THE JOURNAL OF CHEMICAL PHYSICS **128**, 114707 (2008)

Liquid-solid coexistence via the metadynamics approach

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(Received 20 November 2007; accepted 16 January 2008; published online 18 March 2008)

The metadynamics method, recently proposed by Laio and Parrinello as a general tool to map multidimensional free-energy landscapes [A. Laio and M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. **99**, 12562 (2002)], has been exploited with the aim of illustrating the properties of generalized thermodynamic potentials across a discontinuous phase transition. Virtues and limitations of the method are discussed in the exemplifying case of the freezing of a Lennard-Jones fluid in two dimensions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841081]

I. INTRODUCTION

The liquid-solid transition is among the best known and most widely studied first-order phase changes. A common trait of such discontinuous transitions is the emergence of hysteresis, a feature reflecting the existence of long-lived metastable states. This phenomenon produces a dynamical bottleneck on the observation of the ideal equilibrium behavior, which sets in only after times that approach infinity for vanishing deviations from two-phase coexistence. In fact, the nucleation of a crystalline structure out of a liquid drop is an activated phenomenon, which takes place only after the system has eventually overcome a free-energy barrier. As a result, the freezing of a fluid is usually observed after supercooling the system to the extent that a solid cluster with a radius larger than a critical size forms and grows. In a similar way, the melting of the bulk crystal typically occurs when the system is superheated up to the point where the lattice becomes unstable. Hence, in spite of the fact that numerical-simulation techniques, implemented with periodic boundary conditions, are well suited for studying the freezing and melting in a bulk system, owing to the elimination of surface effects, the time scale over which such phase changes typically occur is not ordinarily accessible to currently available computers.

For the earlier reasons, most of the old and even recent numerical studies of liquid-solid equilibria explicitly avoid considering coexisting states and just compute one-phase properties along the stable/metastable branches of both phases via some form of thermodynamic integration.[1] One then identifies the coexistence point as the thermodynamic state that is characterized by equal values of the intensive parameters (i.e., temperature T, pressure P, and chemical potential μ) in the two phases.

Recently, an entirely different method has been proposed by Laio and Parrinello in order to cope with structural changes of general type.[2] Given an arbitrary coarse-grained description of the system in terms of a few collective coordinates, the so-called metadynamics (MD) method exploits an artificial evolution which combines the steepest-descent dynamics that is driven by the generalized free energy (GFE) of the system with an antagonistic, history-dependent force. This force is constructed from a fictitious potential V_G, modeled as a sum of Gaussian-shaped contributions centered along the path traced by the collective variables. As time goes by, V_G fills the GFE valleys that are associated with different arrangements of the system, until the sum of the GFE and V_G becomes roughly constant as a function of the collective variables. In order for the method to work efficiently, the MD algorithm requires the accurate evaluation, step by step, of the GFE derivatives with respect to the collective variables. The main virtue of the MD method lies in the ability to drive the system throughout the macrovariable space, this way allowing a thorough exploration of the existing basins.

In the present work, we apply the MD method to the study of the liquid-solid transition undergone by a simple fluid. As far as we know, the only previous attempts of a similar kind are an analysis of the melting transition of hexagonal ice[3] and a study of crystal nucleation in a Lennard-Jones fluid in three dimensions.[4] However, both these studies significantly depart from the present treatment. The easiest way to distinguish a liquid drop from a crystallite is through the comparison of the relative number densities, though other more sophisticated means could be conceived, such as the structural order parameters that were originally proposed by Steinhardt and co-workers[5] or the concentration of the crystal defects that are suspected to play a crucial role at melting.[3] All such indicators are particularly useful whenever one wants to elucidate the underlying microscopic mechanisms that trigger the freezing/melting transition or when more than one candidate for the stable crystal structure is to be taken into account. By contrast, if there is only one intervening solid phase and the interest is just in the thermodynamic aspects of the transition, using the density as the single macrovariable that discriminates between the liquid and the solid may prove sufficient. In order to deal with such simpler cases, we set up in Sec. II the thermodynamic and statistical-mechanical framework for a MD treatment of the liquid-solid phase transition. Section III is devoted to a practical demonstration of the method. Some concluding remarks are given in Sec. IV.

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II. THERMODYNAMIC FRAMEWORK

In an isolated system at equilibrium, entropy attains the maximum value that is compatible with the given thermodynamic constraints. Hence, for a closed N-particle system with short-range interactions—e.g., a simple fluid—in contact with a heat and volume reservoir, the generalized thermodynamic potential,

$$\widetilde{G}(E,V;T,P,N)=E-TS(E,V,N)+PV, \tag{1}$$

attains its minimum value at equilibrium.[6] In Eq. (1), $S(E,V,N)$ is the entropy of the fluid, while T and P are the values of the temperature and pressure that are fixed by the bath. At variance with T, P, and N, which are thermodynamic control parameters (i.e., fixed numbers), the macrovariables E and V are to be adjusted in order for the fluid and the bath to be in mutual equilibrium. When this condition is fulfilled, the minimum value of $\widetilde{G}$ yields the Gibbs free energy of the fluid, $G(T,P,N)$.

The earlier considerations are fully thermodynamic in character and, as such, they are asymptotically valid for a statistical-mechanical model of a fluid in the thermodynamic limit. In this case, $\widetilde{G}$ is a convex function of E and V—since the microcanonical entropy of the fluid $S(E,V,N)$ is a concave function of the same variables—and shows a unique minimum. Conversely, when N is finite, the function $S(E,V,N)$ may not be everywhere concave. In particular, in the neighborhood of a discontinuous phase transition point, $\widetilde{G}$ develops another minimum, with a smaller depth than the one corresponding to the stable equilibrium state. This secondary minimum is associated with a competing metastable phase. Correspondingly, a whole region of energies and volumes appears where $\widetilde{G}$ has the "wrong" concavity.

For finite N, one can use the MD method to reconstruct the profile of $\widetilde{G}$ as a function of E and V, for fixed values of T and P. To this aim, all that is needed is the computation of the partial derivatives of $\widetilde{G}$ with respect to E and V in the region (Λ) of interest.[7] Since

$$\begin{aligned}\frac{\partial\widetilde{G}}{\partial E}&=1-\frac{T}{T(E,V,N)},\\ \frac{\partial\widetilde{G}}{\partial V}&=-T\frac{P(E,V,N)}{T(E,V,N)}+P,\end{aligned} \tag{2}$$

the problem actually reduces to estimating $T(E,V,N)$ and $P(E,V,N)$, i.e., the temperature and the pressure of the isolated fluid. In a MD run, upon starting, say, from the values of E and V that correspond to the equilibrium state for the given T and P, the simulation algorithm generates a path throughout Λ which, if sufficiently long, will pass many times nearby each Λ point. In this case, the sum of Gaussians which is updated at every step of the procedure will eventually match, though with a reversed sign, the profile of $\widetilde{G}(E,V)$.

To simplify things further, let us suppose that we are only interested in the "slice" of the $\widetilde{G}(E,V)$ surface where the constraint $T(E,V,N)=T$ is satisfied (this condition is actually equivalent to considering the equilibrium value of E for the given values of T, V, and N). In this case, $\widetilde{G}$ reduces to

$$\begin{aligned}\mathcal{G}_{T,P,N}(V)&\equiv\widetilde{G}(E(T,V,N),V;T,P,N)\\ &=E(T,V,N)-TS(T,V,N)+PV\\ &=F(T,V,N)+PV,\end{aligned} \tag{3}$$

and, in place of Eqs. (2), we get

$$\frac{\mathrm{d}\mathcal{G}_{T,P,N}(V)}{\mathrm{d}V}=P-P(T,V,N). \tag{4}$$

In the earlier formula, $P(T,V,N)\equiv P(E(T,V,N),V,N)$ is the pressure of the fluid expressed as a function of T, V, and N. This approach is similar in spirit to the method proposed by Martoňák and co-workers for studying solid-solid transitions.[8]

Note that any local extremum of $\widetilde{G}(E,V)$ is such also for $\mathcal{G}(V)$ since the condition $\partial\widetilde{G}/\partial E=0$ is equivalent to $T(E,V,N)=T$. A straightforward calculation also yields

$$\frac{\mathrm{d}^2\mathcal{G}_{T,P,N}(V)}{\mathrm{d}V^2}=\frac{P_E T_V-P_V T_E}{T_E}=\frac{\widetilde{G}_{EE}\widetilde{G}_{VV}-\widetilde{G}_{EV}^2}{\widetilde{G}_{EE}}, \tag{5}$$

showing that the sign of the second derivative of $\mathcal{G}$ at an extremal point is the same as that of $\widetilde{G}_{EE}=-TS_{EE}$.

The earlier derivation implicitly assumes that $T_E\propto S_{EE}\neq 0$ for any (E,V,N), which in fact is verified in the thermodynamic limit. However, for finite N, the entropy function may have a convex intruder and one is not allowed to invert locally $T(E,V,N)=T$ at those points where S changes from concave to convex as a function of E only. Even in this case, Eqs. (3) and (4) remain well defined as long as $F(T,V,N)$ and $P(T,V,N)$ are interpreted as the canonical Helmholtz free energy and pressure of the fluid.

If, for instance, the fluid pressure is slightly less than the liquid-solid coexistence pressure at temperature T, the deepest minimum of $\mathcal{G}$ is associated with the liquid phase and, correspondingly, the isothermal compressibility attains negative values over a range of volumes (similar considerations apply to the liquid-vapor transition as well). As is well known, on approaching a discontinuous phase-transition point, the profile of $P(T,V,N)$ generally shows, when plotted as a function of V, a van der Waals loop.[9–12] By Eq. (4), this feature suffices to generate a $\mathcal{G}$ profile with two minima.

At each MD step, the calculation of $P(T,V,N)$ can be carried out by a Monte Carlo (MC) simulation of the fluid in the canonical ensemble. In practice, the calculation is feasible for two-dimensional systems only since the MC decorrelation time is enormously long in the transition region (all the more so in three dimensions) and, as a result, the computed $P(T,V,N)$ will be affected by a huge error. This effectively restrains the applicability of the present method to fluids in two dimensions.

We can attach another meaning to $\mathcal{G}_{T,P,N}(V)$. To this aim, we consider the probability that the N-particle fluid has volume V at equilibrium, when the temperature and the pressure are both held fixed

$$\Pi_{T,P,N}(V) = \frac{e^{-\beta PV} Z_{T,V,N}}{Y_{T,P,N}}, \tag{6}$$

$Z_{T,V,N}$ and $Y_{T,P,N}$ being the canonical and isothermal-isobaric partition functions of the fluid. Then, if we define the auxiliary potential

$$\Phi_{T,P,N}(V) \equiv -\frac{1}{\beta} \ln \Pi_{T,P,N}(V) = PV + F(T,V,N) - G(T,P,N), \tag{7}$$

we see that $\mathcal{G}_{T,P,N}(V)$ and $\Phi_{T,P,N}(V)$ do actually differ for an "additive constant" only, i.e., $G(T,P,N)$. In the thermodynamic limit, all statistical ensembles become equivalent for systems with short-ranged potentials and one has

$$\min_{v}\{f(T,v) + Pv\} = \min_{e,v}\{e - Ts(e,v) + Pv\} = g(T,P), \tag{8}$$

where we have used lowercase letters to indicate the values of the extensive quantities per particle (e.g., $v=V/N$). Hence, we obtain

$$\min_{v} \lim_{N\to\infty} \frac{\Phi_{T,P,N}(Nv)}{N} = 0. \tag{9}$$

In the thermodynamic limit, the minimum value of $\mathcal{G}/N$ is exactly equal to the chemical potential of the stable phase. For large but finite values of N, $\mathcal{G}$ shows two minima which we are tempted to identify with the chemical potentials of the two phases. In this case, the condition for phase coexistence turns out to be the equality of the minima displayed by $\mathcal{G}$, which corresponds to a histogram $\Pi_{T,P,N}(V)$ showing two maxima with equal height. It is easy to see that the stated prescription is nothing but Maxwell's rule, which determines the volumes V_1 and V_2 of the coexisting phases of a system whose isotherms $P(T,V,N)$ show a van der Waals loop in the transition region. In fact, one has in general

$$\begin{aligned}\int_{V_1}^{V_2} \mathrm{d}V P(T,V,N) &= F(T,V_1,N) - F(T,V_2,N) \\ &= -P(T,V_1,N)V_1 + \mu(T,V_1,N)N \\ &\quad + P(T,V_2,N)V_2 - \mu(T,V_2,N)N.\end{aligned} \tag{10}$$

At coexistence, the two phases have the same pressure P and chemical potential μ. Hence, the following equation must hold:

$$\int_{V_1}^{V_2} \mathrm{d}V P(T,V,N) = P(V_2 - V_1), \tag{11}$$

which is precisely Maxwell's rule

$$\int_{V_1}^{V_2} \mathrm{d}V (P(T,V,N) - P) = 0. \tag{12}$$

In the light of Eq. (4), Eq. (12) is completely equivalent to $\mathcal{G}_{T,P,N}(V_1)=\mathcal{G}_{T,P,N}(V_2)$, which is what we intended to show.

The equal-height rule for the peaks of $\Pi_{T,P,N}(V)$ should not be regarded as necessarily superior to the prescription of equal areas under the same peaks, a criterion that is also found in the literature, because one can rightly argue that, for sufficiently large values of N, such areas are in fact in the same ratio as the partition functions of the two phases, and are equal, in turn, to the values, respectively, attained by $\exp\{-\beta G_{T,P,N}\}$. In the thermodynamic limit, these quantities coincide for coexisting phases.

We finally want to comment on the meaning of the height of the barrier separating the two minima of $G_{T,P,N}(V)$ when they have equal depth, viz., at coexistence. Let V_1 be the volume of the liquid and V_{mix} the abscissa of the maximum of $\mathcal{G}_{T,P,N}(V)$. One has

$$\Delta\mathcal{G} \equiv \mathcal{G}_{T,P,N}(V_{\mathrm{mix}}) - \mathcal{G}_{T,P,N}(V_1) = P\Delta V + \Delta F. \tag{13}$$

In turn, $\Delta F = F(T,V_{\mathrm{mix}},N) - F(T,V_1,N)$ is the Helmholtz free-energy difference between a liquid-solid mixture of volume V_{mix}, with unspecified proportions N_{A} and N_{B} of the two phases, and the liquid of volume V_1,

$$\begin{aligned}\Delta F &= F_{\mathrm{mix}} - F_1 \\ &= -PV_{\mathrm{A}} - PV_{\mathrm{B}} + \mu N_{\mathrm{A}} + \mu N_{\mathrm{B}} + F_{\mathrm{surf}} + PV_1 - \mu N,\end{aligned} \tag{14}$$

where we have considered that the two competing phases have the same pressure and chemical potential; F_{surf} is the contribution of the interface separating the liquid and the solid components of the mixture. Since $V_{\mathrm{A}}+V_{\mathrm{B}}=V_{\mathrm{mix}}$ and $N_{\mathrm{A}}+N_{\mathrm{B}}=N$, upon inserting Eq. (14) into Eq. (13), one obtains

$$\Delta\mathcal{G} = F_{\mathrm{surf}}. \tag{15}$$

Hence, the height of the barrier is just the Helmholtz free-energy cost associated with the interface separating the two phases. We note that, since $F_{\mathrm{surf}}=\mathcal{O}(N^{1/2})$ in two dimensions, $\Delta\mathcal{G}/N$ vanishes, as expected, in the infinite-size limit.

III. RESULTS

We applied the MD method, in the framework outlined in the previous section, to the description of the freezing transition of a Lennard-Jones (LJ) fluid in two dimensions. The interaction potential,

$$u_{\mathrm{LJ}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{16}$$

was truncated at a distance $r_c=2^{1/6}\times 2.5\sigma$. The system consisted of $N=256$ particles moving in a rectangular box with edge ratio $L_y/L_x=\sqrt{3}/2$ and periodic boundary conditions.

In a typical *NVT* run the particles were initially arranged at the vertices of a triangular lattice and then equilibrated for at least 10^5 sweeps, one sweep corresponding to one attempted Metropolis move per particle. However, whenever possible, we preferred to choose as initial configuration the last configuration produced in a well-equilibrated run carried out at a nearby density, after properly rescaling all particle coordinates. Equilibrium averages were computed over a trajectory 10^6 to 2×10^7 sweeps long, depending on whether the system was homogeneous or heterogeneous. At the beginning of the production run the maximum shift of a particle from its position in a MC move was fixed so as to ensure a fraction of accepted moves close to 50%. The pres-

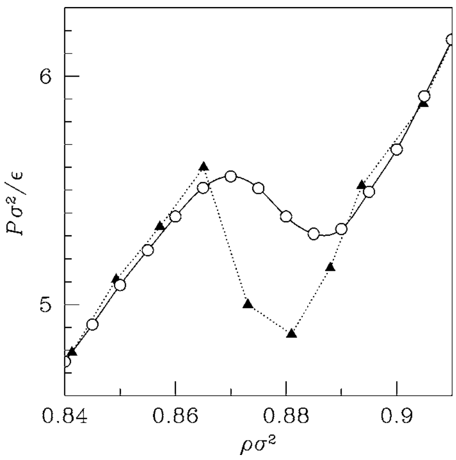

FIG. 1. *NVT* equation of state of a Lennard-Jones fluid in two dimensions, for $N=256$ and $k_BT/\epsilon=1$; open circles: Present Monte Carlo results; triangles: Toxvaerd's molecular-dynamics data (see Table I of Ref. 11). A spline interpolant (solid line) was drawn through the data points in order to guide the eye.

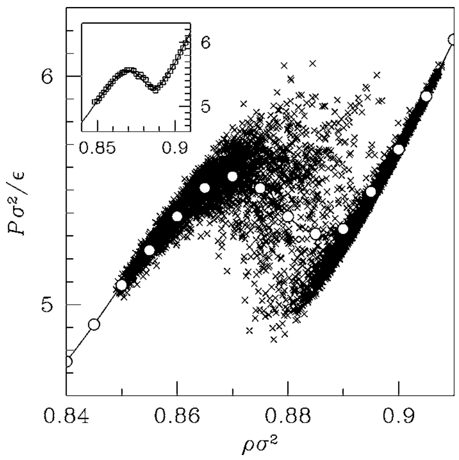

FIG. 2. Equation of state of a Lennard-Jones fluid in two dimensions, for $N=256$ and $k_BT/\epsilon=1$; open circles: Present Monte Carlo results; crosses: (P,V) Data obtained along the metadynamics trajectory. The mean pressure obtained by binning together adjacent crosses is plotted in the inset as a function of the density (open squares) and compared with the spline interpolant of the Monte Carlo data.

sure $P(T,V,N)$ of the system was calculated as the average of the virial of the interatomic forces. At the end, the pressure and the excess energy per particle were corrected so as to remedy the truncation of the potential, the corrections being, respectively, given by

$$P_{\text{tail}} = -\tfrac{1}{2}\pi\rho^2\int_{r_c}^{L_y/2} \mathrm{d}r r^2 g(r)u'(r), \qquad (17)$$

$$u_{\text{tail}} = \pi\rho\int_{r_c}^{L_y/2} \mathrm{d}r r g(r)u(r),$$

where $\rho=N/V$ and $g(r)$ is the radial distribution function of the system with truncated interactions.

In order to calculate $\Pi_{T,P,N}(V)$ we performed *NPT* simulations of a LJ sample with similar specifications as in the *NVT* case but for the choice of the potential cutoff which was taken to be $L_y/2$. We employed the ordinary isothermal-isobaric Metropolis algorithm as described, for instance, in Ref. 1. The volume histogram was updated every single sweep.

We first tried to reproduce the molecular-dynamics data obtained by Toxvaerd ($k_BT/\epsilon=1$).[11] Our results for the pressure, plotted as a function of the reduced density, are compared with those obtained by Toxvaerd in Fig. 1. A neat van der Waals loop is manifest in the transition region. However, the agreement between the present results and Toxvaerd's data is rather poor in this region. We surmise that this discrepancy may be due to insufficient equilibrium sampling in Toxvaerd's simulations. As seen from Fig. 1, the spinodal region is confined in a range of pressures between, approximately, 5.3 and 5.6 (in units of ϵ/σ^2).

As far as the nature of the high-density phase is concerned, one may wonder whether it is a solid or, rather, a hexatic fluid. Actually, there is no way to distinguish between the two phases in a system with 256 particles. As a matter of fact, exact free-energy calculations by Udink and Frenkel[13] indicate that the solid is stable against dislocation unbinding down to the estimated liquid-solid coexistence pressure. Yet, the "two-phase region" of the system is highly unusual in that, apparently, a disclination-unbinding transition occurs within it.

We verified that very long MC simulations (viz., at least 10^7 sweeps long) are needed to ensure an efficient sampling of the system in the coexistence region. On the other hand, an accurate reconstruction of $\mathcal{G}_{T,P,N}(V)$ carried out via metadynamics would require, in a case like ours, some 500 MD steps (this estimate follows from a MD calculation which uses the "exact" pressure of Fig. 1 as an input). As a matter of fact, we found that even a fast, "on-the-fly" sampling of the system at each MD step gives the right result anyway, provided one uses a sufficiently small amplitude for the Gaussians. This unexpected shortcut in the MD calculation, due to a very efficient cancellation of positive and negative errors on the estimate of $P(T,V,N)$, is probably the most significant result of the present paper.

We run our MD code for $P\sigma^2/\epsilon=5.46$. At this pressure, one is close to coexistence for $k_BT/\epsilon=1$, as indicated by the double-peaked structure of $\Pi_{T,P,N}(V)$. We used $\delta v=0.002\sigma^2$ as the step length of the volume dynamics and $w=10^{-5}\epsilon$ as the amplitude of the Gaussians. For each MD step, we equilibrated the LJ sample for 10^4 MC sweeps and computed equilibrium averages over "only" 10^5 sweeps. We also performed the algorithm modifications that are needed to cancel the spurious volume correlations in the last part of the MD trajectory.[14] We show in Fig. 2 the values obtained for $P(T,V,N)$ along a MD trajectory of 5000 steps. Manifestly, in the transition region, the data points do not fall along the "true" isotherm of Fig. 1, the errors being evenly distributed on both sides of the curve (see the inset in Fig. 2).

The MD estimate of $\mathcal{G}$ as a function of MD "time" is shown in Fig. 3. The "liquid" minimum, from which the simulation was started, was filled first, soon followed (starting, approximately, from step No. 500) by the other minimum. After about 3000 steps, the reconstruction of $\mathcal{G}$ was practically completed and, from there onwards, there was room for refinement, especially in the region of the barrier

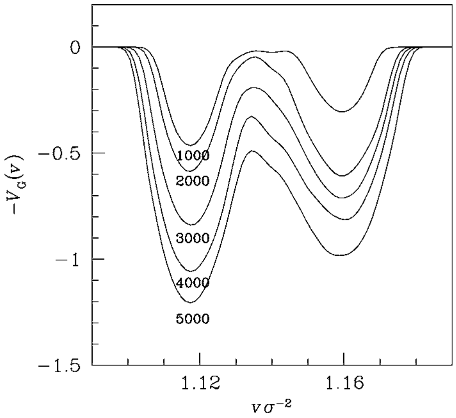

FIG. 3. Values of the quantity $-V_G(v)$, gathered after every 1000 steps of metadynamics, for a Lennard-Jones fluid in two dimensions, for $k_BT/\epsilon=1$ and $P\sigma^2/\epsilon=5.46$. The depths of the minima increase with the number of metadynamics steps. The curve progressively converges to the generalized free energy of the fluid, $\mathcal{G}_{T,P,N}(v)$.

between the two minima. Since the exact $\mathcal{G}$ is perfectly known [it can be inferred from our accurate *NVT* pressure data through Eq. (4)], we can safely judge, in this case, the quality of the MD calculation. The MD prediction for $\mathcal{G}$ and the corresponding Φ are reported in Fig. 4, together with the real shape of $\mathcal{G}$. Overall, the MD outcome is good, except for the region of the maximum which would manifestly require a yet smaller value of w. Conversely, the output of the *NPT* simulation is far from the expected result, a disagreement which we attribute to the choice, made in order to speed up the simulation, of calculating the *NVT* pressure by first truncating the tail of the potential and later correcting for the finite cutoff.

In conclusion, a fairly accurate reconstruction of $\mathcal{G}$ by the MD method is certainly at hand, at least for two-dimensional fluids, though with a still significant computational effort. In fact, a better result can be obtained more rapidly with a single (sufficiently long) *NPT* simulation or, even, with a collection of *NVT* runs carried out in the liquid-solid coexistence region. For three-dimensional systems, the $\mathcal{G}$ profile near the freezing transition is definitely much harder to obtain. The better way to do so is through the histogram of volumes in the *NPT* ensemble, which could be estimated with one of the many smart Monte Carlo methods expressly suited for enhancing the occurrence of low-probability configurations (such as the multicanonical-ensemble method,[15] the Wang–Landau method,[16] or the time-honored umbrella sampling technique[17]).

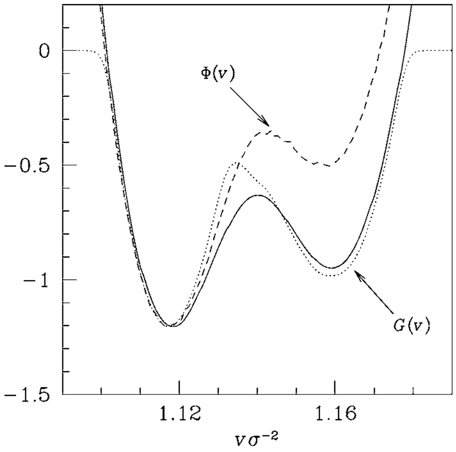

FIG. 4. Comparison between $\mathcal{G}_{T,P,N}(V)$ (dotted line) and $\Phi_{T,P,N}(V)$ (dashed line) for a Lennard-Jones fluid in two dimensions, for $k_BT/\epsilon=1$ and $P\sigma^2/\epsilon=5.46$. The Φ curve was shifted vertically so as to coincide with $\mathcal{G}$ at the absolute-minimum point. The real shape of $\mathcal{G}$ is also reported (solid line). The Φ curve shows a neat deviation from the other two estimates that is due to the slightly different methods employed for computing the pressure in the *NVT* and *NPT* simulations, respectively.

IV. CONCLUDING REMARKS

In this paper, we have revisited the solidification transition of a simple fluid as a case study in MD. We have shown that the generalized Gibbs free energy of the system, which signals the phase transition in a finite system through a crossing of minima, can be reconstructed with a MD calculation of moderate computational effort, at least in two dimensions. For fixed temperature, the only quantity needed for carrying out the steepest-descent dynamics that is part of the MD procedure is the canonical pressure. We found out that it is not strictly necessary to fully equilibrate the system at each MD step, since the errors in the estimate of the pressure, which turn out to be evenly distributed between positive and negative values, have no sizable effect on the overall quality of the final result.

ACKNOWLEDGMENTS

The authors are grateful to Professor Michele Parrinello for a critical reading of the manuscript.

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