Equilibrium and nonequilibrium molecular dynamics methods for determining solid–liquid phase coexistence at equilibrium

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The solid–liquid equilibrium phase transition of a one-component Lennard-Jones system is determined by equilibrium and nonequilibrium molecular dynamics simulation methods. One method uses the observation that the scaling exponent of the pressure or energy of a shearing Lennard-Jones liquid is approximately 1 at the solid phase. This enables us to locate the density of the coexisting solid phase. The coexisting liquid phase density is then obtained by constructing a tie line between the coexisting solid phase point and the liquid phase curve. Alternatively, the coexisting liquid phase density can be efficiently obtained by observing the change in pressure as a function of strain rate and density. The coexisting solid phase density can be then obtained from a tie line from the liquid curve to the solid curve. These calculations are the first reported use of combined equilibrium and nonequilibrium molecular dynamics methods for phase coexistence at equilibrium. Our results are in very good agreement with those obtained by alternative simulation methods for phase equilibria. © 2003 American Institute of Physics. [DOI: 10.1063/1.1623476]

I. INTRODUCTION

It is often difficult to determine the solid–liquid transition by conventional simulation techniques because of the computational challenges posed by two dense phases. Hansen and Verlet1 reported the first molecular simulation results for solid–liquid phase coexistence using a thermodynamic integration algorithm that involves the accurate evaluation of free energies. The widely used Gibbs ensemble simulation algorithm2,3 has proven to be a successful technique to determine vapor–liquid and liquid–liquid phase equilibria. However, it is of limited usefulness for solid–liquid phase equilibria because of the difficulty of inserting particles in the solid phase. This limitation has been addressed by the Gibbs–Duhem integration technique4 that does not require particle insertions to determine solid–liquid phase equilibria. Unlike the Gibbs ensemble, the main disadvantage of Gibbs–Duhem integration is that it requires prior knowledge of at least one pair of coexistence points to start the algorithm. The success in predicting the phase boundary largely depends on the accuracy of this starting point.

Nonequilibrium molecular dynamics (NEMD) simulation has proven to be a powerful technique in studying the transport phenomena of liquids.5 Traditionally, NEMD is mainly confined to the liquid phase. In this study, we demonstrate that the NEMD technique can be a useful tool to determine the solid–liquid phase coexistence at equilibrium.

Part of this work stems from the insights gained from our previous work,6,7 which demonstrated that the pressure and energy of a shearing simple liquid can be expressed as

\[ p^* = p_{0*}^* + a \dot{\gamma}^{*a} , \]

where \( p_{0*}^* \) and \( E_{0*}^* \) are the equilibrium reduced values of pressure and energy, respectively, \( \dot{\gamma}^* \) is the reduced strain rate, \( a \) and \( b \) are constants, and \( \alpha \) is an exponent that may be expressed as a linear function of density and temperature,

\[ \alpha (\rho^*, T^*) = A + B T^* - C \rho^* . \]  

A, B, and C are constants; and \( \rho^* \) and \( T^* \) are the reduced density and temperature, respectively. For the Lennard-Jones fluid they have the values \( A = 3.67 \pm 0.04, B = 0.69 \pm 0.03, \) and \( C = 3.35 \pm 0.03 \) in reduced units, and we note that \( \alpha \) is independent of strain rate. All quantities in Eqs. (1) and (2) are expressed in terms of reduced units as described below.

For the liquid system we found typical values of \( \alpha \) to lie continuously in the range \( \sim 1.2 \leq \alpha \leq 2 \), where the exponent decreases as a function of density. Further examination of Eq. (2) reveals that the solid phase is entered once the value of the exponent is approximately 1.

In this work, we outline how to estimate the solid–liquid phase transition by this method. We, furthermore, demonstrate that the imposition of a small strain rate can greatly facilitate the transition from solid to liquid phases, and show how this method may be used for fast and accurate determination of the solid–liquid phase transition at equilibrium, and how the melting and freezing curves can be efficiently computed. Both these methods provide alternatives to thermodynamic integration,1 Gibbs ensemble,2 and Gibbs–Duhem3 algorithms. Comparison of our results to those in the literature indicates that there is very good agreement. The results also verify our previous observation7 that the scaling exponent is a continuous function of temperature and density, and should not be assumed to have the predicted mode-coupling theory value of 3/2.
II. SIMULATION METHOD

Our system consists of 500 Lennard-Jones atoms. Homogeneous NEMD simulations were conducted using the standard thermostatted SLLOD equations of motion, the details of which may be found elsewhere. A Gaussian thermostat is used to constrain the kinetic temperature. The normal convention is adopted for the reduced density, which is itself calculated by the standard Irving–Kirkwood expression for a homogeneous nonequilibrium liquid. We calculate is given as one third the trace of the pressure tensor, \( \langle \frac{\partial^2 E}{\partial \rho^2} \rangle \). As previously noted, we do not assume any value of the \( \gamma \) exponent in the pressure equation or the \( \lambda \) exponent in the temperature equation of state. These values are determined by a least-squares fit of the pressure as a function of strain rate, based on Eq. (1). The pressure we calculate is given as one third the trace of the pressure tensor, which is itself calculated by the standard Irving–Kirkwood expression for a homogeneous nonequilibrium liquid. We then extract the value of \( \frac{\gamma}{\eta} \) for each \( (\rho, T) \) state point, probing the range \( 0 \leq \gamma \leq 0.6 \) in steps of 0.1 reduced strain rate units. All our simulations were performed at a potential cut-off radius of 3.5\( \sigma \).

III. DETERMINATION OF THE EQUILIBRIUM SOLID–LIQUID PHASE BOUNDARY

A. Melting transition

We performed NEMD simulations at three temperatures in the dense liquid phase region according to Fig. 1. Figure 1 illustrates the regions of both vapor–liquid (obtained by Gibbs ensemble simulation) and liquid–solid equilibria obtained for the Lennard-Jones intermolecular potential. For liquid–solid equilibria, literature data obtained from both thermodynamic integration and Gibbs–Duhem calculations are illustrated. A comparison with our results is also given, the details of which are discussed below. 

When the system density is close to the solid–liquid phase boundary the system’s pressure becomes unstable. For example, consider an (NVT) simulation that commences from an initial face-centered-cubic (fcc) lattice structure, at a density slightly greater than the density at which the liquid freezes into the solid. After an initial equilibrium simulation of several tens of thousands of time steps, the time averaged system pressure can remain in an unstable value much lower than that of the corresponding metastable equilibrium liquid state after a run of several million time steps. This is an indication that the system is in the close vicinity of the freezing transition, wherein the system is more solidlike compared to the equilibrated liquidlike state. We further find that within the solid–liquid phase envelope, at any density and nonzero strain rate, the system will reach a nonequilibrium steady-state relatively quickly, after only several thousand time steps. We will return to the topic of the metastable liquid branch and how NEMD simulations greatly facilitate computation of the metastable liquid pressures in Sec. III B.

We have tested the effect of applied strain rate on the time taken to reach a nonequilibrium steady state and found...
that this occurs at about 20,000 time steps for a strain rate of 0.01. Figure 3 shows the comparison of the effect of small strain rates on the steady-state relaxation time for systems at density of 0.92 and 0.96, and $T = 1.00$. Even for the system with density 0.96 (close to the melting transition) at the smallest strain rate of 0.001 only around 170,000 time steps are needed to attain steady state. This compares very favorably to an equilibrium simulation with no shear, in which millions more time steps are needed to equilibrate within the two-phase liquid/solid region.

Figure 4 shows the effect of strain rate on time taken for the pressure to relax to its nonequilibrium steady-state value. All runs start at the same face-centered-cubic lattice configuration. A time step of 0.001 is used. The system density and temperature are 0.96 and 1.0, respectively. It is well known that the time taken to reach steady state decreases with increasing strain rate, and this is clearly observed. The important feature of Fig. 4, and what makes it useful for our purposes, is that even a very weak strain rate is sufficient to enhance the melting of the crystal. This is particularly useful as we are interested in the solid–liquid phase transition. After about 170,000 time steps the crystal has melted for even the weakest field strength of $\dot{\gamma} = 0.001$. This is evidenced by the increase in pressure in going from the solid to the solid–liquid two-phase region. Contrast this to the bottom curve on Fig. 4, which is the system pressure with no shear, i.e., at equilibrium. After 170,000 time steps the solid has still not melted. We conducted simulations up to two million time steps at equilibrium and melting had still not occurred. In general, only after many millions of time steps would melting occur for the equilibrium (i.e., no shear) system.

The dynamical behavior at weak nonzero shear rates encourages us to consider the possibility of using NEMD to investigate the melting transition. In the high density two-phase region it is a computationally intensive task to obtain the melting and freezing points by standard equilibrium techniques. However, with the help of a small strain rate the equilibration process is significantly speeded up, saving a considerable amount of simulation time. If we wish to return to an equilibrium state, switching the field off once the solid has yielded and steady state has been attained does not result in the liquid freezing back into the solid phase. This is demonstrated in Fig. 5. For example, for the weakest strain rate of $\dot{\gamma} = 0.001$ an initial fcc lattice is sheared for 170,000 time steps, at which point the solid has yielded and the resulting liquid has reached steady state. The field is then switched off at $t = 250,000\tau$ and the liquid allowed to relax to equilibrium for a further two million time steps (we only show times up to 450,000$\tau$ in Fig. 5). The difference in pressure between the nonequilibrium steady state and the final equilibrium liquid state is very small, difficult to observe visually from the plot at the field strengths probed here, and reflects only the structural effects of the shear. Clearly, the liquid has not resolidified, which would result in a significant pressure drop.

The essential question is, can we use NEMD techniques to predict the equilibrium (i.e., zero-shear) melting transition? By examining Fig. 2 in conjunction with Eq. (2), it is apparent that the exponent in the strain rate, $\alpha$, decreases with increasing density at constant temperature. Significantly, it turns out that at a value of $\alpha = 1.0$ the predicted density is very close to that of the melting transition. At this
stage we do not propose a theoretical justification for this, and the value of $\alpha=1.0$ is based purely on observation. We use this observation as the basis of a working hypothesis that allows us to estimate the melting transition. Clearly, further work is required to justify its use and to apply it to other systems. Nevertheless, as a demonstration of this phenomenon, let us extrapolate the three lines in Fig. 2 to the value of $\alpha=1.0$. Recall that each line represents the variation of $\alpha$ as a function of density for a constant temperature. At $\alpha=1.0$ the lines intersect the $x$ axis and we can easily read off three densities. After performing a simple \((NVT)\) equilibrium molecular dynamics simulation, the system pressure at each interpolated density can be obtained. These three solid phase densities are shown in Fig. 1, and are depicted by filled squares. They sit on or close to the melting transition curve and are in very good agreement with the calculations reported in the literature, as can also be seen in Table I. We also make the observation that liquidlike behavior is observed for values of $\alpha>1$, whereas solidlike behavior is observed for $\alpha\leq1$.

Figure 6 gives the results of pressure with varying strain rate at $T=1.00$ and a number of densities. At lower densities the data points are well represented by curves of varying exponent $\alpha$, as suggested by Eq. (2). However, at higher densities the upper four curves show a significantly different feature. At $\dot{\gamma}=0$ the pressures are even lower than those corresponding to lower densities. This is because at these densities we are in the two-phase liquid–solid region of the phase diagram. When the strain rate is switched on the solid yields and the pressure jumps up suddenly and remains almost linear with increasing $\dot{\gamma}$. As seen by a comparison with Figs. 1 and 2, a value of $\alpha=1.0$ gives us the approximate density at the melting transition. In order to obtain the approximate density of the melting transition at any given temperature, set $\alpha=1.0$ in Eq. (2), i.e.,

$$\rho = \frac{A+BT - 1}{C}.$$  

In the case of $T=1.00$, this gives a value of $\rho=1.00$ to two significant digits.

There is a limitation to this method. Equation (3) is linear, which means that the predicted solid line can only have a linear form. Clearly, this is not the case in general, and is not the case in Fig. 1. However, Eq. (3) is based upon coefficients that were determined only from data obtained within the liquid region of the phase diagram. Thus, within the temperatures spanned by this region ($0.687 \leq T \leq 1.26$), Eq. (3) approximates the true solid curve by a line. This limitation could be removed if it was known exactly what the extrapolated value of $\alpha$ is at the melting phase transition. In this work we only assume an approximate value of $\alpha=1.0$, based upon observation as discussed above. There is no theory available at present that predicts an accurate or reliable value of $\alpha$. It is likely that at the melting phase transition the value of $\alpha$ is not a constant value of 1.0 for all values of temperature and density, but varies slightly as functions of these phase variables. Thus, a more accurate melting curve can result. It is worth exploring this phenomenon in future work.

There is another more accurate and efficient method that combines both equilibrium and nonequilibrium techniques that we can use to determine the melting transition, and this is indicated by the hollow circle data in Fig. 1. These data do not depend on any limiting assumptions made on the value of $\alpha$. We will discuss how these data are obtained after the following section, in which the underlying principles are discussed.

**B. Freezing transition**

The preceding considerations indicate how the boundary between the single solid phase and the two-phase liquid/solid region (the melting transition) was determined. To complete the phase equilibria calculation, we must also determine the transition between the single liquid phase and the two-phase liquid/solid region, i.e., the freezing transition. The procedure for obtaining the densities and pressures for the freezing transition is illustrated with the aid of Fig. 7, which represents the pressure–density isotherm at a constant temperature of $T=1.00$.

The pressure–density isotherm is constructed using equilibrium pressures from Gibbs ensemble Monte Carlo (GEMC), \((NVT)\) equilibrium molecular dynamics (MD) and NEMD simulations. In Fig. 7, the filled squares are data from GEMC simulations, and the crosses represent data from \((NVT)\) MD simulations in the gas phase. The gap between the two densities of the vapor–liquid phase equilibrium is the normal two-phase region. Open diamonds represent the dense liquid phase that is obtained by normal \((NVT)\) MD
equilibrium MD and NEMD simulations, and one that does not rely upon the approximation that \( \alpha = 1 \) in the solid phase, utilizes the fact that a small strain rate applied to the system disturbs its two-phase state. We can see this clearly by, again, referring to Fig. 6. In these results, each simulation starts from an initial fcc lattice configuration. It is important to realize that the system is not compressed gradually from liquid to solid densities to observe the liquid–solid transition. In a conventional molecular simulation involving a finite number of molecules, a metastable extension of the liquid line is observed at densities above the freezing point and the solid line extends to densities below the melting density. This van der Waals loop (hysteresis effect) means that the exact location of the phase transition is difficult to determine with absolute certainty. As will be evident in the following discussion, we observe that our results for the liquid–solid transition are in very good agreement with values in the literature.

For each density simulated, our initial fcc system is allowed to relax to equilibrium (\( \gamma = 0 \) simulations) or reach a nonequilibrium steady state (\( \gamma \neq 0 \)). At lower densities that correspond to the liquid phase the pressure follows the simple power law relationship of Eq. (1). At higher densities we enter the two-phase liquid–solid region and there is a sharp drop in pressure at \( \gamma = 0 \). In principle, one could determine this transition by performing only equilibrium MD simulations and noting where this pressure drop occurs. However, this is a tedious process and would require many equilibrium MD simulations, each separated in density by a very small incremental amount \( \Delta \rho \), and spanning a wide range of densities that encompassed the transition density. Furthermore, one could easily miss the transition point by choosing too large a value of \( \Delta \rho \). This can be illustrated by reference to Fig. 7. If, at densities that span the metastable liquid/solid phase, one computes equilibrium pressures in relatively large steps of \( \Delta \rho \), it would be possible to move from the liquid to the solid branch without noticing any significant difference in the pressure. One might then be deceived into believing one is in the liquid phase, whereas in fact the solid phase has already been entered.

This ambiguity can be eliminated with the aid of NEMD simulations. This is because there is such a sharp and easily distinguishable discontinuity in the pressure versus strain rate curves when the two-phase liquid/solid freezing transition has been entered, as observed in Fig. 6. In fact, all one needs is just one nonzero strain rate point in addition to the zero strain rate point to see this (e.g., \( \dot{\gamma} = 0, 0.1 \)). If, for each state point, we perform simulations at \( \gamma = 0, 0.1 \), we can easily judge whether we are in the single liquid phase or the two-phase metastable or solid phase; if there is a small difference in pressure then the system is in the single liquid phase (see Fig. 6). This allows one to initially coarsely sample a wide range of densities quickly, saving considerable excess simulation time. Once it is clear whereabouts the transition density is, it is a simple matter of fine tuning. Starting in the liquid phase and increasing the density in incremental amounts of \( \Delta \rho \), in the limit as \( \Delta \rho \to 0 \) the density at which we
first observe this discontinuity of the pressure versus strain rate curve corresponds to the density of the freezing curve of the equilibrium phase diagram in Fig. 1. Note that this is accurate to within \( \Delta \rho \). We plot these results as open squares on the two-phase curve in Fig. 1, where the horizontal error bars indicate the value of \( \Delta \rho \). Note, also, that we use very small values of \( \Delta \rho \) in the vicinity of the phase transition to compute the freezing curve density. This is not apparent in Fig. 7 (e.g., between \( 0.92 \leq \rho \leq 0.94 \) we probe the densities in steps of \( \Delta \rho = 0.01 \)). Very good agreement is found with our method and corresponding results in the literature.\(^1\)\(^4\) It is of interest to note that our results are in better agreement with the results obtained from thermodynamic integration\(^1\) than those obtained from the Gibbs–Duhem algorithm.\(^4\) This may possibly reflect the influence of the choice of starting point used for the Gibbs–Duhem calculations, or different cutoff conditions in the different reported simulations.

We note here that this method is extremely efficient in obtaining the metastable points, and was used to calculate these in Fig. 7 (crossed open diamond symbols). We stress here that NEMD assists us in forcing the solid to yield. Once this is done, the field is switched off and the fluid is allowed to relax back to equilibrium. Thus, equilibrium MD (EMD) simulations proceed, in which state the liquid does not re-freeze into the solid state, but remains in the metastable liquid state. NEMD alone cannot, of course, determine the liquid–solid phase transition at equilibrium. In fact, because we are able to accurately determine these metastable points by the combination of NEMD/EMD simulation we lessen the risk of over-running the phase transition in determining the freezing line. As mentioned above, our predictions are accurate to within \( \Delta \rho \). One cannot easily obtain metastable points by conventional Monte Carlo or equilibrium molecular dynamics simulations in the two-phase region due to the long simulation times required. However, the application of a very small strain rate can easily force the solid to yield, thus breaking the crystalline structure of a starting fcc lattice to reach the metastable phase. The alternative standard way to calculate the two-phase region is by condensing or quenching the system at very slow rates,\(^10\) which takes considerably more CPU time.

Our work differs from that recently reported by Butler and Harrowell,\(^11\)\(^12\) who examined the coexistence between a strained crystal and its shearing melt. While their work focused on the coexistence away from equilibrium using inhomogeneous methods (i.e., physical modeling of the walls, and moving them to simulate planar couette flow), our work applies the standard homogeneous NEMD algorithm [i.e., SLLOD (Ref. 5)] to determine the equilibrium coexistence of the solid–liquid phase transition.

C. Melting transition revisited

Once the freezing point has been determined (Sec. III B), it is relatively straightforward to determine the melting point. As discussed in Sec. III B and illustrated in Fig. 7, at any temperature the liquid branch of the coexistence curve and its metastable extension can be easily calculated by a combination of equilibrium MD and NEMD simulations. For any liquid density, extending an isobaric tie line from the liquid branch onto the solid branch can identify the melting point on this curve. The point of intersection with the solid branch gives the corresponding density of the melting transition. These data are shown in Fig. 1 as hollow circles, where again the error in density corresponds to \( \Delta \rho \), as discussed before. Very good agreement is found between our data and that of previous workers.\(^1\)\(^4\) Again, we note that our data agree better with thermodynamic integration results\(^1\) than the Gibbs–Duhem data.\(^5\)

D. Comparison with other algorithms

It is of interest to compare our procedure with the alternative methods for obtaining solid–liquid phase coexistence. Thermodynamic integration is arguably the least routine method because it requires accurate values of free energies that are difficult to obtain. In principle, the Gibbs ensemble could be applied to obtain solid–liquid equilibria. However, the low probability of exchanging particles between the dense liquid and solid phases means that it is not a practical option in most cases. Gibbs–Duhem integration is the most computationally efficient method but it suffers from the disadvantage that it is not self-starting, requiring knowledge of one coexistence point. The accuracy of the Gibbs–Duhem method critically depends on this initial starting point. We note that recently\(^13\) a new algorithm for solid–liquid equilibrium has been proposed, which uses histogram reweighting techniques to overcome this limitation.

In common with the Gibbs–Duhem method, our procedures have the advantage that they do not involve particle interchanges. In addition, they have the further advantage that they do not require an initial starting point and the solid–liquid phase transition can be determined entirely \(a\) \(p\)\(r\)i\(a\)\(n\)\(t\)\(a\)\(p\)riori. Our method of determining the melting transition by setting \( \alpha = 1 \) does have a limitation at present in that it can only approximate the solid phase transition curve as a line. It is hoped that this limitation will be removed once a theoretical determination of the exact value of \( \alpha \) at the solid phase transition is obtained. Our alternative method of determining both the two-phase solid–liquid freezing and melting coexistence curves by applying a small strain rate to yield an initial crystal configuration is completely general and suffers from no such limitation. It is both accurate and computationally efficient.

IV. CONCLUSIONS

We have computed the melting and freezing curves for an equilibrium Lennard-Jones system of atoms by a combination of equilibrium and nonequilibrium molecular dynamics simulations. One method relies upon a previous discovery that the strain rate power exponent of the pressure is a continuous linear function of temperature and density, and ranges within approximately \( 1.2 \leq \alpha \leq 2 \) in the liquid phase. In this work we demonstrate that the exponent takes on an approximate value of \( \alpha = 1.0 \) at the solid–liquid melting phase transition. Knowledge of this exponent allows us to estimate the melting density at any temperature, and enables us to construct the melting curve. The solid phase density
observed is consistent with that of other work.\textsuperscript{1,4} The corresponding freezing curve can also readily be obtained by intercepting a tie line from the solid phase with the isotropic liquid curve. This method is limited by the approximation we necessarily place upon the value of $\alpha$ at the melting phase transition. Further theoretical work is required to extend and validate this approach to other systems.

To overcome this limitation we have used a combination of equilibrium MD and NEMD methods that rely upon no such approximation. By noting that there is a discontinuity in the pressure versus strain rate curve once the two-phase region is entered we can quickly and accurately compute both the freezing and melting equilibrium phase transition curves. We note that it is nearly impossible to get the two-phase metastable region by conventional Monte Carlo and equilibrium molecular dynamics simulations starting from a fcc lattice. However, the application of a very small strain rate can easily force the starting crystal to yield and break the crystalline structure to reach the two-phase metastable region.

Finally, we comment that while this series of calculations was performed on the Lennard-Jones liquid, there is no reason why it should not work for other single-component liquids (atomic or molecular) with different potentials that exhibit relatively simple phase diagrams. By observing the abrupt change in pressure exponent for the pressure versus strain rate curve, which corresponds to the solid yielding by application of a small shearing field, it is straightforward to compute the freezing transition, from which the melting transition can be computed.

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