Freezing transition of two- and three-dimensional classical fluids using double Yukawa potential

Y Pathania & P K Ahluwalia

Physics Department, Himachal Pradesh University, Shimla 171 005

Received 26 July 2004; revised 26 May 2005; accepted 13 September 2005

Employing the techniques of molecular dynamics computer simulation, the onset of the freezing region of two and three-dimensional classical fluids interacting via Double Yukawa potential have been investigated. The radial distribution function \( g(r) \) for unique, qualitative and quantitative structural characteristics associated with the onset of freezing and for the validity of a universal freezing criterion has been studied. We have compared our results with those of Lennard Jones, when parameters occurring in Double Yukawa potential are chosen to fit the Lennard Jones potential. Later, the attractive and repulsive parameters of Double Yukawa potential have been varied to study the effect of attractive and repulsive part of the potential separately on the freezing criterion.

Keywords: Freezing transition, Classical fluids, Double Yukawa potential, Molecular dynamics computer simulation

IPC Code: G06N3/10, F15D

1 Introduction

The Lennard-Jones potential is undoubtedly the most widely used intermolecular potential for molecular simulation. It is a simple continuous potential that provides an adequate description of intermolecular interactions for many applications. It is a parameterised potential with the following form.

\[
u(r) = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right]
\]

where \( \varepsilon \) is an arbitrary energy scale, \( \sigma \) is the effective diameter and is the distance where the potential becomes zero. Although, it is treated as a pairwise potential, it is more accurately described as an ‘effective’ potential and as such it does not truly represent two-body interactions in a very sophisticated and accurate way\(^1\).

The nature of intermolecular interactions is discussed in greater detail by Stone\(^2\). Many effective potentials have been developed in literature\(^3\) and applied to atoms. Computer simulation permits the theoretical rigorous evaluation of the accuracy of such intermolecular potentials. However, very few potentials have been tested extensively using molecular simulation. Notable exceptions are the hard sphere, Lennard-Jones (LJ), and exp-6 potentials.

An alternative to Lennard-Jones potential is Double Yukawa (DY) potential. This potential can be fitted to any realistic potential to facilitate the calculations of real systems. For example, it is possible to fit DY potential with the LJ potential by choosing appropriate parameters, which provides accurate thermodynamic properties of classical fluids\(^4,6\). This potential has also been used to deal with long-range correlations\(^7\).

A freezing criterion based on the structural properties of three-dimensional (3D) dense fluids and two-dimensional (2D) dense fluids has been formulated and investigated for the particles interacting with LJ potential\(^8,9,10\). Wendt and Abraham\(^11\) defined an empirical parameter \( R \), which is the ratio of the first minimum, \( g_{\text{min}} \), to the first maximum, \( g_{\text{max}} \), of the radial distribution function (RDF) to characterize the onset of amorphous state. By employing Monte-Carlo methods to study the radial distribution function of LJ fluids, they stated that the onset of freezing occurs when \( R \) is approximately equal to 0.14 for 3D LJ fluids. For 2D LJ fluids, Ranganathan and Pathak\(^10\) found \( R \) to be 0.07 by employing the techniques of molecular dynamics simulation.

This paper focuses on the onset of glass transition in 2D and 3D DY fluids through an investigation of the salient features of the RDF, when parameters occurring in DY potential are chosen to fit the LJ potential, to compare our results with those of LJ fluids. The onset of glass transition has also been presented, when parameters occurring in DY potential i.e. \( \lambda_1 \) (repulsive part) and \( \lambda_2 \) (attractive part) are varied.
Double Yukawa Potential

The form of this potential is:

\[ u(r) = E\varepsilon(\sigma/r)[\exp(-\lambda_1 ((r/\sigma) - 1)) \]
\[ -\exp(-\lambda_2 ((r/\sigma) - 1))] \]  \hspace{1cm} \ldots (2)

where \( \sigma \) is the value of \( r \) at which \( u(r)=0 \). \( E \) is the depth of the potential and \( \varepsilon \) is an arbitrary energy scale. \( \lambda_1 \) and \( \lambda_2 \) control the decay range of the repulsive and attractive contributions to the potential. If suitably parameterised, DY potential provides a close fit to LJ potential as shown in Fig. 1.

The nature of the potentials for different \( \lambda_1 \) and \( \lambda_2 \) are shown in Figs 2 and 3. \( \lambda_1 \) affects considerably the repulsive and, to a lesser extent, the attractive parts of the potential. On the other hand, \( \lambda_2 \) affects mainly the attractive part of the potential. The impact of \( \lambda_2 \) on the range of attractive part can be clearly seen. The locations and depths of the minima of the attractive potentials, however, are strongly dependent on both \( \lambda_1 \) and \( \lambda_2 \). We can calculate the locations \( r_{\text{min}}^* \) of the minima from Eq. 2, giving:

\[ r_{\text{min}}^* = 1 + [1/(\lambda_1 - \lambda_2)] \ln[(\lambda_1 r_{\text{min}}^* + 1)/(\lambda_2 r_{\text{min}}^* + 1)] \]  \hspace{1cm} \ldots (3)

For a given \( \lambda_2 \), \( r_{\text{min}}^* \) decreases whereas \( |u_{\text{min}}| \) increases with increasing \( \lambda_1 \). Similarly, \( r_{\text{min}}^* \) also decreases with increasing \( \lambda_2 \) but \( |u_{\text{min}}| \) decreases considerably as shown in Table 1. For LJ potential, Eq. (3) becomes:

\[ r_{\text{min}}^* = (2)^{1/6} \]  \hspace{1cm} \ldots (4)

3 Molecular-Dynamics Simulation

We have chosen to start our simulation with 1024 particles on a simple cubic lattice for three-dimensional (3D) fluids and on a square lattice for two-dimensional (2D) fluids. In both 2D and 3D fluids, MD calculations were performed for the two systems each interacting with LJ and DY potentials respectively. Total momentum was conserved via shifting all velocities. We scaled the resulting velocities to adjust the mean kinetic energy to the desired value and thus adjusted the instantaneous temperature to match the desired temperature. Newton's equations of motion were integrated using...
Verlet’s algorithm. The potential was truncated at approximately half the box length and then shifted. The periodic boundary conditions were imposed in the usual fashion. With the periodic boundary conditions, we had eliminated the surfaces and created a quasi-infinite volume/area to represent the macroscopic system more closely.

After establishing equilibrium configurations, the MD simulations were carried out for 10,000 time steps with $\Delta t = 0.001$. In a MD simulation, successive time steps are correlated and do not contain significantly new information. So, position vectors $\mathbf{r}(t)$ and velocity vectors $\mathbf{v}(t)$ were stored at every 10th time step for subsequent analysis. The dimensionless units, that are being used in this paper are $u^* = u/\epsilon$, $r^* = r/\sigma$, $n^* = n\sigma^2$, for 2D system and $n^* = n\sigma^3$ for 3D system, $t^* = (\epsilon/m\sigma^2)^{1/2}$ and temperature $T^* = K_B T/\epsilon$. The state points chosen for 3D and 2D fluids were taken close to their respective freezing lines\(^7,12\).

### 4 Positional Correlation Function

The calculation of $g(r)$ involves the relation:

$$\langle n(r) \rangle = 2\pi r \Delta r n g(r)$$

…(5)

for 2D fluids, and for 3D fluids, the relation is

$$\langle n(r) \rangle = 4\pi r^2 \Delta r n g(r)$$

…(6)

where $\langle n(r) \rangle$ is the average number of particle in the annulus of radius $r$ and thickness $\Delta r$, centred at a given particle.

Figure 4 shows the structural information for the isotherm $T^* = 0.48$ (which corresponds to 57.5K in case of Argon) at different densities for 2D DY system as well as for 2D LJ system, when parameters occurring in DY potential are chosen to fit the LJ potential (i.e. when $E=2.0198$, $\lambda_1=14.735$ and $\lambda_2=2.6793$). The curves are in good agreement. The function $g(r)$ becomes firstly zero at short distances, where repulsive forces prevent overlapping of the molecules. When $r$ is close to the collision diameter $\sigma$, $g(r)$ increases rapidly to a maximum corresponding to the first peak. As $r$ increases gradually, $g(r)$ decreases showing that influence of the central atom is disappearing and there is no order at long distances. Concentrating on first two peaks of the RDF, we note that two smooth peaks exist at $n^*=0.76$ and as the density increases, the first peak becomes more pronounced in magnitude and narrower in width and the first minimum decreases in magnitude. The second peak starts to show signs of gradual flattening at $n^*=0.80$ and if density were further reduced, an eventual bimodal splitting would have been seen. The peaks are sharper than that in liquid but not as sharp as that of solid. This shows that the system is in solid-liquid phase equilibrium. However, we are interested in looking for the ‘signature’ that the glass transition region has been reached. The start of the flattening of
second peak in \( g(r) \) then likely indicates the freezing transition, which in our case is probably closer to 0.80. Calculating various values of \( R \) at different densities, we find that for the onset of freezing, \( R=0.07 \) for 2D DY system. Similarly, from Fig. 5, the onset of freezing for 3D DY system occurs at \( R=0.14 \). These results are in good agreement with those of 2D and 3D LJ system results respectively. When the parameters \( \lambda_1 \) and \( \lambda_2 \) of DY system are varied, there is slight change in the triple point. But the freezing criterion i.e. the value of \( R \) remains constant (0.07 for 2D system and 0.14 for 3D system) as shown in Figs 6-11.

We have also determined the diffusion coefficient from the slope of the mean square displacement at long times and it was found that diffusion coefficient \( D^*=D\tau/\sigma^2 \), where \( \tau=(m\sigma^2/\varepsilon)^{1/2} \), did not fall abruptly to zero as the transition was crossed. It was found to be still quite appreciable around the transition density as shown in Table 2. Similar behaviour was noted with the LJ potential\(^1\) and with the inverse-twelvth-power repulsive potential\(^1\) .

![Fig. 6—Radial distribution function along the isotherm \( T^*=0.42 \) at various densities for the 2D DY system, when parameters occurring in DY potential are chosen to be \( \lambda_1=14.735, \lambda_2=3.0, E=2.0198\varepsilon \). The curves are displaced for clarity](image1)

![Fig. 7—Radial distribution function along the isotherm \( T^*=0.43 \) at various densities for the 2D DY system, when parameters occurring in DY potential are chosen to be \( \lambda_1=12.0, \lambda_2=2.6793, E=2.0198\varepsilon \). The curves are displaced for clarity](image2)

---

Fig. 5—Radial distribution function along the isotherm \( T^*=0.72 \) at various densities indicated by solid curves for the 3D DY system, when parameters occurring in DY potential are chosen to fit the LJ potential represented by dots. The curves are displaced for clarity.
Fig. 8—Radial distribution function along the isotherm $T^*=0.40$ at various densities for the 2D DY system, when parameters occurring in DY potential are chosen to be $\lambda_1=6.0$, $\lambda_2=2.6793$, $E=2.0198\varepsilon$. The curves are displaced for clarity.

Fig. 9—Radial distribution function along the isotherm $T^*=0.70$ at various densities for the 3D DY system, when parameters occurring in DY potential are chosen to be $\lambda_1=12.0$, $\lambda_2=2.6793$, $E=2.0198\varepsilon$. The curves are displaced for clarity.

Fig. 10—Radial distribution function along the isotherm $T^*=0.70$ at various densities for the 3D DY system, when parameters occurring in DY potential are chosen to be $\lambda_1=14.735$, $\lambda_2=3.0$, $E=2.0198\varepsilon$. The curves are displaced for clarity.

Fig. 11—Radial distribution function along the isotherm $T^*=0.70$ at various densities for the 3D DY system, when parameters occurring in DY potential are chosen to be $\lambda_1=6.0$, $\lambda_2=2.6793$, $E=2.0198\varepsilon$. The curves are displaced for clarity.
Table 2—Diffusion coefficient calculated along the transition density for different parameters of Double Yukawa potential at their respective isotherms

<table>
<thead>
<tr>
<th>System</th>
<th>( n^* )</th>
<th>( D^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>At ( (\lambda_1, \lambda_2, E) = (14.735, 2.6793, 2.0198 \varepsilon) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D</td>
<td>0.92</td>
<td>0.019</td>
</tr>
<tr>
<td>2D</td>
<td>0.78</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>0.025</td>
</tr>
<tr>
<td>At ( (\lambda_1, \lambda_2, E) = (14.735, 3.0, 2.0198 \varepsilon) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D</td>
<td>0.90</td>
<td>0.022</td>
</tr>
<tr>
<td>2D</td>
<td>0.78</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>0.029</td>
</tr>
<tr>
<td>At ( (\lambda_1, \lambda_2, E) = (12.0, 2.6793, 2.0198 \varepsilon) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D</td>
<td>0.94</td>
<td>0.019</td>
</tr>
<tr>
<td>2D</td>
<td>0.78</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>0.027</td>
</tr>
<tr>
<td>At ( (\lambda_1, \lambda_2, E) = (6.0, 2.6793, 2.0198 \varepsilon) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D</td>
<td>1.76</td>
<td>0.099</td>
</tr>
<tr>
<td></td>
<td>1.82</td>
<td>0.003</td>
</tr>
<tr>
<td>2D</td>
<td>0.92</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>0.96</td>
<td>0.011</td>
</tr>
</tbody>
</table>

5 Conclusions

We have investigated behaviour of the RDF of 2D and 3D DY fluid when (1) The parameters in DY potential are chosen to fit the LJ potential; (2) The attractive and repulsive parameters of DY potential are varied.

Based on the analysis, it has been inferred that a ‘universal’ freezing criterion based on the value of \( R \) (0.07 for 2D and 0.14 for 3D) exists for 2D as well as for 3D DY systems. The first appearance of a shoulder in case of a 2D system and the simple flattening in case of 3D system shows that the glass transition region has been reached. Also the diffusion coefficient near the transition region does not fall abruptly to zero indicating that system is in solid-liquid phase equilibrium and has not reached solid phase.

References