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Phase Diagram of Kob-Andersen-Type Binary Lennard-Jones Mixtures

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The binary Kob-Andersen (KA) Lennard-Jones mixture is the standard model for computational studies of viscous liquids and the glass transition. For very long simulations, the viscous KA system crystallizes, however, by phase separating into a pure A particle phase forming a fcc crystal. We present the thermodynamic phase diagram for KA-type mixtures consisting of up to 50% small (B) particles showing, in particular, that the melting temperature of the standard KA system at liquid density 1.2 is 1.028(3) in A particle Lennard-Jones units. At large B particle concentrations, the system crystallizes into the CsCl crystal structure. The eutectic corresponding to the fcc and CsCl structures is cutoff in a narrow interval of B particle concentrations around 26% at which the bipyramidal orthorhombic PuBr$_3$ structure is the thermodynamically stable phase. The melting temperature’s variation with B particle concentration at two constant pressures, as well as at the constant density 1.2, is estimated from simulations at pressure 10.19 using isomorph theory. Our data demonstrate approximate identity between the melting temperature and the onset temperature below which viscous dynamics appears. Finally, the nature of the solid-liquid interface is briefly discussed.

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Standard models are invaluable in physics by providing well-understood reference systems for testing new ideas. Well-known examples are the ideal gas model, the Ising model for critical phenomena [1,2], and the $\phi^4$ scalar field theory for renormalization [1,3]. In computational studies of viscous liquids and the glass transition [4–9], the Kob-Andersen (KA) binary Lennard-Jones (LJ) mixture has been the standard model for 20 years [10]. The KA model is a mixture of 80% large A particles and 20% small B particles. The model is characterized by a strong AB attraction, which disfavors phase separation into a pure A phase by making it energetically costly. When the model crystallizes in very long computer runs, this nevertheless happens by phase separation into a pure A phase forming a face-centered cubic (fcc) crystalline structure [11,12]. This may be contrasted with the Wahnström 50/50 binary LJ mixture [13], which has a much more complex crystal structure [14].

In the KA mixture, all particles have the same mass and interact via LJ pair potentials $v(r) = 4\varepsilon[(r/\sigma)^{-12}-(r/\sigma)^{-6}]$ truncated and shifted to zero at $2.5\sigma$ with $\sigma_{BB}/\sigma_{AA} = 0.88$, $\sigma_{AB}/\sigma_{AA} = 0.8$, $\varepsilon_{BB}/\varepsilon_{AA} = 0.5$, and $\varepsilon_{AB}/\varepsilon_{AA} = 1.5$. The large $\varepsilon_{AB}$ favors stability toward phase separation. The parameters of the KA model were chosen to mimic the nickel-phosphor mixture [10] that has a eutectic at 20% P atoms [15]; eutectic mixtures [16] are generally regarded as optimal for glass formation [17].

Crystallization of binary LJ models has been simulated by several groups [18–21]. In 2001, Wales and co-workers showed that the KA system possesses low-lying crystalline minima [22], confirming the prevailing view that the KA viscous liquid is not in true thermodynamic equilibrium [23]. Two years later, Fernandez and Harrowell reported rapid crystal growth for the 50/50 KA mixture [24] and argued that, for general KA-type mixtures, the lowest-energy ordered state consists of coexisting phases of single-component fcc and equimolar CsCl crystal structures [25]. In 2009, Kob and co-workers reported that the standard 80/20 KA mixture crystallizes in two dimensions, whereas the 65/35 composition does not [26]. Royall and co-workers in 2015 showed that locally favored structures impede crystallization if they do not tile space [27]. In 2016, Bhattacharyya and co-workers showed that the entropic penalty for demixing is a nonmonotonic function of composition with a maximum at a composition close to that of the standard KA model [28].

The below study utilized the software packages RUMD [29], LAMMPS [30], VMD [31], and a home-written code [32]. The majority of the simulations involved 8000 particles, and a few had 10 000 particles.

Most KA-model papers focus on density 1.2 in the LJ unit system defined by the A particle parameters. We determined the melting temperature of the standard KA liquid at this density from two-phase simulations by proceeding as follows. First, the pressure of the liquid was calculated as a function of temperature at density 1.2 [Fig. 1(a)]. Next, we determined the lattice parameters of pure A particle fcc crystals at the temperatures and pressures of Fig. 1(a) [33,34]. The final step was to simulate at each temperature and pressure a two-phase system composed initially of half KA liquid and half pure A crystal, choosing a box size compatible...
with the determined lattice constant and using a “longitudinal” barostat, ensuring constant pressure perpendicular to the crystal-liquid interface. Over time, the pure A crystal either grows or shrinks, which changes the ratio of A to B particles in the liquid phase. When equilibrium has been reached, the temperature is the melting temperature of that particular liquid composition [35]. Figure 1(b) shows the fraction of B particles where the abscissa is the melting temperature at the pressure identified in Fig. 1(a). For the standard 80/20 KA system, we see that, at pressure \( p = 10.19(3) \) and liquid-phase density 1.2, freezing occurs at the temperature 1.028(3).

Figure 2 shows a snapshot of the two-phase equilibrium KA system at \( T = 1.028 \) and \( p = 10.19 \). A few B particles (red) have diffused into the pure A crystal, which is to be expected given the relatively high temperature. The lower panel shows the density of B particles (red) and of all particles (black), confirming that the liquid phase has density 1.2 and contains 20% B particles.

Having determined the pressure of the state point at which the KA liquid at freezing has density 1.2, we proceed to establish the composition-temperature phase diagram at this pressure (Fig. 3). The phase diagram was arrived at by the above method in which the solid-liquid interface is “pinned” due to the composition constraint in the liquid.
We also studied the Al on triangular prisms is the thermodynamically stable phase.

When the liquid has the same composition as the crystal, this constraint is absent, however, in which case we used the interface-pinning method [36]. At small B particle concentrations, the solid phase is a pure A-phase fcc crystal. Upon increasing the B particle concentration, at some point the system crystallizes instead into the 50/50 CsCl structure of two interpenetrating cubic lattices of A and B particles [24,28]. The eutectic of these two crystal phases is located around 26% B particles, but interestingly there is a narrow region around the eutectic in which the bipyramidal orthorhombic PuBr3 structure based on triangular prisms is the thermodynamically stable phase. We also studied the Al2Cu, Fe3C, and Ni3P structures shown by Fernández and Harrowell to be of low energy at T = 0 and p = 0 [37], but found that their melting temperatures are all lower (compare Fig. 3 and Table I). In Fig. 3, “layered” denotes a structure of alternating layers of CsCl and pure A particle fcc crystals, which is known to have low energy at T = 0 [22,24].

To investigate the dynamics of crystallization, we utilized the following protocol for a range of compositions and temperatures (p = 10.19): First, one equilibrates up to ten liquid configurations at the coexistence temperature. Subsequently, the temperature is changed to the desired value and one computes the crystallization time t∗, defined as the average time at which 10% of the particles are in a crystalline environment (monitored by the crystal order parameter defined as the absolute value of the density’s Fourier transform at the fundamental lattice k vector [38]). The blue and red areas in Fig. 3 are regions with rapid crystallization. As expected, the spontaneously formed crystals are fcc for 0%–15% B’s and CsCl for 41%–50% B’s. The green crosses show for each composition the temperature Tmin at which the crystallization time is at a minimum, t∗min. The upper panel shows t∗min.

The melting line in Fig. 3 is for p = 10.19, the pressure at which the coexisting liquid for the standard 80/20 KA system has density 1.2. The melting temperature’s variation with B particle concentration at other pressures or at constant liquid-phase density may be estimated from the p = 10.19 results from the fact that the melting line to a good approximation follows a liquid isomorph [8,39]. The estimate, which makes use of the fact that LJ-type systems are R-simple, i.e., have strong virial potential-energy correlations [40–42], works as follows. For any mixture of LJ particles, if the melting temperature at liquid density ρ0 is T0, the melting temperature T at liquid density ρ is approximately given [43,44] by

\[
T/T_0 = (\gamma_0/2 - 1)(\rho/\rho_0)^4 - (\gamma_0/2 - 2)(\rho/\rho_0)^2. \tag{1}
\]

\[
T/T_0 = (\gamma_0/2 - 1)(\rho/\rho_0)^4 - (\gamma_0/2 - 2)(\rho/\rho_0)^2. \tag{1}
\]

### TABLE I. State point data for the liquid in coexistence with different crystalline states at pressure p = 10.19 at the specified B particle concentrations in the liquid phase (A particle LJ units). Crystal structures are identified by prototype, Hermann-Mauguin space group, and International Union of Crystallography number. Tm is the melting temperature, ρs and ρl are the solid and liquid densities, us and ul are the average potential energies per particle of the solid and liquid phases, ΔS is the constant-pressure entropy of fusion calculated from the parameters and the phase-equilibrium condition ΔG = 0.

<table>
<thead>
<tr>
<th>Structure</th>
<th>χB</th>
<th>Tm (K)</th>
<th>ρs (LJ units)</th>
<th>ρl (LJ units)</th>
<th>us (LJ units)</th>
<th>ul (LJ units)</th>
<th>ΔS (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc [Fm(\overline{3}m); 225]</td>
<td>0%</td>
<td>1.341(4)</td>
<td>1.0535</td>
<td>0.9796</td>
<td>−3.6460</td>
<td>−2.7971</td>
<td>1.177</td>
</tr>
<tr>
<td>PuBr3 [Cmcm; 63]</td>
<td>25.5%</td>
<td>0.935(8)</td>
<td>1.3515</td>
<td>1.2712</td>
<td>−7.1192</td>
<td>−6.3170</td>
<td>1.367</td>
</tr>
<tr>
<td>Fe3C [Pnma; 62]</td>
<td>25.0%</td>
<td>0.820(8)</td>
<td>1.3501</td>
<td>1.2950</td>
<td>−7.1446</td>
<td>−6.5360</td>
<td>1.134</td>
</tr>
<tr>
<td>Ni3P [I(\overline{4}); 82]</td>
<td>24.8%</td>
<td>0.767(6)</td>
<td>1.3582</td>
<td>1.2878</td>
<td>−7.0759</td>
<td>−6.6409</td>
<td>1.102</td>
</tr>
<tr>
<td>Al2Cu [I(\overline{4})(m)(c); 140]</td>
<td>33.4%</td>
<td>0.875(8)</td>
<td>1.4256</td>
<td>1.2858</td>
<td>−7.1720</td>
<td>−6.9785</td>
<td>1.109</td>
</tr>
<tr>
<td>CsCl [Pm(\overline{3}m); 221]</td>
<td>49.4%</td>
<td>1.394(4)</td>
<td>1.6427</td>
<td>1.4392</td>
<td>−7.5850</td>
<td>−5.9561</td>
<td>1.798</td>
</tr>
</tbody>
</table>

![FIG. 4. Isomorph-theory estimated melting temperature as a function of B particle concentration at fixed liquid-phase density ρ = 1.2 (triangles), as well as at pressures ρ = 0 and ρ = 30 (squares and diamonds). The circles connected by colored full lines are the results from Fig. 3, giving the reference states from which the open symbols are predicted. Red crosses are the actual melting temperatures. (Inset) Melting temperature Tm versus the onset temperatures T0 (not to be confused with the above isomorph reference temperature), identified by Coslovich and Pastore at which the A and B particle dynamics (black and red) change from Arrhenius to non-Arrhenius temperature dependence [45]. The four points show represent different densities (pressures) of the standard 80/20 KA model.](image-url)
TABLE II. Thermodynamic quantities along the $p=10.19$ melting line used for estimating the melting temperatures at constant liquid-phase density, as well as at two other pressures (Fig. 4).

<table>
<thead>
<tr>
<th>$\gamma_B$</th>
<th>$T_0$</th>
<th>$\rho_0$</th>
<th>$\gamma_0$</th>
<th>$u_0$</th>
<th>$w_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.341</td>
<td>0.980</td>
<td>5.16</td>
<td>−4.817</td>
<td>9.056</td>
</tr>
<tr>
<td>0.085</td>
<td>1.230</td>
<td>1.062</td>
<td>5.15</td>
<td>−5.256</td>
<td>8.372</td>
</tr>
<tr>
<td>0.106</td>
<td>1.200</td>
<td>1.084</td>
<td>5.11</td>
<td>−5.372</td>
<td>8.204</td>
</tr>
<tr>
<td>0.135</td>
<td>1.150</td>
<td>1.117</td>
<td>5.12</td>
<td>−5.548</td>
<td>7.971</td>
</tr>
<tr>
<td>0.163</td>
<td>1.100</td>
<td>1.151</td>
<td>5.10</td>
<td>−5.724</td>
<td>7.752</td>
</tr>
<tr>
<td>0.200</td>
<td>1.028</td>
<td>1.200</td>
<td>5.11</td>
<td>−5.974</td>
<td>7.444</td>
</tr>
<tr>
<td>0.255</td>
<td>0.935</td>
<td>1.278</td>
<td>5.10</td>
<td>−6.343</td>
<td>7.042</td>
</tr>
<tr>
<td>0.291</td>
<td>1.000</td>
<td>1.305</td>
<td>5.13</td>
<td>−6.354</td>
<td>6.808</td>
</tr>
<tr>
<td>0.319</td>
<td>1.100</td>
<td>1.316</td>
<td>5.18</td>
<td>−6.263</td>
<td>6.641</td>
</tr>
<tr>
<td>0.362</td>
<td>1.200</td>
<td>1.433</td>
<td>5.18</td>
<td>−6.202</td>
<td>6.384</td>
</tr>
<tr>
<td>0.410</td>
<td>1.300</td>
<td>1.375</td>
<td>5.19</td>
<td>−6.118</td>
<td>6.115</td>
</tr>
<tr>
<td>0.494</td>
<td>1.395</td>
<td>1.439</td>
<td>5.21</td>
<td>−5.953</td>
<td>5.691</td>
</tr>
</tbody>
</table>

Here $\gamma_0$ is the density-scaling exponent at $(\rho_0, T_0)$ computed from equilibrium, constant-density canonical-ensemble fluctuations via $\gamma_0 = \langle \Delta U \Delta W \rangle / \langle \Delta U \rangle^2$, in which $U$ is the potential energy and $W$ is the virial [8]. At liquid density 1.2, the predictions based on Eq. (1) are shown as triangles in Fig. 4.

If one wishes to estimate from the $p = 10.19$ results the melting temperature at other pressures, the following procedure is employed. Along a LJ isomorph, the pressure varies as $p = k_B T + (2w_0 - 4u_0)(\rho/\rho_0)^4 - (w_0 - 4u_0) \times (\rho/\rho_0)^2$, in which $w_0$ and $u_0$ are the virial and potential energy per particle at the reference state point $(\rho_0, T_0)$ [46]. Equation (1) is inserted into this expression, resulting in $p(\rho)/\rho = A(\rho/\rho_0)^4 - B(\rho/\rho_0)^2$, in which $A = k_BT_0(\gamma_0/2 - 1) + 2w_0 - 4u_0$ and $B = k_BT_0(\gamma_0/2 - 2) + w_0 - 4u_0$. This relation is inverted numerically and the melting temperature is estimated by inserting $\rho(\rho)$ into Eq. (1). The parameters used in the predictions are given in Table II.

The estimated melting temperature at $p = 0$ and $p = 30$ are shown in Fig. 4 as open squares and diamonds, respectively. These compare reasonably well to the actual melting temperatures (crosses). At the standard 80/20 composition, the zero-pressure melting temperature is estimated to be 0.547(8). The actual melting temperature is 0.525(4), which is 4% below the estimate. The largest deviation from the isomorph-theory estimated melting temperatures are found for the CsCl structure. In this case, there is a four times larger difference between the liquid and crystal density-scaling exponents than for the A particle fcc crystal, implying that the melting line is less accurately represented as an isomorph [39]. We note that for single-component systems, a more accurate melting-line theory exists based on a first-order Taylor expansion from the approximate melting isomorph [39].

By fitting relaxation times for the standard 80/20 KA system to the frustration-limited-domain theory of the glass transition [47], Coslovich and Pastore determined the “onset temperature” below which the non-Arrhenius temperature dependence of the relaxation time initiates [45]. The inset of Fig. 4 compares their data to the melting temperature at different pressures. There is good agreement, which tentatively confirms physical pictures of Sastry et al. [48,49] and Yanagishima et al. [50]. Though the identity of onset and melting temperatures may not apply universally, this suggests that a class of liquids exists for which it applies.

The two main crystal structures have different formation dynamics. Figure 5 shows how the crystal order parameter fluctuates at solid-liquid equilibrium. The coexisting fcc-liquid situation is more noisy than the CsCl-liquid case. We interpret the former as reflecting a rough interface, whereas in the latter case the interface is flat, i.e., grows layer by layer [51]. This is consistent with general findings [52] since the melting entropy is larger in the latter case (Table I).

In summary, we have mapped out the phase diagram of KA-type binary LJ mixtures showing, in particular, that the standard 80/20 KA liquid at density 1.2 crystallizes at $T = 1.028(3)$. Our findings suggest that KA systems more stable against crystallization are those of 26%–30% B particles. This is consistent with recent results of Ingebrigtsen and co-workers, who have simulated the density 1.2 KA viscous liquid with 25% and 33.33% B particles for months on a GPU cluster without being able to crystallize these systems [53].

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