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Determination of a melting curve using the one-phase approach

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ABSTRACT

The melting curve of the modified Lennard-Jones solid is derived using a one-phase approach. The Padé approximation employed for solving the melting-curve equation converges at the middle stage, giving rise to the well-known Simon curve that satisfactorily captures the actual melting curve found from a molecular dynamics simulation over a pressure range of four orders of magnitude. This situation is justified because the solid under consideration was shown to satisfy the thermodynamic condition under which Simon's curve becomes exact.

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1. Introduction

Melting has been studied extensively. Theoretical viewpoints, including the classical one leading to Lindemann's theory of melting phenomena [1], are beautifully reviewed in Ref. [2].

A major issue in melting phenomena is to determine the transition temperature, i.e., the melting point. Two approaches are possible. The first, referred to as a two-phase approach, is to look for the temperature at which the free energies of the crystalline and liquid phases equilibrate [2]. The second, one-phase approach, is to assess the melting point from the properties of the crystalline phase. The terms "one- (two-) phase simulation" were first coined by Belonoshko [3]. Here, the terms "one- (two-) phase approach" have a wider meaning and can refer to methods other than simulation. The two melting points derived by the two approaches do not necessarily coincide for a given substance; the melting point determined from the two-phase approach is consequently the equilibrium one, whereas that from the one-phase approach may involve kinetic effects. A major strategy in the one-phase approach to identify the stability limit of a solid state is to exploit the weakening of the restoring forces against shear deformation with increasing temperature [4]. However, defects are claimed to be responsible for forming liquid droplets below the nominal melting point [5]. The essential mechanism that makes a solid thermodynamically unstable is therefore still controversial. The situation is even worse at high pressures. Indeed, Liu et al. [6] stated that "the prediction of the pressure dependence of the melting temperature is problematic".

In this Letter, we examine the pressure dependence of the melting temperature based on the one-phase approach proposed by Kumari and Dass [7] and Kechin [8]. We have already reported that the procedure works well for a model molecular solid [9]. We employ here a simpler system of point particles to confirm the main findings in Ref. [9], thereby consolidating the Kumari–Dass–Kechin one-phase approach. This approach relies on the thermodynamic information of the solid phase in question. In our numerical simulation presented below, the size of the model is chosen so that it is large enough to extract the thermodynamic quantities, but small enough to inhibit the heterogeneous nucleation of liquid droplets before reaching the catastrophe. No free surfaces are involved in our model.

2. Model and method

A classical ensemble consisting of point particles is considered in this study. The essential ingredient to be included in the model when considering melting is the attractive interactions between the particles. The Lennard-Jones (LJ) potential is often employed in such statistical mechanical problems. Indeed, the aforementioned mechanism of shear instability upon melting was identified by a model that employed the LJ potential [4]. Its attracting tail, however, extends to infinity, and a truncation is unavoidable when treated numerically. We must therefore invoke a large system size, thereby allowing a large cutoff length of the tail, to assess the intrinsic thermodynamic properties of the LJ system. (This motivated the investigation of effective recipes for truncating the tail [10].

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The equilibrium melting curve of Xe was extensively discussed based on a two-phase simulation utilizing the LJ potential [11].)

With this circumstance in mind, we have proposed adopting as a substitute for the LJ potential the modified Lennard-Jones (mLJ) potential [12], which mimics the shape of the LJ potential as closely as possible but has a *finite* tail. The functional form of the mLJ potential is as follows [12]:

$$\phi_{\rm m} = \begin{cases} 4(r^{-12} - r^{-6}) + C_1 & (r \le 2.3) \\ C_2 r^{-12} + C_3 r^{-6} + C_4 r^2 + C_5 & (\,2.3 < r \le 2.5) \\ 0 & (2.5 < r), \end{cases}$$

where the interparticle distance r is measured in units of the length parameter σ and the potential $\phi_{\rm m}$ in units of the energy parameter ϵ. (For example, it is appropriate for argon to choose $\sigma = 3.389 \times 10^{-1}$ nm and $\epsilon = 1.930 \times 10^{-21}$ J [13].) The numbers $\{C_i\}$ $(i = 1, \ldots, 5)$ were refined as $C_1 = 0.0163169237$, $C_2 = 3136.5686$, $C_3 = -68.069$, $C_4 = -0.0833111261$, and $C_5 = 0.746882273$ [14]. We have thus far concentrated our effort on standardizing the mLJ system through our studies of the phase diagram [14,15] and the equations of state (EOSs) for the fluid [13] and solid [16] states. The mLJ system is superior, not only in the unambiguity associated with the treatment of the tail, but also in the ability to predict thermodynamic properties from the rich knowledge base for the LJ system [17].

We now examine the melting curve of the mLJ solid. Note that here we use the term “melting curve” in a somewhat different way than usual. Refer to the last paragraph in this section. To this end, we first conducted an isothermal–isobaric molecular dynamics (MD) simulation to find the melting point, $T_{\rm m}$. (From now on, the values for temperature, T, and pressure, p, are given in reduced units, i.e., in units of $\epsilon/k_{\rm B}$, where $k_{\rm B}$ is Boltzmann’s constant, and ϵ/σ^3, respectively.) The method of the simulation was essentially the same as that described in Ref. [14], with an improvement to enhance parallelization [16]. A system consisting of 6912 particles was employed throughout the simulation to reduce finite-size effects as much as possible [18]. For other technical details of the simulation, see Ref. [14].

The melting point was determined for $p \in [10^{-4}, 10]$ as follows. For a given p in the range, the system, in which the particles were initially located on the fcc lattice points, was equilibrated at the temperature $T_0 = 0.2$. Five thousand MD steps were sufficient for this equilibration and the subsequent 5000 steps were used to evaluate the average system’s volume. The system was then heated using temperature steps of 8.35×10^{-3} (which corresponds to 1.2 K for argon) and the average volume was evaluated after equilibration. This procedure was repeated until the system experienced a sudden jump in the average density. The melting point was defined to be the midpoint of the sudden jump. The melting point thus determined has an ambiguity equal to the width of the temperature step. This ambiguity was very small compared with the ambiguities associated with the EOSs and is ignored in the following argument.

As evident from the method of determination, the melting point under consideration represents the thermodynamic stability limit of the solid state and hence gives an upper bound for the equilibrium melting point defined from the two-phase approach.

3. Results and discussion

To keep the mathematical expressions to be developed below simple, the specific volume $v \equiv V/V_0$, where V_0, the volume at (T_0, p_0), is used instead of V. p_0 denotes the reference pressure. (In this study, we chose rather arbitrarily $p_0 = 2.417 \times 10^{-3}$, which corresponds to 1.2 atm for argon [13].) With the one-phase approach, a melting curve is then given by the solution to the following thermodynamic identity [7,8]:

$$\frac{{\rm d}\ln T_{\rm m}}{{\rm d}p} = \frac{\Gamma_{\rm m}}{K_{\rm m}}, \tag{1}$$

where $K_{\rm m}$ is the bulk modulus at the melting point and $\Gamma_{\rm m}$ is defined by

$$\Gamma_{\rm m} = -\frac{{\rm d}\ln T_{\rm m}}{{\rm d}\ln v_{\rm m}}. \tag{2}$$

(Quantities with the suffix “m” represent throughout those quantities measured along the melting curve.) Instead of evaluating the right-hand side (RHS) of Eq. (2), $\Gamma_{\rm m}$ was usually reduced [7,19–21], assuming the validity of Lindemann’s melting law [1], to Grüneisen’s parameter $\gamma_{\rm m}$:

$$\Gamma_{\rm m} = 2\left(\gamma_{\rm m} - \frac{1}{3}\right). \tag{3}$$

By referring to the appropriate or approximate value for $\gamma_{\rm m}$ and by using the measured value for $K_{\rm m}$, Kechin and others have attempted to rationalize the melting curves of some substances [7,22].

An important step in the derivation of the melting curve based on Eq. (1) was the evaluation of Eq. (3) and $K_{\rm m}$ (i.e., the numerator and the denominator of the RHS of Eq. (1)) separately as functions of p [7]. Kechin (independently) proposed introducing the Padé approximation to the RHS of Eq. (1) [8]:

$$\frac{\Gamma_{\rm m}}{K_{\rm m}} = \frac{\Gamma_{\rm m0} + \Gamma'_{\rm m0}\Delta p + \cdots + \Gamma^{(L)}_{\rm m}{}_0(\Delta p)^L}{K_{\rm m0} + K'_{\rm m0}\Delta p + \cdots + K^{(M)}_{\rm m}{}_0(\Delta p)^M}, \tag{4}$$

where $\Delta p = p - p_0$, and hence the subscript “0” is understood to represent the quantity evaluated at p_0. In Eq. (4), $\Gamma_{\rm m}$ and $K_{\rm m}$ are expanded up to the Lth and the Mth orders, respectively. As stressed by Kechin [8], the ingenious approximation of Eq. (4), when substituted for the RHS of Eq. (1), can give a solution with a melting maximum. Equation (4) tries to represent the RHS simply as a quotient in which the numerator and denominator are evaluated separately around p_0. Because the p-dependence of the RHS is not completely known for the entire p range (unless a drastic approximation such as that represented by Eq. (3) is invoked), the coefficients involved in Eq. (4) are not determined uniquely at this moment. Therefore, the use of “Padé approximation” is not strict in this context.

One important viewpoint is missing, however: the substitution tacitly assumes that even though it is abnormally shaped with a maximum, the melting curve is *smooth*, i.e., everywhere differentiable. The validity of Eq. (4) is open to serious question when the melting curve under consideration has a singularity. This seems to be the case, for example, for the melting curves of molecular crystalline $\rm SnI_4$ [23] and $\rm GeI_4$ [24]. The slope of the melting curve changes abruptly at ~ 1.5 GPa for $\rm SnI_4$ [23] and at ~ 3 GPa for $\rm GeI_4$ [24]. According to a theoretical consideration, the breakpoint of the melting curve is speculated to be the triple point between the solid and the two liquid phases [25].

We call a melting curve “normal” when it is a smooth, upward convex function of p. The melting curve obtained through solving Eq. (1) seemed to converge with increasing L and M in Eq. (4) to the normal part of $\rm SnI_4$’s [26] and $\rm GeI_4$’s melting curve [24] when the values extracted from the EOS for each solid phase [24,27] were substituted into the RHS of Eq. (4). The existence of an apparent singular point on the melting curve, however, prevented us from firmly confirming the convergence. We could not identify the microscopic origin that makes the shape of the melting curves abnormal, and we therefore could not reproduce the melting curve of $\rm GeI_4$ [9]. This failure to reproduce the singularity became, on the other hand, an advantage in demonstrating the convergence behavior [9]. This motivated us to examine a simpler system to

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