Inverse melting and phase behaviour of core-softened attractive disks

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Outline

- Why this potential?
- Increase inverse melting
- Phase diagram
- More interesting stuff
Square shoulder-square well pair potential

\[ U(r)/\varepsilon = \begin{cases} 
0 & \text{if } r = 0 \\
-0.5 & \text{if } 0 < r < b \\
0 & \text{if } b \leq r < c \\
-1.0 & \text{if } c \leq r < \infty 
\end{cases} \]

\[ b = \sqrt{2} \]

\[ c = \sqrt{3} \]

Motivation for the potential: water

Average over relative orientations of two water molecules to obtain a radial potential. There are two characteristic distances in the result.

Square shoulder-square well

Square and low density triangular crystals have the same potential energy.

\[ b = \sqrt{2} \]
\[ c = \sqrt{3} \]
All transitions in the phase diagram appear to be first-order phase transitions.

Monte Carlo simulations:
- NPT
- Frenkel-Ladd Integration
- Gibbs-Duhem Integration
- Gibbs Ensemble (for L-G)

P-T Phase Diagram


(not previously reported)
P-T Phase Diagram

The L-S melting curve exhibits a maximum temperature, indicating that at higher pressure, the liquid is more dense than the solid.

Also it exhibits a maximum pressure, indicating that the inverse melting occurs in a small range of pressure.

Inverse melting is a rare phenomenon and confirming it for a simple model will allow for deeper exploration into the basic physics surrounding it.

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Increasing range of inverse melting

What changes can we make to the potential in order to increase the pressure range for which inverse melting can be obtained?
This technique allows one to obtain a phase diagram of a new model \( u_2 \) starting from the known phase diagram (for \( u_1 \)).

\[
u = (1 - \lambda) u_1 + \lambda u_2
\]

At \( \lambda = 0 \) we recover the original potential and at \( \lambda = 1 \) we transform the potential to the new one.

Technique tells you e.g. how the coexistence pressure will shift if you change the potential and keep temperature constant (or vice versa).

Parameters to be changed are \( e \), \( b \) and \( c \).
Inverse melting becomes more obvious

Pick $b=1.46$ and confirm transition.

Carry out umbrella sampling Monte Carlo to calculate the free energy as a function of density at constant $T$ and $P$, which are taken to be on the coexistence line.

Confirming transition

Carry out umbrella sampling Monte Carlo to determine the free energy as a function of density at constant T and P, which are taken to be on the coexistence line.

Hexatic Phase: Colloidal Experiment

Frank’s constant in the hexatic phase

P. Keim,1 G. Maret,2 and H. H. von Grünberg1

\[ G_6(r) = \langle \psi(\vec{r}) \psi^*(\vec{0}) \rangle \]

\[ \psi(\vec{r}) = \psi_k = \frac{1}{N_j} \sum_j e^{i6\theta_{jk}}. \]

KTNHY Theory
Kosterlitz, Thouless, Halperin, Nelson and Young

\[ \lim_{r \to \infty} G_6(r) \neq 0 \]
\[ G_6(r) \sim r^{-\eta_6} \quad \text{crystal: long-range order,} \]
\[ G_6(r) \sim e^{-r/\xi_6} \quad \text{hexatic: quasi-long-range order,} \quad \eta_6 < 1/4 \]
\[ G_6(r) \sim e^{-r/\xi_6} \quad \text{isotropic: short-range order.} \]
Checking for hexatic phase, \( N=65536, P=5.6 \)

Direct Confirming with MD

Start with S crystal at P=5.6, T=0.30 and see what happens.
What about the rest of the phase diagram?

\[ b = \sqrt{2} \quad 1.414 \]

\[ b = 1.46 \]

HDT melting line would need to curve a lot.
Add HDT-L Coexistence Curve

HDT-S-L triple point disappears

HDT-L line inflects (?)
Add HDT-L Coexistence Curve

Is this a channel of liquid super stability with no crystals in the way?
Let’s take a look at the liquid here.
Liquid at
It has various local environments
Close-packed
Squares
And pentagons
(surrounded by triangles and little squares or rhombuses)
And pentagons
(surrounded by triangles and little squares or rhombuses)

O-phase (Outphase? ... still looking for a name)
And pentagons
(surrounded by triangles and little squares or rhombuses)

I-phase
(Inline phase? ... still looking for a name)
New Phases

I crystal

O crystal

O crystal
A look at metastability

I-phase not stable above $T=0.4$
HDT-S-L triple point disappears
HDT-L line inflects (?!)
This is a very strange point, as we shall later see.
HDT-L Coexistence Curve

\[ P^2 / k_B T \]

\[ \Delta G / k_B T \]

\[ T = 0.60 \]
\[ T = 0.70 \]
\[ T = 0.80 \]
\[ T = 0.90 \]
\[ T = 1.00 \]
HDT-L Coexistence Curve

$T=0.5$

$P_s^2/e = b = 1.46$

$\Delta G/k_B$ vs $\rho/\sigma^2$

Regular NPT simulation

Umbrella sampling

HDT-L Coexistence Curve

MC steps per particle

HDT

L

S

T=0.5

L+HDT
Below this temperature, we can use Gibbs-Duhem integration.

\( T=0.46 \)

(umbrella sampling)
Conclusions

• Calculated phase diagram for a tricky potential developed to produce liquid anomalies.
• Found inverse melting – weak effect.
• Tweaked potential (made shoulder wider) to amplify inverse Melting.
• Really does look like first-order melting.
• New crystal phases thwart liquid’s stability down to $T=0$.
• A funny point, where free energy barrier between HDT and L vanishes, appears at $T=0.5$. 
Thank you for your attention