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Melting and critical superheating

A. B. Belonoshko,[1,2] N. V. Skorodumova,[3] A. Rosengren,[2] and B. Johansson[1,3]
[1]*Department of Material Science and Engineering, The Royal Institute of Technology (KTH), SE-10044 Stockholm, Sweden*
[2]*Department of Physics, AlbaNova University Center, The Royal Institute of Technology, SE-106 91 Stockholm, Sweden*
[3]*Department of Physics, Box 530, Uppsala University, S-75121 Uppsala, Sweden*

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Two mechanisms of melting are known, heterogeneous, where melting starts at surfaces, and homogeneous, where the liquid nucleates in the bulk crystal. If melting occurs homogeneously, a crystal can be superheated significantly above its melting temperature (T_m). At present, the physical meaning of the limit of superheating (T_{LS}) is unknown. We demonstrate, by molecular dynamics simulations, that the total energy of a solid at T_{LS} is equal to the total energy of its liquid at T_m at the same volume. In the high pressure limit T_{LS} and T_m are connected by the constant $k_{AB}=ln\,2/3$ via the relation $k_{AB}=T_{LS}/T_m-1$.

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Melting is the most common structural transition, yet the nature of melting is not completely understood.[1,2] The melting, as we usually observe it, is the so-called heterogeneous melting,[3] where melting is initiated due to inhomogeneities. Under special conditions, it is possible to melt a solid in a homogeneous way.[4–6] It has been observed, that if a crystal melts homogeneously, it can be overheated substantially above its T_m. However, there is a critical T_{LS}, above which one cannot heat a solid without transforming it into a liquid structure. For the case of heterogeneous melting we have a number of criteria which tell us the physical content of T_m, for example, the equality of the Gibbs or Helmholtz free energies of the solid and liquid phases at T_m. A number of criteria has been suggested[7–12] for T_{LS}. For example, Born[9] suggested that the solid loses its shear strength at T_{LS}. Recently, it has been demonstrated that all of these criteria, including the Born criterion, are preceded by the nucleation of liquid at T_{LS}.[11,13–16] This nucleation, once initiated, leads to a complete melting. Therefore, at present the physical meaning of T_{LS} is not clear. While explaining in detail the microscopic mechanism of the solid-liquid transition at T_{LS}, recent studies[13–16] tell us little about the meaning of T_{LS} other than this is the temperature (T) at which the solid-liquid transition occurs, which is merely the definition of T_{LS}. Superheating is a comparably rare phenomenon in nature, still it is routinely simulated by researchers who attempt to determine the T_m of a substance. This is because a perfect crystal with periodic boundary conditions (PBC) is simulated in a typical molecular dynamics (MD) run. A perfect crystal with PBC has no surfaces which are required to avoid superheating. Therefore, atomistic simulations without an interface are perfectly suited to study homogeneous melting.

In this study, we establish a connection between T_{LS} and T_m. We simulate a perfect crystal using the MD method. As a model for describing the interactions between atoms we have chosen the Lennard-Jones (LJ) potential. This model has also been employed in a similar study.[15] The LJ model is exceptionally well studied, and a number of its properties is established.[15,17]

When studying superheating, it is important how the simulated crystal is heated. Usually, two methods are applied. The velocities are either scaled to the desired T, while in the second one the crystal is coupled to a thermal bath. In our study, the major question is: What happens to a superheated crystal when T reaches T_{LS}? An obvious answer is that it melts, however, it is not obvious how this would change the T of the system. To be able to answer this question, we must not interfere with the evolution of the crystal in our simulations. Apparently, neither the scaling nor the thermal bath method is suitable for that purpose. In our simulations, we have instead chosen a third approach. Namely, a certain amount of kinetic energy is provided to the face-centered cubic (fcc) crystal in the very beginning of the MD simulations. After that, the system is allowed to evolve on its own, equilibrating to some T.

We have performed MD simulations of the initialy perfect fcc LJ crystal. The parameters of the LJ potential were $\epsilon/k_B=119.8$ K (k_B—Boltzmann constant) and $\sigma=3.41$ Å, which are the physical parameters of argon. The number of particles was 4000 ($10\times10\times10$ cells) and 32 000 ($20\times20\times20$ cells) on to check the size effect PBC were applied. The timestep was set equal to 0.25×10^{-15} s to ensure a very good conservation of energy. Normally, 250 thousands timesteps were sufficient to get statistically reliable results. We calculated three isochores for the unit cells with $a=4.2$ Å, $a=4.4$ Å, and $a=5.37$ Å (a—the fcc unit cell parameter) to ensure that our observations are not volume specific. The results are shown in Figs. 1(a) and 1(b). We observe the identical phenomenon [Fig. 1(c)] in exactly the same way, but for a different, embedded-atom potential model for copper.[18]

When we heat a crystal at a constant volume (V), the pressure (P) increases with T. This is what we see for all isochores (Fig. 1). When T approaches T_{LS}, a very small increase in the initial kinetic energy leads to melting (Fig. 1). Remarkably, at all volumes T, to which the system evolves, drops down to T_m (Fig. 1). Because of our way of heating the crystal, we know that the total energies at T_{LS} and at T_m, at the same volume, are equal. This allows us to uncover the physical meaning of the T_{LS}, which can be written as follows:

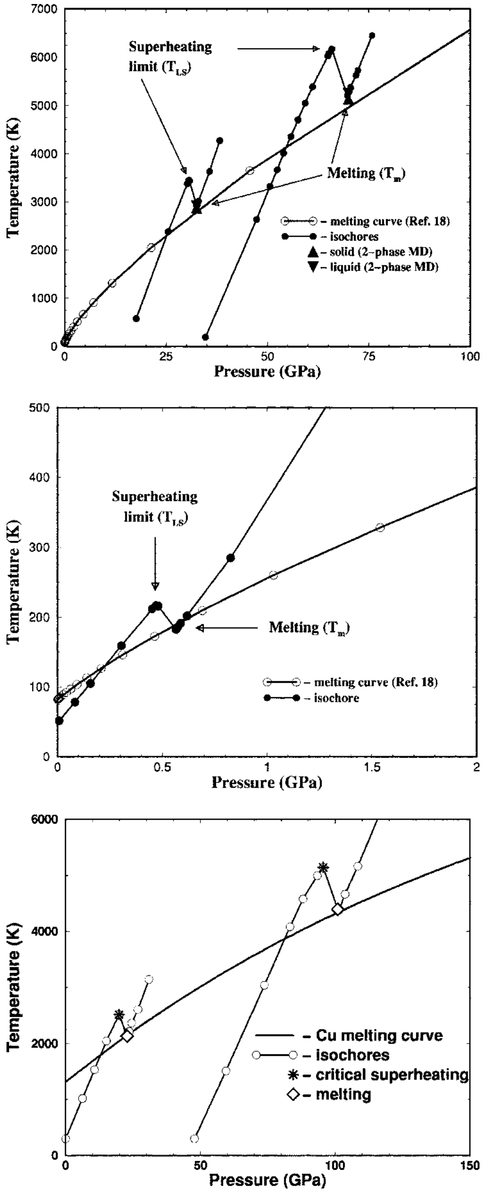

FIG. 1. The relation between the limit of superheating (T_{LS}) and the melting temperature (T_m) of LJ solid at high (a) and low (b) pressures and embedded-atom model (EAM) of Cu (Ref. 18) (c). The melting curve of a LJ fcc crystal (Ref. 17) is shown by a solid line with open circles (a) and (b). The calculated isochores of the LJ are shown by solid curves with filled circles. Since the LJ melting curve was calculated in Ref. 17 with a large step in P, we performed two-phase simulations (Refs. 19, 21, and 22) to determine more precisely the T_m at the pressures of 32.5 and 70 GPa. (The upper and lower bounds of T_m are shown by inverted and right filled triangles, respectively; their numerical values at the $P=32.5$ GPa are 2871 and 2921 K and at the $P=70.0$ GPa they are 5133 and 5251 K; after T_{LS} is reached the emerging, PT conditions are 32.56 GPa and 2918 K and at higher pressure 69.7 GPa and 5208 K.) One can see in (a) and (b) that the lower ends of the liquid parts of the isochores indeed correspond to the melting temperatures of the LJ solid. The same phenomenon holds for EAM Cu (c). After reaching the limit of superheating, the temperature of the system spontaneously drops to exactly (within the size of the symbols, which roughly represents the numerical error) the temperature of melting.

$$U^{Solid}(V,T_{LS}) = U^{Liquid}(V,T_m), \tag{1}$$

where $U(V,T)$ is the total energy of the system at volume V and temperature T. After reaching T_{LS} the T decreases because of the latent heat. We want to emphasize that Eq. (1) in no way follows from our simulation procedure. The drop of T to exactly T_m after reaching T_{LS} is quite unexpected. We also note that in the MD runs, where we observed melting in the close vicinity of T_{LS}, the T remained constant for about 60 000 timesteps. This is an indication that the initial assignment of velocities to the atoms does not initiate a melting. The melting is initiated at a later stage of evolution by the creation and accumulation of defects, possibly according to the mechanism described in previous works.[15,16]

The identity in Eq. (1) has an obvious physical meaning: the homogeneous melting occurs when the internal energy of the atoms in the solid state is sufficient to explore the potential energy landscape of the liquid state. When this happens, the crystal melts to minimize the Helmholtz free energy. In heterogeneous melting a liquid gets stabilized by entropy. In a solid at $T<T_{LS}$ this mechanism is suppressed until, at T_{LS}, the internal energy of the crystal becomes high enough to allow the atoms to leave their crystalline positions and diffuse within the sample. Equation (1) also tells us that one cannot provide a solid with an energy which is higher than that of a liquid without melting the solid. We have been able to derive this relation because we indeed reached the limit of superheating. We have noticed that scaling of velocities or connecting the system to a thermostat leads to homogeneous melting temperatures well below the T_{LS}. Therefore, it is possible that some of the previous studies have not reached T_{LS}.

To demonstrate that the absence of the states with high entropy is the reason for superheating, we performed two-phase MD simulations.[19–22] Normally, in a two-phase *NPT* MD simulation the solid is placed in contact with a liquid of the same composition, ensuring the equality of the Gibbs free energies of the solid and liquid at T_m.[19,21,22] We also performed a two-phase MD simulation, however, the LJ parameters for the liquid were chosen quite differently from those for the solid. Therefore, the Gibbs free energies of the solid and liquid were different. Nevertheless, the solid in these two-phase MD simulations melted without superheating. This confirms that the heterogeneity itself (i.e., the solid-liquid interface, in this case) is sufficient to ensure the equilibrium melting of the solid. In the context of our present study this means that if states with higher entropy were accessible, atoms would readily enter those states. Nowadays, it is assumed that in two-phase simulations[19,20] one has to place a solid in contact with a liquid of the same composition. Our simulation demonstrates that an arbitrary liquid in contact with a solid also allows one to simulate melting without superheating. This also explains why the knowledge of the properties of a solid, without reference to the properties of the corresponding liquid phase, is sufficient to predict its melting curve.[23]

In computer simulations of melting it was noticed that T_{LS} is higher than T_m by about 20–30%. So far this observation did not have a quantitative explanation. Equation (1) provides the basis for the quantitative evaluation of the super-

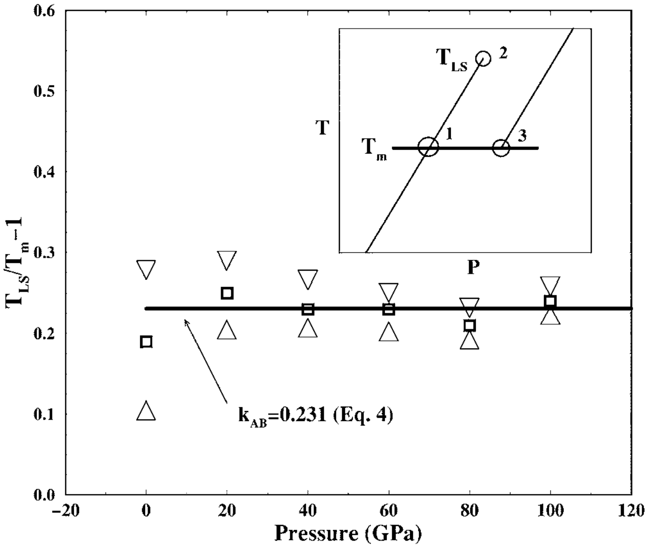

FIG. 2. The relation between T_{LS} and T_m for Al (Ref. 25) as a function of P (open squares). The triangles represent the error bars for each point. The horizontal solid line indicates the numerical value of the constant k_{AB} [Eq. (4)]. The inset illustrates the derivation of the constant k_{AB} [Eqs. (2)–(4)].

heating limit. In the high pressure limit most of the melting curves of simple solids become rather flat because of the small difference between the volumes of the liquid and solid due to the high pressure (see inset in Fig. 2). If we consider points 1, 2, and 3 (Fig. 2, inset), then from Eq. (1) it follows that

$$U_2(T_{LS},V) - U_1(T_m,V) = U_3(T_m,V) - U_1(T_m,V), \qquad (2)$$

where U_i is the internal energy at the conditions (V and T) at the point i. Let us assume that the heat capacity of the solid at volume V and the temperature between T_{LS} and T_m is equal to $3k_B$, and the energy change at melting is equal to $T_m k_B\, ln\, 2$ ($\Delta S = k_B\, ln\, 2$ is the asymptotic value of the entropy of melting.[24] Then, Eq. (2) can be written in the following form:

$$3k_B(T_{LS} - T_m) = T_m k_B \ln 2 \qquad (3)$$

from which it follows that

$$\frac{T_{LS}}{T_m} - 1 = \frac{\ln 2}{3}. \qquad (4)$$

This constant, $k_{AB}=ln\,\frac{2}{3}$, is roughly equal to 0.231, and is the asymptotic value for the superheating limit. If one compares this value with what was previously observed (e.g., Table VI in Ref. 25; see also Fig. 2), one comes to the conclusion that our consideration allows us to explain the particular value of superheating repeatedly observed in computer simulations for as long as attempts to simulate melting have been undertaken.

Since our simulations cover a wide range of pressures and include such different models of interaction as the Lennard-Jones and embedded-atom method, we conjecture that Eq. (1) is a general law. This law [Eq. (1)] allows us to introduce a simple method to determine T_m of a solid. However, in this method both a rather large number of atoms and long runs are needed; therefore, it might be impractical to use it for *ab initio* simulations. On the other hand, our method is simple, quite general, and can be used to determine T_m of any substance.

The constant $k_{AB}=ln\,2/3$ [Eq. (4)] relates T_{LS} and T_m in the high pressure limit. The relation (4) allows us to explain the magnitude of critical superheating routinely observed in simulations of melting.

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[1] R. W. Cahn, Nature (London) **323**, 668 (1986).
[2] R. W. Cahn, Nature (London) **413**, 582 (2001).
[3] J. G. Dash, Rev. Mod. Phys. **71**, 1737 (1999).
[4] B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. Dwayne Miller, Science **302**, 1382 (2003).
[5] S. N. Luo and T. J. Ahrens, Appl. Phys. Lett. **82**, 1836 (2003).
[6] K. Sokolowski-Tinten *et al.*, Nature (London) **422**, 287 (2003).
[7] F. A. Lindemann, Z. Phys. Chem., Stoechiom. Verwandtschaftsl. **11**, 609 (1910).
[8] J. J. Gilvarry, Phys. Rev. **102**, 308 (1956).
[9] M. Born, J. Chem. Phys. **7**, 591 (1939).
[10] H. J. Fecht and W. L. Johnson, Nature (London) **334**, 50 (1988).
[11] J. L. Tallon, Nature (London) **342**, 658 (1989).
[12] P. R. Okamoto, N. Q. Lam, and L. E. Rehn, Solid State Phys. **52**, 1 (1999).
[13] K. Lu and Y. Li, Phys. Rev. Lett. **80**, 4474 (1998).
[14] Z. H. Jin and K. Lu, Philos. Mag. Lett. **78**, 29 (1998).
[15] Z. H. Jin, P. Gumbsch, K. Lu, and E. Ma, Phys. Rev. Lett. **87**, 055703 (2001).
[16] M. Forsblom and G. Grimvall, Nat. Mater. **4**, 388 (2005).
[17] R. Agrawal and D. A. Kofke, Mol. Phys. **85**, 43 (1995).
[18] A. B. Belonoshko, R. Ahuja, O. Eriksson, and B. Johansson, Phys. Rev. B **61**, 3838 (2000).
[19] A. B. Belonoshko, Geochim. Cosmochim. Acta **58**, 4039 (1994).
[20] J. R. Morris, C. Z. Wang, K. M. Ho, and C. T. Chan, Phys. Rev. B **49**, 3109 (1994).
[21] A. B. Belonoshko, R. Ahuja, and B. Johansson, Phys. Rev. Lett. **84**, 3638 (2000).
[22] A. B. Belonoshko, R. Ahuja, and B. Johansson, Nature (London) **424**, 1032 (2003).
[23] L. Burakovsky, D. L. Preston, and R. R. Silbar, Phys. Rev. B **61**, 15011 (2001).
[24] S. M. Stishov, Usp. Fiz. Nauk **114**, 3 (1974).
[25] S.-N. Luo *et al.*, Phys. Rev. B **68**, 134206 (2003).