Phase Diagram of a modified Lennard-Jones system

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Abstract. The well-known Lennard-Jones potential is modified in such a way that it smoothly vanishes at a certain distance. A system whose interparticle interaction is given by such a potential is referred to as a modified Lennard-Jones system, and is served as a standard system describing simple solids and fluids. A phase diagram is determined based on the free energies obtained through thermodynamic integration.

1. Introduction
The Lennard-Jones (LJ) potential has been used to describe the interparticle interaction in simple solids and fluids. A phase diagram of the LJ system has been recently updated by Toxvaerd utilizing large-scale molecular dynamics simulations [1]. In such numerical treatments, the potential tail is neglected, whose effects will be tried to be compensated later on. However, this potential cutoff should be avoided in the following reasons. The error in the pressure owing to the cutoff is estimated to be roughly equal to the pressure itself in a low-pressure (density) region below the triple point. In estimating the error, the virial is averaged over the distances beyond the cutoff, where the radial distribution function is usually assumed to be that of an ideal gas. In the solid state, however, the distribution is still oscillating around the cutoff distance. Hence, such a treatment of the error is definitely inappropriate for a low-pressure solid.

Here, we employed a potential which smoothly vanishes at a certain distance, while the most part, except for an immediate vicinity of the vanishing point, remains unmodified. This latter potential is referred to as a modified LJ potential, and a system that employs the potential as interparticle interactions is called a modified LJ system. The equilibrium melting point, $T_m$, of the modified LJ system was precisely determined at zero pressure. In the present study, the phase diagram in a low-pressure region is investigated. $T_m$s are known to shift towards the high-temperature side with increasing system size [2]. This size dependence becomes less remarkable when the number of particles exceeds ~ 5000 [2]. From the viewpoint of the computational cost, however, a 256-particle system is provided for the calculation at the cost of accuracy. The deviation of the phase boundaries from those at the thermodynamic limit is estimated.

2. Methods
The following modified LJ potential [3], $\phi_m$, was employed.

$$\phi_m(r) = \begin{cases} 
4\epsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + c_1 & (r \leq 2.3\sigma) \\
2^6\epsilon \left( \frac{\sigma}{r} \right)^{12} + c_2 \left( \frac{\sigma}{r} \right)^{6} + c_3 \left( \frac{\sigma}{r} \right)^2 + c_5 & (2.3\sigma < r < 2.5\sigma) \\
0 & (r \geq 2.5\sigma),
\end{cases}$$

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where \( r \) is the interparticle distance, and the coefficients, \( c_i \), are given by \( c_1 = 0.016132 \epsilon \), \( c_2 = 3.1366 \times 10^3 \epsilon \), \( c_3 = -6.8069 \times 10^6 \epsilon \), \( c_4 = -0.083312 \epsilon \), and \( c_5 = 0.74689 \epsilon \), respectively. The well-established argon parameters [4] were used for the energy and length parameters, \( \epsilon \) and \( \sigma \). Note that both \( \phi_m \) and its derivative vanish at and beyond 2.5\( \sigma \).

Thermodynamic integration (TI) [3] was employed for the evaluation of free energies. The system under consideration is coupled to a reference system, whose free energy is exactly known, by a coupling parameter. The system is then converted to the reference system by gradually varying the strength of the parameter. The reversible work for the conversion is then calculated by integration with respect to the parameter under a given thermodynamic condition. An Einstein solid and an ideal gas were chosen as the reference system on the solid and the fluid sides, respectively. For further details, refer to [3]. In order to calculate the infinitesimal work upon the variation, it is required to generate isothermal-isobaric or isothermal-isochore ensembles. Molecular dynamics method was used for the generation of these ensembles; the Nosé-Hoover thermostat [5, 6] and the Andersen barostat [7] were adopted to realize isothermal and isobaric conditions, respectively. The fourth-order Runge-Kutta-Gill scheme [8] was used for the numerical integration of the equations of motion. The time mesh was fixed to 10\(^3\) steps, and 50000 steps were used for the ensemble average. As is well recognized, the thermodynamic integration is time consuming and is not necessarily an effective means for the evaluation of free energy. Hence, only several free energies were calculated using the thermodynamic integration under a given pressure. The free energies were then interpolated by integrating the Gibbs-Helmholtz (GH) relationship [3].

In the following, unless otherwise explicitly stated, pressure and temperature are given in units of \( \epsilon/\sigma^3 \) and \( \epsilon/k_B \), respectively, where \( k_B \) is Boltzmann’s constant.

3. Results and discussion

The free energy of solid, liquid and gas states was calculated at a fixed pressure, \( p \), as a function of temperature, \( T \), and is plotted in figure 1. The \( T_m \) is then obtained from a cross point between the two. The errors of the free energy are estimated by assuming that each integrand upon the TI is statistically independent.

| \( p/\sigma^3 \) | \( T_m/\epsilon/k_B \) |
|-----------------|-----------------|
| 0.0001          | 0.611\(^{+0.034}_{-0.033}\) |
| 0.001           | 0.629\(^{+0.034}_{-0.033}\) |
| 0.002           | 0.606\(^{+0.034}_{-0.033}\) |
| 0.003           | 0.571\(^{+0.034}_{-0.033}\) |
| 0.01            | 0.633 \( \pm \) 0.033 |
| 0.1             | 0.653 \( \pm \) 0.033 |

Table 1 summarizes the \( T_m \) thus determined under a pressure shown. Estimation of the error \( \Delta T \) associated with a \( T_m \) was made based on the following consideration. Let \( \Delta g(T_0) \) be the error of the free energy (per particle) evaluated at \( T_0 \) under given \( p \). The free energy at another \( T \) is found by integrating the GH relationship from \( T_0 \). It is then proven that \( \Delta g \) is conserved at any \( T \) provided that \( p \) is unchanged. Projection of \( \Delta g \) to the \( T \)-axis allows us to estimate \( \Delta T \), which amounts 0.03 when \( \Delta g \) of the solid branch is used. However, this is smaller as compared with that originating from uncertainty of the liquid free energy. The latter is largely attributable to the uncertainty of the free energy in the ideal-gas limit. This makes estimating the intrinsic error of the liquid free energy difficult. If a reference
liquid with the exact free-energy formula is available, the uncertainty will be reduced to the same order of magnitude as that of the solid branch. Here, we regard the principal value of the free energies as the true value. This idea is partially supported by the fact that the free energies calculated from the GH relationship using the thermodynamically integrated free energy as an initial input coincide with those obtained independently through the TI (see figure 1). From these observations, the intrinsic uncertainty of the fluid-state free energy is inferred to be the same order of magnitude as that of the solid-state free energy. The errors presented in table 1 were thus estimated from the ambiguities in the solid-state free energies. These errors are then reduced with increasing system size. Indeed, they attain $O(10^{-3})$ for an $N = 4000$ system [2].

$T_m$ under nonzero pressures becomes higher than that at $p = 0$. This is evident from the Clausius-Clapeyron (CC) relationship:

$$\frac{dp}{dT} = \frac{\Delta L}{T_m \Delta V},$$

in which the latent heat, $\Delta L$, is a positive quantity upon melting. The change in volume, $\Delta V$ is also positive (see figure 2(b)) for such a simple system composed of modified LJ particles.

As seen from figure 2(a), the slope of the melting curve becomes steep towards $p \to 0$. This behavior is qualitatively understood also from the CC relationship in the following way. Although $\Delta V$ of sublimation is larger than that of fusion (see figure 2(b)), the entropy change $\Delta L/T_m$ on sublimation is much larger than that on fusion, because a solid loses the global crystalline order completely on sublimation. This latter change overcomes the former volume change multiplied by $T_m$, and as a result, the slope, $dp/dT$ becomes much larger on the solid – gas transition side.

Finally, we have to give warning once again to making little of the effects of potential tails when discussing thermodynamic properties of LJ systems. The cutoff of the tail at $2.5\sigma$ is usually employed in most of numerical simulations for the ordinary LJ system. The error caused by the cutoff to the total potential energy was shown to amount to $\sim 5\%$ [9], by manipulating the sum of the potential so as to be taken without the cutoff operation. The generalized Ewald method [10] was invoked to this end. However, the Ewald method is so costly that can handle a system consisting only of $O(10^2)$ LJ

Figure 1. Free energies in units of $\epsilon$ per particle of the solid, liquid and gas states at $p = 0.1$ are plotted against temperature, $T$. Those obtained through the TI are marked by the symbols, whereas those obtained by integrating the GH relationship are delineated by the lines.
particles. The results will suffer from the finite-size effects, then. In this context, the modified LJ system is attractive in that the potential tail is “cut off” at the outset. We hope that the system is treated as a standard system in investigating thermodynamic properties of a simple system under low pressures.

Figure 2. (a) The $p$–$T$ phase diagram of a low-pressure region of the modified LJ system. Pressure is plotted on a logarithmic scale. The triple point, marked by an asterisk, is from [3]. The melting points are marked by pluses, whereas the boiling point is marked by a cross. No error estimation was made for the latter. The lines showing the phase boundaries are only a guide to the eye. (b) The densities in coexistence state under the pressure indicated are plotted. The error in density was obtained from the root-mean-square variation of volume on either side of the phase separated by the melting point.

4. Conclusion
The phase diagram of the modified LJ system consisting of 256 particles was obtained. The equilibrium melting point at zero pressure is 0.60, which is 0.03 lower than the one at thermodynamic limit [2]. Therefore, the phase boundaries shown in figure 2 are expected to be shifted upward by an amount roughly equal to 0.03 in the thermodynamic limit. Investigations using an $N = 6912$ system are now in progress, and the results involving less effects of finite size will be reported in the no distant future.

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