computationally, is extremely inaccurate in practice.] Recently, based on results of very accurate numerical calculations, Evans and Searles demostrated that for finite times the Kawasaki distribution preserves its norm [7]. This means that the difference in the phase-space contractions of the two systems is correctly represented by the integral in Eq. (7).

The simplest way of performing the calculations is to separate the equilibrium and the switched-on nonequilibrium part of the calculations. The random insertion process provides a correct representation of the $(N+1)$-particle system. Therefore we can assume that determining the α's of the two systems separately, starting from their equilibrium state, is correct because this is the way we move to their representative NESS states.

In NESS the system is on a strange attractor in phase space without a further loss of dimensionality. Our calculation must be able to separate that part of the dissipation which characterizes the phase-space contraction for transient times from the permanent and (apart from fluctuations) constant dissipation of the steady state. This task is more than mere technicality (see Sec. IV).

III. CPA EXPRESSION FOR STEADY STATES

The expression of Eq. (7) exploits the information present in the transition region. Considering a numerical realization of the Widom or test-particle method sampling of the steady state seems a more attractive alternative. We expect to avoid the explicit time dependence because macroscopic properties of NESS systems are independent of time. In order to make the derivation clearer we change the variable in the equation of the partition function. Then

$$Q_N = \int_{-\infty}^{\infty} W_N(E,\beta)\exp(-\beta H_N)dE \quad (8)$$

where $W_N(E,\beta)$ is a phase-space volume defined as

$$W_N(E,\beta)\delta E \equiv \frac{1}{N!h^{3N}}\int_{E \leq H \leq E+\delta E} \delta[H(\Gamma)-E]d\Gamma. \quad (9)$$

Then the expression for the equilibrium chemical potential is

$$\beta\mu = -\ln\left\langle \frac{W_{N+1}(E+\Delta E,\beta)}{W_N(E,\beta)} \times \exp[(-\beta(H_{N+1}-H_N))] \right\rangle_{E,\Delta E}. \quad (10)$$

The average in the logarithm should be taken for different E and ΔE values. We can obtain exactly the same expression for NESS systems

$$\beta\mu* = -\ln\left\langle \frac{W_{N+1}^*(E+\Delta E,\beta)}{W_N^*(E,\beta)} \times \exp[-\beta(H_{N+1}-H_N)] \right\rangle_{E,\Delta E}, \quad (11)$$

where the stars indicate that these quantities were measured far from equilibrium. The reason why Eq. (11) is formally identical with Eq. (10) follows from the energy-constrained dynamics of Eqs. (1)–(3). The Boltzmann-factor for the same energy difference remains the same but the equilibrium phase-space volumes and volume ratios of the corresponding energies or energy differences will change under the impact of the external field.

Equation (10) can be simplified by the factorization of $W_N(E,\beta)$

$$W_N(E,\beta) = \frac{(Vh^{-3})^N}{N!}W_N(\Phi)_\beta\prod_{i=1}^N W_i(\beta)p^{3N}, \quad (12)$$

where Φ is the potential energy of the system and p is the unit of the momentum. Since $W_i(\beta)=1$ for all i, we get

$$\beta\mu = \beta\mu^{id} - \ln\left\langle \frac{W_{N+1}(\Phi+\phi)_\beta}{W_N(\Phi)_\beta}\exp(-\beta\phi) \right\rangle_{\Phi,\phi}. \quad (13)$$

This expression is the same as Eq. (6) with the difference that here the averages are formed over the energy; therefore, the corresponding weight functions (phase-space volumes) are shown explicitly. During an equilibrium simulation (Monte Carlo or molecular dynamics) the frequency with which the system visits different regions of the phase space correctly represents the $W_N(\Phi)_\beta$ values, while simultaneous random insertions of the test-particle estimate the phase-space volume of $W_{N+1}(\Phi+\phi)_\beta$.

The simplification of Eq. (10) utilized the implicit assumption that particle velocities are mutually uncorrelated and there is no correlation with the positions either. This is not true for NESS systems. If we still want to obtain an analogous excess-chemical-potential-type expression we cannot get substantially further in simplicity from Eq. (11). Although the denominator values in the logarithm are reproduced during an NEMD run, velocity-velocity and position-velocity correlations prohibit the previous factorization. It is well-known that there are multiple collision patterns in nonequilibrium liquids at higher densities [13].

We performed some exploratory calculations on a Sllod system thermostatted by a Nosé-Hoover integral feedback [2]. Distribution of the random kinetic energy is no longer isotropic

$$\sum_i p_{ix}^2 \neq \sum_i p_{iy}^2 \neq \sum_i p_{iz}^2 \text{ and } \langle p_{ix}p_{iy}\rangle \neq 0$$

in these systems. In addition to this, the total energy of a particle is correlated with its random kinetic energy. Unfortunately, one cannot tell *a priori* how much of the phase-space contraction is represented by the easily calculable one-particle correlations. This restricts the calculations to an approximate value, in fact, to an upper bound for the CPA.

To do such an approximate calculations for hard particles reduces the complications somewhat by removing the potential energy. (This was utilized in our previous study [8].) However, the problem of higher-order correlations applies to hard particles as well; therefore we will not discuss the numerical details of this method here.

IV. CPA CALCULATIONS FROM THE TRANSIENTS

We tested Eq. (7) using a model liquid of WCA particles at a state point on the Lennard-Jones liquid-vapor coexistence curve with the number density of 0.758 and the temperature of 0.9 [14]. (Here we apply the usual reduced units of computer simulations [15].)

Particles of the WCA model are defined as a short-range version of the Lennard-Jones interaction. The pair-potential $\phi(r)$ is also spherically symmetric, pairwise additive and is given in terms of the distance between two particles r as follows:

$$\phi(r) = \begin{cases} 4[r^{-12} - r^{-6}] + 1, & r < 2^{1/6}, \\ 0, & r > 2^{1/6}. \end{cases}$$

The calculations were performed using the Sllod algorithm of planar Couette flow [2] at the reduced shear rate of 1.0. We started nonequilibrium trajectories from the equilibrium systems containing N or $N+1$ particles at regular intervals (50 time-steps). The length of each trajectory was 2000 time steps. We used a fourth order Runge-Kutta integrator for this purpose with 0.001 reduced time step. To save computer time, after five steps we fitted a polynomial to the positions and momenta and switched to a fifth order Gear integrator by determining the higher order derivatives of the predictor steps. The dissipation function recorded at each time step was averaged for both systems. Then we determined the average dissipation difference according to Eq. (7). We had three different systems containing 32, 108, and 256 particles in order to see the systematic behavior and the size-dependence of the method. The averaged values were calculated from 2×10^5 or 1×10^5 individual trajectories for the 32-, 108-, and 256-particle systems, respectively.

In Fig. 1 we show enlarged curves for the thermostatting multipliers for the three different system pairs. Systems with $N+1$ particles were at the target density of 0.758. The large waves apparent in the curves are not random fluctuations.
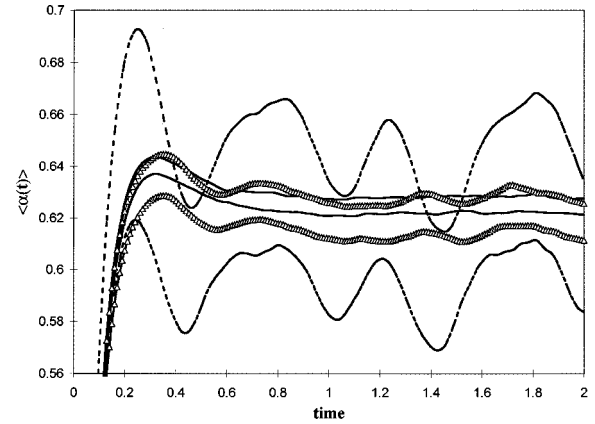

FIG. 1. Dissipation as function of time for three system pairs (dashed lines: 31 and 32; triangles: 107 and 108; solid lines: 255 and 256). The temperature is 0.9 in each system. The density, $N/V = 0.758$, for the larger members of the pairs and $(N-1)/V$ for the smaller members. Every quantity is given in reduced units.

They have the same characteristics for the members of each pair and are related to the non-autonomous property of the Sllod algorithm [16].

In Fig. 2 we show the dissipation differences for the three systems. Despite the 2×10^5 individual trajectories, these curves contain considerable fluctuations. There may also be certain amount of systematic behavior, especially in the case of the two smaller system pairs (108-107, 32-31). Nevertheless, after the reduced time of 0.7–0.8 the running integral of these curves provides a linear function which indicates that transient effects became asymptotically weak, in practice, we reach the plateau (see Fig. 3). We can fit of a straight line to the long-time part of this curve. The y intercept will represent the loss of the transient dissipation relative to a fictive steady state dissipation having the plateau value from $t = 0$ (a Newtonian fluid without time dependence).

A trivial way to separate the transients from the steady state contribution is to identify the first crossing point of the dissipation difference curve and its long-time average. The value of the running integral at this point can be viewed as the extra contraction of the phase-space volume caused by
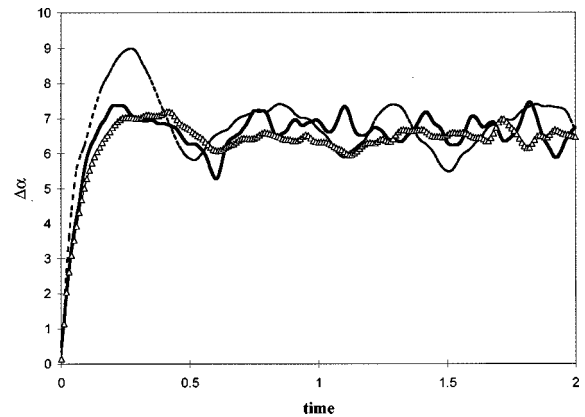

FIG. 2. Dissipation differences for the three system pairs (dashed line, 32-31; triangles, 108-107; solid line, 256-255). $\Delta\alpha = 3[(N+1)\langle\alpha(t)\rangle_{N+1} - N\langle\alpha(t)\rangle_N]$. Waves on the curves of the smaller systems seem more systematic, while, in the case of the large system, they are merely noise.
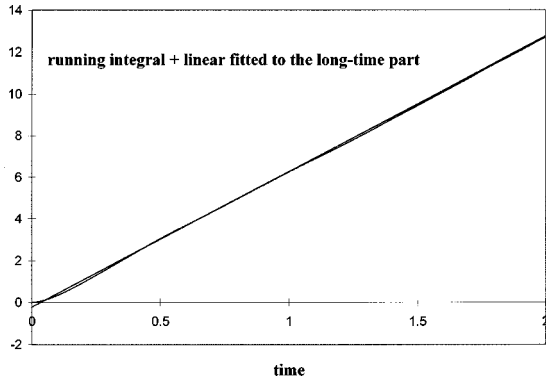
FIG. 3. The running integral of the exponent in Eq. (7) for the (107-108) pair and the linear fitted to the second half of the curve. Despite the seemingly noisy character of the curves shown in the previous figure, with the exception of the short initial part, the fit is hardly distinguishable from the running integral.

the presence of the extra particle. However, this method fails to explain what to do with the so-called "overshoot" region where the dissipation has higher values than its long time average. A more reasonable but computationally simple way is to identify the linear viscoelastic behavior of the fluid. Linear effects make no contributions to changes in thermodynamic potential functions. The simplest model for this is the Maxwell fluid in which the constitutive relation is non-Markovian but linear [2]. The transient dissipation response of the Maxwell fluid to a step-function strain rate can be written as

$$\langle \alpha(t) \rangle = \langle \alpha \rangle (1 - \exp[-t/\tau_M]), \qquad (14)$$

where $\langle \alpha \rangle$ is the $t \to \infty$ expectation value of the thermostatting multiplier and τ_M is the Maxwell relaxation time. Our choice of τ_M is $1/\lambda_{max}$ where λ_{max} is the largest Lyapunov exponent of the steady state system. This exponent represents the most unstable mode of collective motions, i.e., the fastest relaxation in the system. In the case of weak fields, Eq. (14) is a reasonable approximation of the time-dependence of the average multiplier. We assume that this behavior can be extended to strong fields and must be subtracted from the total response.

An alternative argument can be given for Eq. (14) by turning to dynamical systems theory. The ostensible phase-space-volume contraction contains a contribution which is the result of the increasingly fractal character of the phase space of NEMD models. In addition to the real contraction of the phase space volume, this virtual contribution is always there; in fact, in steady state this is the only effect left. Unfortunately, we cannot provide a quantitative theory or present convincing numerical results of exploratory calculations performed in the short transient region which could refine Eq. (14). We accept the form of Eq. (14) as the simplest approximation. One may argue that the minimal value of the coarse-graining length scale ε which provides accurate enough results for the fractal dimension of the systems, should vary as the smallest (largest negative) Lyapunov exponent. In this case we can replace λ_{max} by $-\lambda_{min}$. In Fig. 4 we show the simulated and the calculated dissipation difference curves for one of the systems. The latter curves were determined using Eq. (14) with both λ_{max} and $-\lambda_{min}$. From
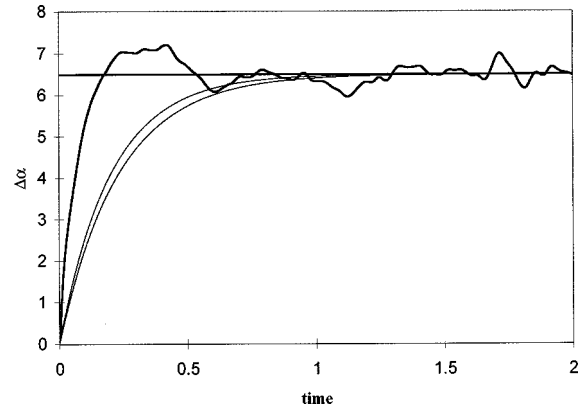

FIG. 4. Separation of the transient from the steady-state contribution using Eq. (14) with λ_{max} and $-\lambda_{min}$. The long-time dissipation difference value of 6.49 (shown as a line parallel with the x axis) has been calculated from the fit of a straight line to the previous figure (108-107 particles). Functions for the linear terms, $3[(N+1)\langle \alpha \rangle_{N+1} - N\langle \alpha \rangle_N][1 - \exp(-\lambda_{max}t)]$ and $3[(N+1)\langle \alpha \rangle_{N+1} - N\langle \alpha \rangle_N][1 - \exp(\lambda_{min}t)]$, respectively, are also shown.

our earlier calculations for the smallest system we obtained the $\lambda_{max} = 4.3$ value. From the conjugate pairing rule ($\lambda_{max} + \lambda_{min} = -\langle \alpha \rangle$) we can determine λ_{min} [17].

In Table I we present the results of the calculations using the data shown in the figures. Values of the simple separation scheme are also shown for comparison. We also calculated the integral between the overshoot curves and the long-time averages to correct for the obvious failure of this crude approximation. Results using Eq. (14) take into account the effect of the overshoot automatically. Because of its large first maximum, the smallest system provided a large chemical potential by this method. The rest of the data indicates an increase of a little more than unity over the equilibrium chemical potential.

V. CONCLUSIONS

We have investigated a possible approach to derive computationally feasible chemical potential analogs for NEMD model liquids in order to be able to simulate phase coexistence in NESS systems. We argued that minimum dissipation-type criteria are unsuitable as markers for this purpose. In the derivation we exploited the analogy with the

TABLE I. Change in the chemical potential relative to the same system (WCA, $N/V = 0.758$, $T = 0.9$) in equilibrium. The first column (a) refers to the value determined from the simple separation scheme. The second column (b) shows the value when the integral under the excess contribution of the overshoot curve was also added. The third (c) and the fourth (d) columns show results using Eq. (14) with λ_{max} and $-\lambda_{min}$, respectively.

	$\Delta \mu_{NESS}$			
N	a	b	c	d
31-32	0.48	0.96	1.80	1.60
107-108	0.78	0.95	1.22	1.02
255-256	0.58	0.68	1.21	1.00

Widom or test-particle method of equilibrium simulations.

Following this approach, we found two different ways of prescribing the numerical recipe. The first approach is related to the Kawasaki formalism of Evans and Morriss and relies on the norm-preserving property of this function. The information is collected from the transient region of the switch-on experiment. The other possibility is to consider the model in NESS and determine the relative phase-space volumes of insertion attempts. We showed that in the latter method one cannot get an exact answer without computing many-particle correlations. However, it can be used for approximate calculations. In this respect, the lack of NESS data prevents us from estimating the accuracy of the method.

We performed representative calculations for the chemical potential analog determined from the transients of the switch-on experiment. The essence of this technique is to estimate the relative phase-space contraction of the N- and $(N+1)$-particle NESS systems. To be sufficiently accurate the calculation requires numerous transient trajectories. Still, the real problem is the separation of the transient contribution (which indicates the difference in dimensional contraction) from the steady state one. For this purpose we applied an intuitive method of separation based on the Maxwell model of linear viscoelasticity.

The results seem sensible but cross-checks might be necessary to test the accuracy of the method. Unfortunately, we know of no simpler models as replacements of our many particle NEMD systems. At present there is no simple map which could be used for such a purpose [18]. Having only two or three particles in the NEMD model in order to allow a thorough numerical study might be a way for determining other partial derivatives of the entropy such as temperature or pressure. However, in the case of the chemical potential, the derivation does not permit such extremely small system sizes.

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