PHYSICAL REVIEW B **82**, 052101 (2010)

Liquid-solid phase transition in the Lennard-Jones system

Sergey A. Khrapak,[1,2] Manis Chaudhuri,[1] and Gregor E. Morfill[1]
[1]*Max-Planck-Institut für extraterrestrische Physik, D-85741 Garching, Germany*
[2]*Joint Institute for High Temperatures, 125412 Moscow, Russia*
(Received 28 June 2010; published 24 August 2010)

The liquid-solid phase transition of the Lennard-Jones (LJ) system is investigated. It is found that the properly normalized second derivative of the interaction potential is practically constant at freezing. Using this relation a simple equation for the freezing curve is derived. The obtained equation is used to estimate the triple-point parameters of the LJ system. Results are compared with available numerical simulation studies.

DOI: 10.1103/PhysRevB.82.052101 PACS number(s): 64.60.−i, 64.70.D−

Exploring phase behavior of different substances is an outstanding physical problem with applications to both basic and applied research. One of the numerous approaches is to use model pair potentials which capture the essential features of interactions in real substances. A remarkable example is the Lennard-Jones (LJ) system—an ensemble of classical structureless particles interacting via the potential energy of the form

$$U(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{1}$$

where r is the interparticle distance, ϵ and σ are the energy and length scales. The long-range attractive term ($\propto r^{-6}$) corresponds to the dipole-dipole attraction between neutral atoms at large distances while the repulsive ($\propto r^{-12}$) term mimics the steep repulsion at short distances.[1] Apart from providing a reasonable description of the interaction between rare-gas atoms, the LJ potential is one of the most simple models reproducing the complete thermodynamic behavior of conventional classical fluids. Not surprisingly, the phase diagram of the LJ model has been extensively investigated using various theoretical and computational methods (see, e.g., Refs. 2–10 and references therein).

The purpose of this paper is to discuss an interesting property of the LJ system related to its liquid-solid phase transition. Using the available data from numerical simulations we show that the properly normalized second derivative of the potential remains approximately constant along the liquid boundary of the liquid-solid coexistence (freezing curve). This property is used to construct a simple approximate equation for the freezing curve. The obtained equation is then compared with those proposed earlier. As an example of its application, we estimate the temperature and density of the LJ system at the triple point.

We performed a systematic scan of the numerical data related to the liquid-solid phase transition in the LJ system. The quantity we are monitoring is the dimensionless second derivative of the interaction potential evaluated at the mean interparticle distance Δ

$$\mathcal{L}=U''(\Delta)\Delta^{2}/T, \tag{2}$$

where T is the particle temperature and Δ is related to the particle density via $\rho\Delta^{3}=1$. Figure 1 summarizes the values of $\mathcal{L}$ at the liquid (open symbols) and solid (solid symbols) boundaries of the liquid-solid phase coexistence. These values are calculated from the simulation data of Refs. 4, 5, and 8–12. The values of $\mathcal{L}$ at melting exhibit a pronounced decrease with increasing density. In contrast, no systematic dependence of $\mathcal{L}$ on density is evident at freezing. All the data lie between $\mathcal{L}\simeq 270$ and $\mathcal{L}\simeq 320$. There are no well-established standards to assess the accuracy of a particular simulation method. In addition, finite-size and finite-cutoff radius effects are known to be responsible for some discrepancies between simulation results.[10,11] So we do not elaborate further on possible reasons for scatter and deviations between different numerical results. For our present purposes it is sufficient to note that the data points are scattered in the relatively narrow range, $\mathcal{L}\simeq 290\pm 10\%$.

We do not yet have a complete physical interpretation of why the normalized second derivative of the LJ potential is approximately constant along the freezing curve. We note, however, that the LJ model is not the only example exhibiting such a property. A similar behavior was previously reported for a system of particles interacting via the purely repulsive Yukawa potential at the liquid-solid

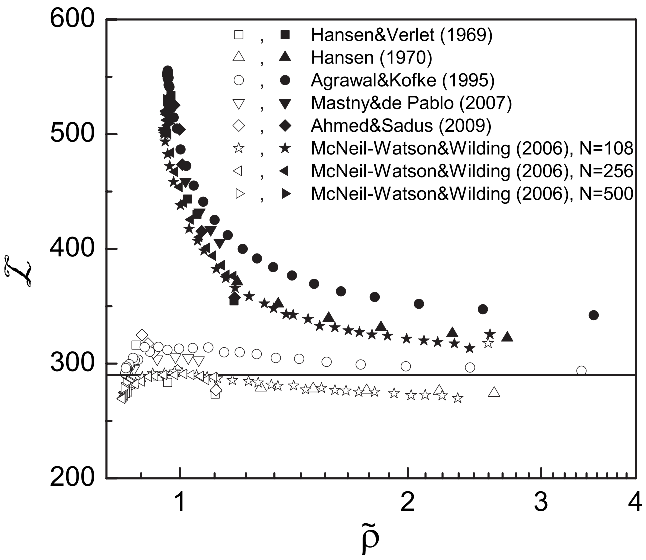

FIG. 1. The value of the normalized second derivative of the interaction potential $\mathcal{L}=U''(\Delta)\Delta^{2}/T$ as a function of normalized density $\tilde{\rho}=(\sigma/\Delta)^{3}$ at freezing (open symbols) and melting (solid symbols) of the LJ system. Symbols denote available data from numerical simulations as indicated in the figure. The horizontal line corresponds to $\mathcal{L}=290$.

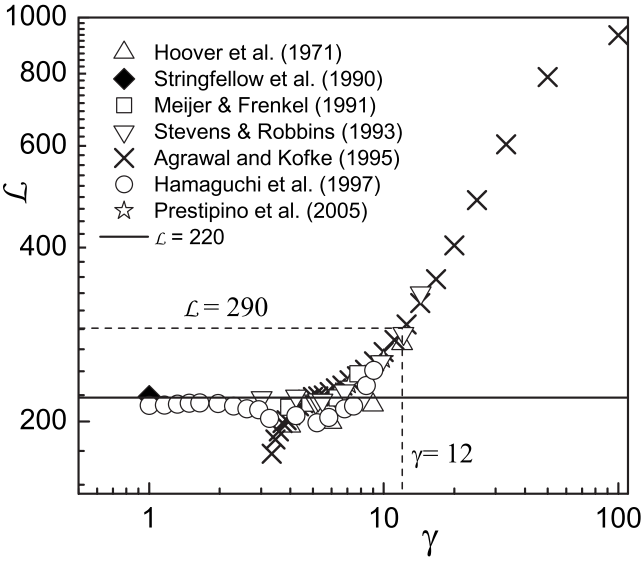

FIG. 2. The values of the parameter $\mathcal{L}=U''(\Delta)\Delta^2/T$ at freezing of the Yukawa and IPL systems versus the potential steepness γ. Symbols denote available data from numerical simulations as indicated in the figure. The horizontal solid line corresponds to $\mathcal{L}=220$. Dashed lines indicate the point $\mathcal{L}=290$ at $\gamma=12$ which emerges from the analysis of the LJ system freezing data. For a discussion see text.

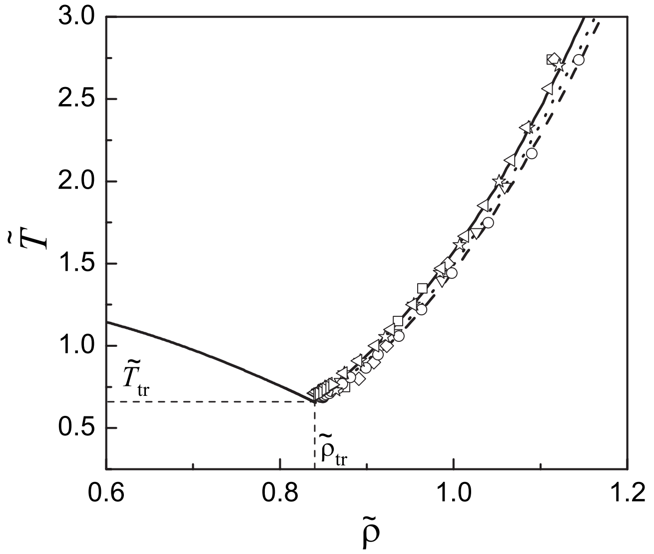

FIG. 3. Portion of the phase diagram of the LJ system on the plane of the normalized density $\tilde{\rho}$ and temperature $\tilde{T}$. The solid curve on the left corresponds to the liquid boundary of the vapor-liquid phase calculated using Eq. (4). The solid curve on the right is the liquid boundary of the liquid-solid phase (freezing curve) calculated using Eq. (3). Their intersection gives the following triple-point parameters: $\tilde{T}_{\mathrm{tr}}\simeq 0.66$ and $\tilde{\rho}_{\mathrm{tr}}\simeq 0.84$. Symbols correspond to the low-temperature portion of numerical data on freezing for the LJ system. Notation is the same as in Fig. 1. The dotted and dashed curves correspond to the fits proposed in Refs. 10 and 24, respectively.

phase transition. Namely, a decade ago Vaulina *et al.*[13,14] proposed a freezing criterion for Yukawa systems utilizing Lindemann-type arguments.[15] Consider a one-dimensional harmonic system with nearest-neighbors interaction between the particles. Average-particle displacements from their equilibrium positions are related to the particle temperature, viz., $U''(\Delta)\langle\delta r^2\rangle\propto T$. According to Lindemann's rule $\langle\delta r^2\rangle/\Delta^2 \simeq$ const at melting, which immediately leads to the condition $\mathcal{L}=$const. This argument is not convincing enough (for a number of obvious reasons) to employ such criterion generically. Moreover, even for repulsive Yukawa systems it works reasonably well only when the ratio of the interparticle distance to the plasma screening length is not too large. In view of the pronounced similarities with respect to freezing in Yukawa and inverse-power-law (IPL) systems reported recently[16] it makes sense to discuss this subject further. This will also provide some insight regarding the obtained value of $\mathcal{L}$ at freezing of the LJ system.

Figure 2 shows the available numerical data related to the values of the parameter $\mathcal{L}$ at freezing for Yukawa and IPL repulsive potentials. For the Yukawa (Debye-Hückel) potential of the form $U(r)=(U_0/r)\exp(-r/\lambda)$, we have $\mathcal{L}=[U(\Delta)/T](2+2\kappa+\kappa^2)$, where U_0 is the parameter regulating the strength of the interaction, λ is the screening length, and $\kappa=\Delta/\lambda$ is the screening parameter. The data shown in Fig. 2 are taken from Refs. 17–19. For the IPL potential of the form $U(r)=\varepsilon(\sigma/r)^n$, we have $\mathcal{L}=[U(\Delta)/T]n(n+1)$, where ε and σ are energy and length scales and n is the index. The data shown in Fig. 2 are taken from Refs. 20–23. In order to unify the data for the two different potentials we plotted $\mathcal{L}$ as a function of the potential steepness evaluated at the mean interparticle distance,[16] viz., $\gamma=|d\ln U(r)/d\ln r|_{r=\Delta}$. Note that in terms of the conventional notation we have $\gamma=1+\kappa$ for the Yukawa potential and $\gamma=n$ for the IPL potential. Figure 2 demonstrates that the data points corresponding to different potentials are scattered in a close vicinity of a single curve. The emerging curve has the following properties. For weak and moderate steepness of the potentials ($\gamma\lesssim 8$) all the data points fall in the vicinity $\mathcal{L}=220$ with an accuracy of approximately ±15% and show little systematic dependence on γ. This is the regime where the original criterion for freezing of Yukawa systems[13,14] is applicable. For $\gamma\gtrsim 8$ the quantity $\mathcal{L}$ exhibits a systematic growth. Interestingly, the value of $\mathcal{L}\simeq 290$ closely corresponds to $\gamma=12$ on the emerging curve (see Fig. 2) which obviously reflects the r^{-12} repulsive term in the LJ potential. This is not surprising since if $\mathcal{L}$ is nearly constant along the freezing line of the LJ system, the value of the constant can be determined from the high-temperature limit, which is governed by $\propto r^{-12}$ repulsion. This correlates with the conventional philosophy that the freezing transition in simple fluids is mainly determined by repulsive forces.[6] In addition, this finding gives hope that freezing for LJ-type potentials (e.g., n-6 and exp-6 models) can be approached in a similar manner. At the same time, certain value of the properly normalized second derivative of the potential cannot serve as a universal criterion of freezing. An obvious example is the hard-sphere system, where the second derivative of the potential is undefined at all.

Now let us discuss some direct applications of the observed property of the LJ system. The constancy of $\mathcal{L}$ at freezing suggests a very simple approximate equation for the freezing curve. Assuming $\mathcal{L}\simeq 290$ we immediately get for the LJ potential

$$\tilde{T}\simeq \frac{24}{290}(26\tilde{\rho}^4-7\tilde{\rho}^2), \tag{3}$$

where $\tilde{T}=T/\epsilon$ is the reduced temperature and $\tilde{\rho}=(\sigma/\Delta)^3$ is the reduced density. The resulting freezing curve is shown in Fig. 3 along with numerical data and two other fits proposed in the literature.[10,24] These two fits have the same functional form $\tilde{\rho}=\tilde{T}^{1/4}\Sigma_{j=0}^{j=5}a_j\tilde{T}^{-j}$, but different values of the coefficients a_j. The agreement between Eq. (3) and these fits is rather good in the considered low-temperature regime. Note, however, that in the high-temperature regime the proposed equation for the freezing curve is expected to be much more reliable. In order to demonstrate this we take the simulation data point with the highest density and temperature: $\tilde{T}\simeq 274$ at $\tilde{\rho}\simeq 3.39$.[8] For $\tilde{\rho}=3.39$, our Eq. (3) yields $\tilde{T}\simeq 278$ while the fit from Ref. 10 predicts $\tilde{T}\simeq 196$ and that from Ref. 24 yields $\tilde{T}\simeq 193$. Both latter values are considerably lower than those from simulation and Eq. (3).

As an example of the application of the proposed equation for the freezing curve, let us estimate the triple-point parameters of the LJ system. We adopt a simple empirical expression for the liquid boundary of the liquid-vapor coexistence suggested by Guggenheim[25]

$$\frac{\rho}{\rho_c}=1+\frac{3}{4}\left(1-\frac{T}{T_c}\right)+\frac{7}{4}\left(1-\frac{T}{T_c}\right)^{1/3}, \tag{4}$$

where ρ_c and T_c are the density and temperature at the critical point. Using the values $\tilde{T}_c\simeq 1.313$ and $\tilde{\rho}_c\simeq 0.304$ reported in Ref. 9 we get the curve shown in Fig. 3. The intersection of the liquid-solid and vapor-liquid coexistence curves yields the following triple-point parameters of the LJ system: $\tilde{T}_{tr}\simeq 0.66$ and $\tilde{\rho}_{tr}\simeq 0.84$. We can compare these numbers with the LJ triple-point parameters reported earlier, e.g., $\tilde{T}_{tr}=0.68\pm 0.02$ and $\tilde{\rho}_{tr}=0.85\pm 0.01$ in Ref. 4; $\tilde{T}_{tr}=0.687\pm 0.004$ and $\tilde{\rho}_{tr}=0.850$ in Ref. 8; $\tilde{T}_{tr}=0.694$ in Ref. 10; $\tilde{T}_{tr}=0.661$ and $\tilde{\rho}_{tr}=0.864$ in Ref. 12; and $\tilde{T}_{tr}=0.67\pm 0.01$ and $\tilde{\rho}_{tr}=0.818\pm 0.004$ in Ref. 26. The agreement is remarkably good taking into account the simplifications involved in the present estimate.

To summarize, we reported an interesting property of the LJ system. The properly normalized second derivative of the interaction potential remains practically constant at freezing. The value of the constant was shown to be close to that of the purely repulsive $\propto r^{-12}$ potential at freezing. This observation was used to construct a simple equation for the freezing curve, which yields adequate results in the entire temperature-density range investigated so far. Using the obtained equation we estimated the triple-point parameters of the LJ system. These agree well with those reported earlier. Finally, we suggest that the approach discussed in this work in the context of the LJ system can be expected to work for the entire family of LJ-type potentials. This, however, requires further detailed investigation.

This work was partly supported by DLR under Grant No. 50WP0203.

---

[1] J. E. Lennard-Jones, Physica (Amsterdam) **4**, 941 (1937).

[2] L. Verlet, Phys. Rev. **159**, 98 (1967).

[3] J. A. Barker and D. Henderson, J. Chem. Phys. **47**, 4714 (1967).

[4] J.-P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).

[5] J.-P. Hansen, Phys. Rev. A **2**, 221 (1970).

[6] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[7] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, Mol. Phys. **78**, 591 (1993).

[8] R. Agrawal and D. A. Kofke, Mol. Phys. **85**, 43 (1995).

[9] H. Okumura and F. Yonezawa, J. Chem. Phys. **113**, 9162 (2000).

[10] E. A. Mastny and J. J. de Pablo, J. Chem. Phys. **127**, 104504 (2007).

[11] G. C. McNeil-Watson and N. B. Wilding, J. Chem. Phys. **124**, 064504 (2006).

[12] A. Ahmed and R. J. Sadus, J. Chem. Phys. **131**, 174504 (2009).

[13] O. S. Vaulina and S. A. Khrapak, JETP **90**, 287 (2000).

[14] O. S. Vaulina, S. A. Khrapak, and G. E. Morfill, Phys. Rev. E **66**, 016404 (2002).

[15] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Elsevier, New York, USA, 2006).

[16] S. A. Khrapak and G. E. Morfill, Phys. Rev. Lett. **103**, 255003 (2009).

[17] E. J. Meijer and D. Frenkel, J. Chem. Phys. **94**, 2269 (1991).

[18] M. J. Stevens and M. O. Robbins, J. Chem. Phys. **98**, 2319 (1993).

[19] S. Hamaguchi, R. T. Farouki, and D. H. E. Dubin, Phys. Rev. E **56**, 4671 (1997).

[20] W. G. Hoover, S. G. Gray, and K. W. Johnson, J. Chem. Phys. **55**, 1128 (1971).

[21] R. Agrawal and D. A. Kofke, Phys. Rev. Lett. **74**, 122 (1995); Mol. Phys. **85**, 23 (1995).

[22] S. Prestipino, F. Saija, and P. V. Giaquinta, J. Chem. Phys. **123**, 144110 (2005).

[23] G. S. Stringfellow, H. E. DeWitt, and W. L. Slattery, Phys. Rev. A **41**, 1105 (1990).

[24] M. A. van der Hoef, J. Chem. Phys. **113**, 8142 (2000).

[25] E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945).

[26] A. J. C. Ladd and L. V. Woodcock, Mol. Phys. **36**, 611 (1978).