Inverse melting and phase behaviour of core-softened attractive disks

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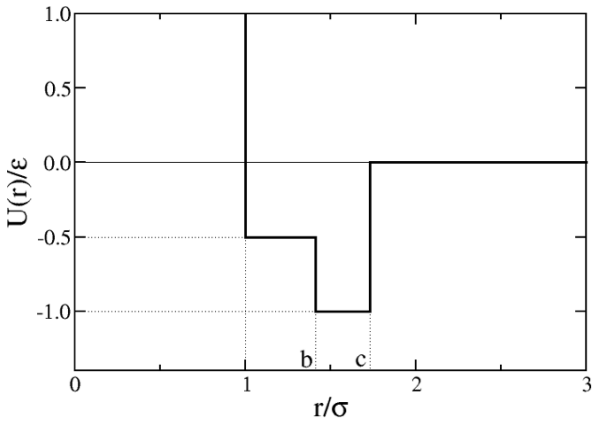
CAP Congress

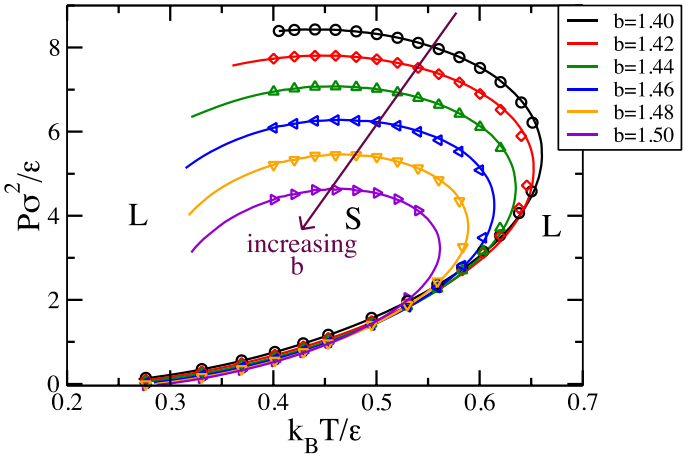
June 18, 2014

Outline

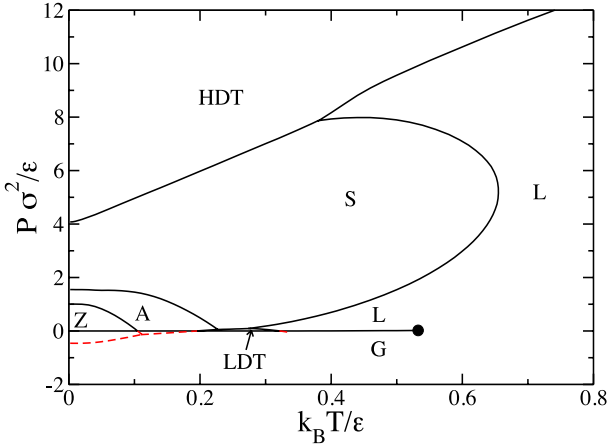
- Why this potential?



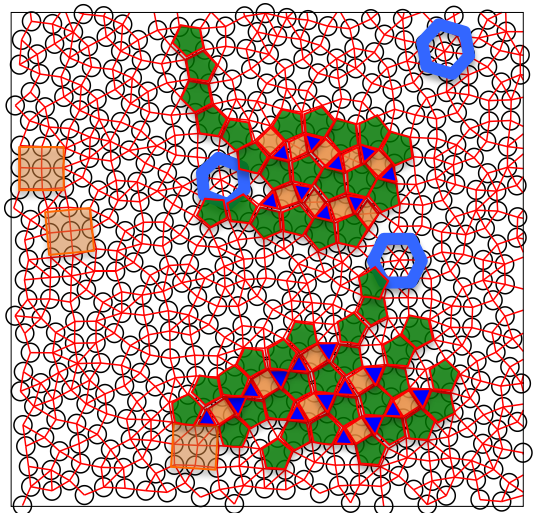
- Increase inverse melting



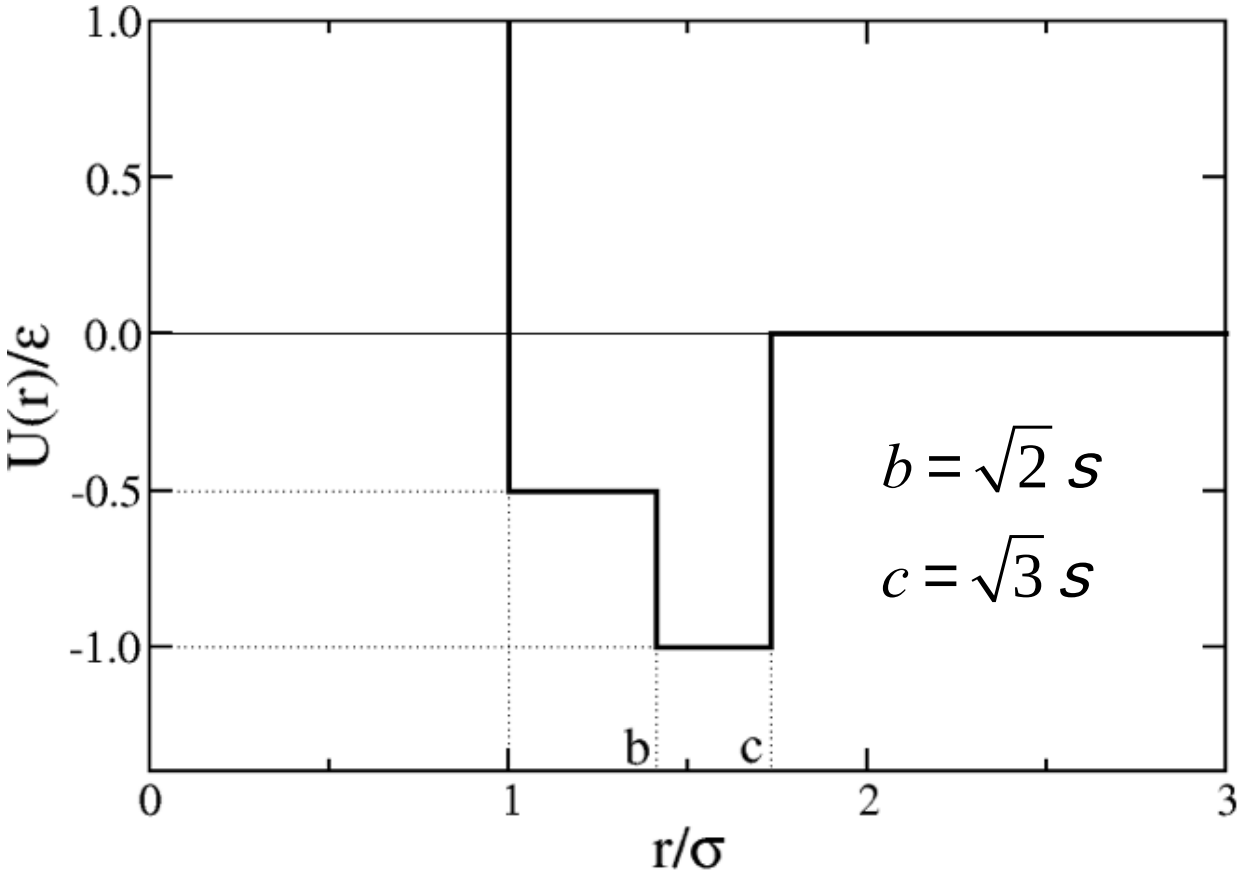
- Phase diagram



- More interesting stuff

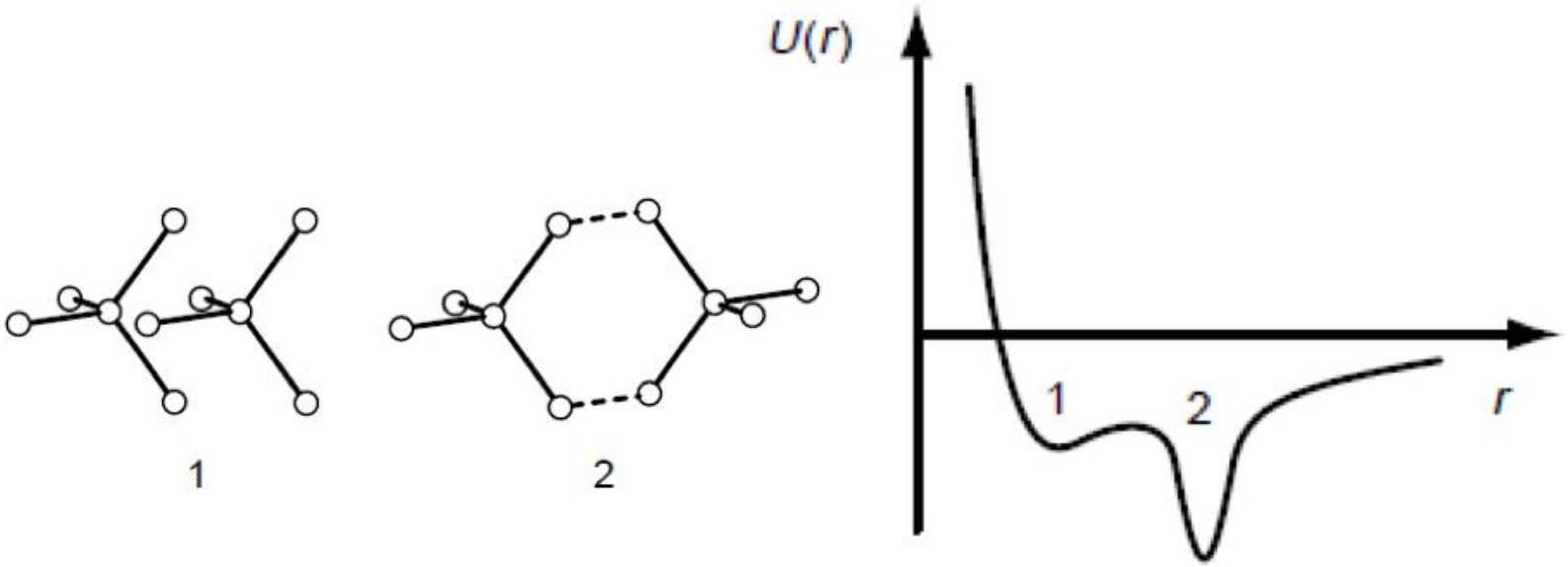


Square shoulder-square well pair potential



A. Scala, M. R. Sadr-Lahijany, N. Giovambattista, S. V. Buldyrev, H. E. Stanley, Phys. Rev. E **63**, 041202 (2001).

Motivation for the potential: water

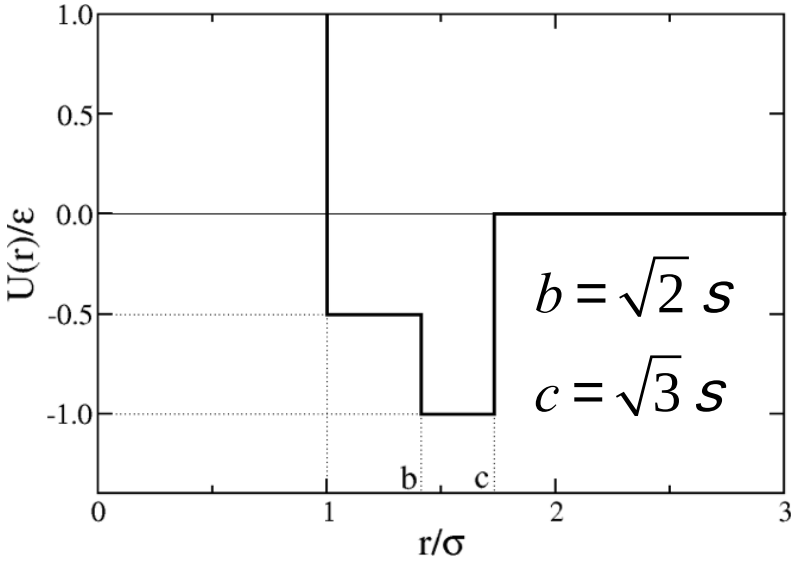


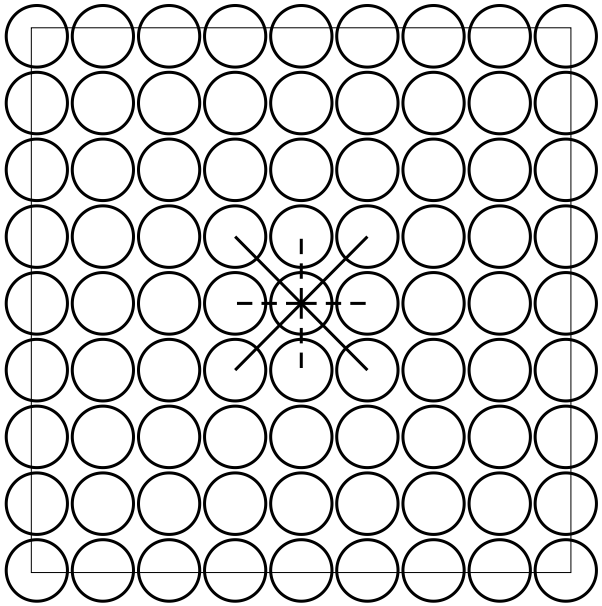
Average over relative orientations of two water molecules to obtain a radial potential. There are two characteristic distances in the result.

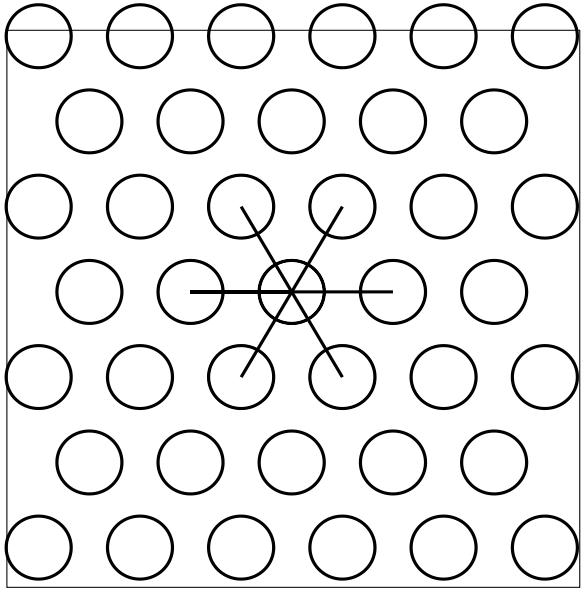
O. Mashima and H.E. Stanley, Nature 396, 329 (1998)

Square shoulder-square well

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



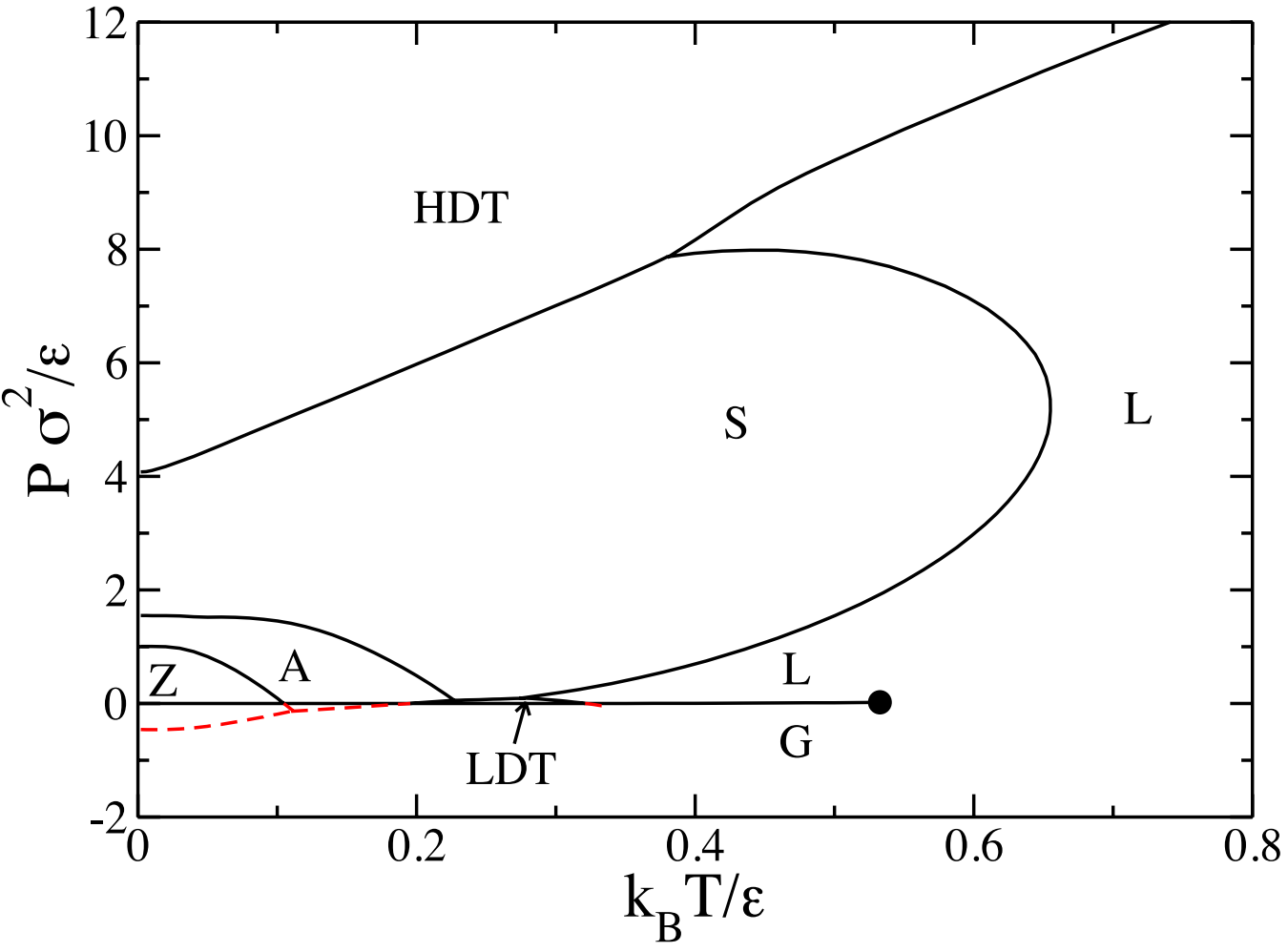




Bond with energy - e

Bond with energy - $e/2$

P-T Phase Diagram (2D system)

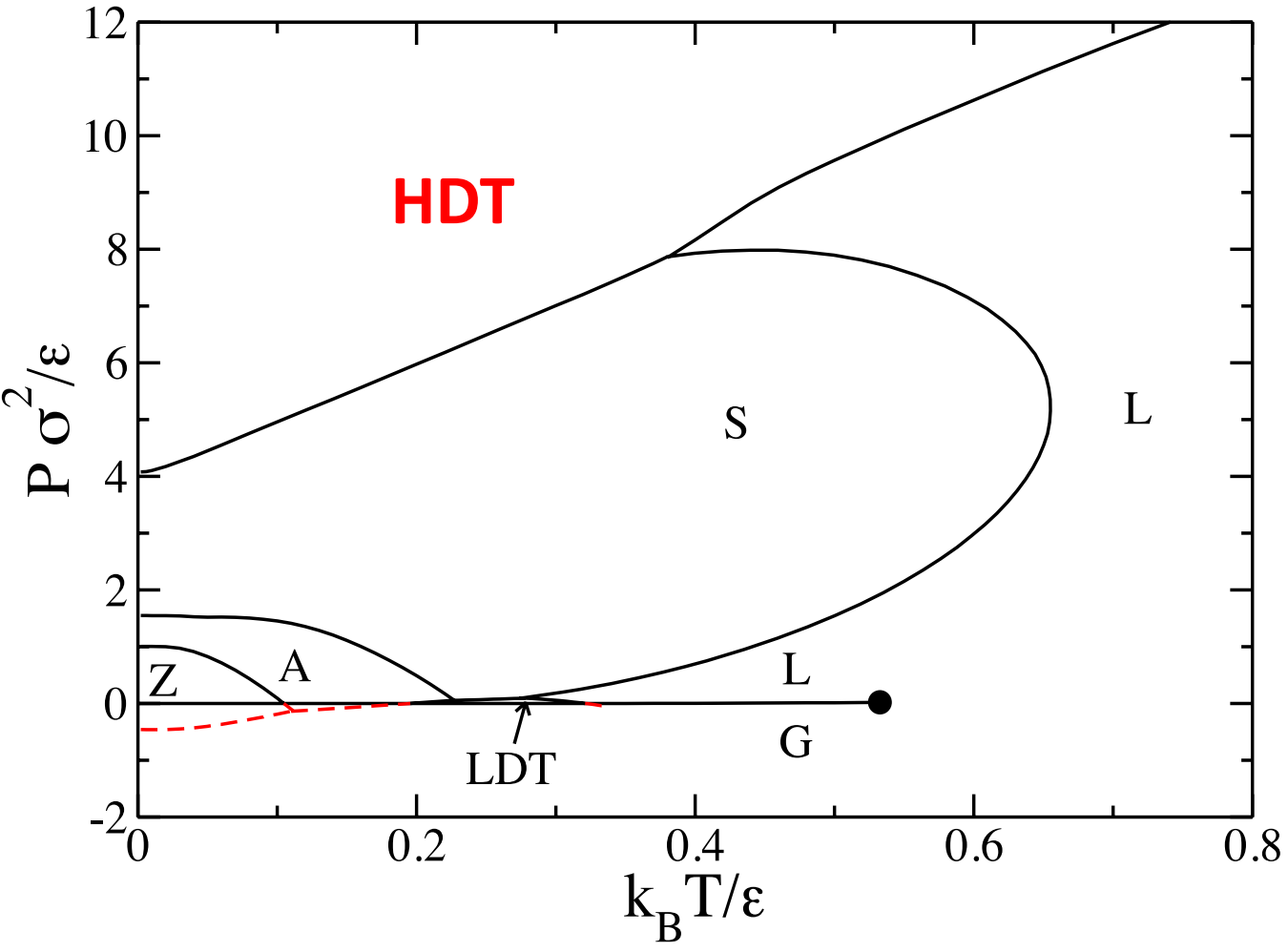


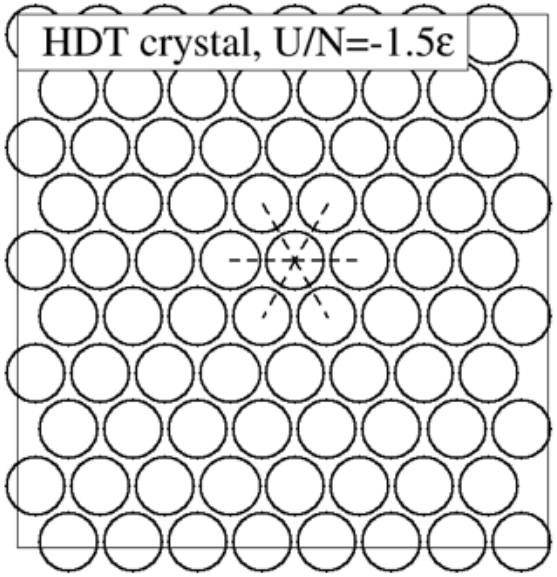
Monte Carlo simulations:
-NPT
-Frenkel-Ladd Integration
-Gibbs-Duhem Integration
-Gibbs Ensemble (for L-G)

All transitions in the phase diagram appear to be first-order phase transitions.

A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 137, 034507 (2012).

P-T Phase Diagram





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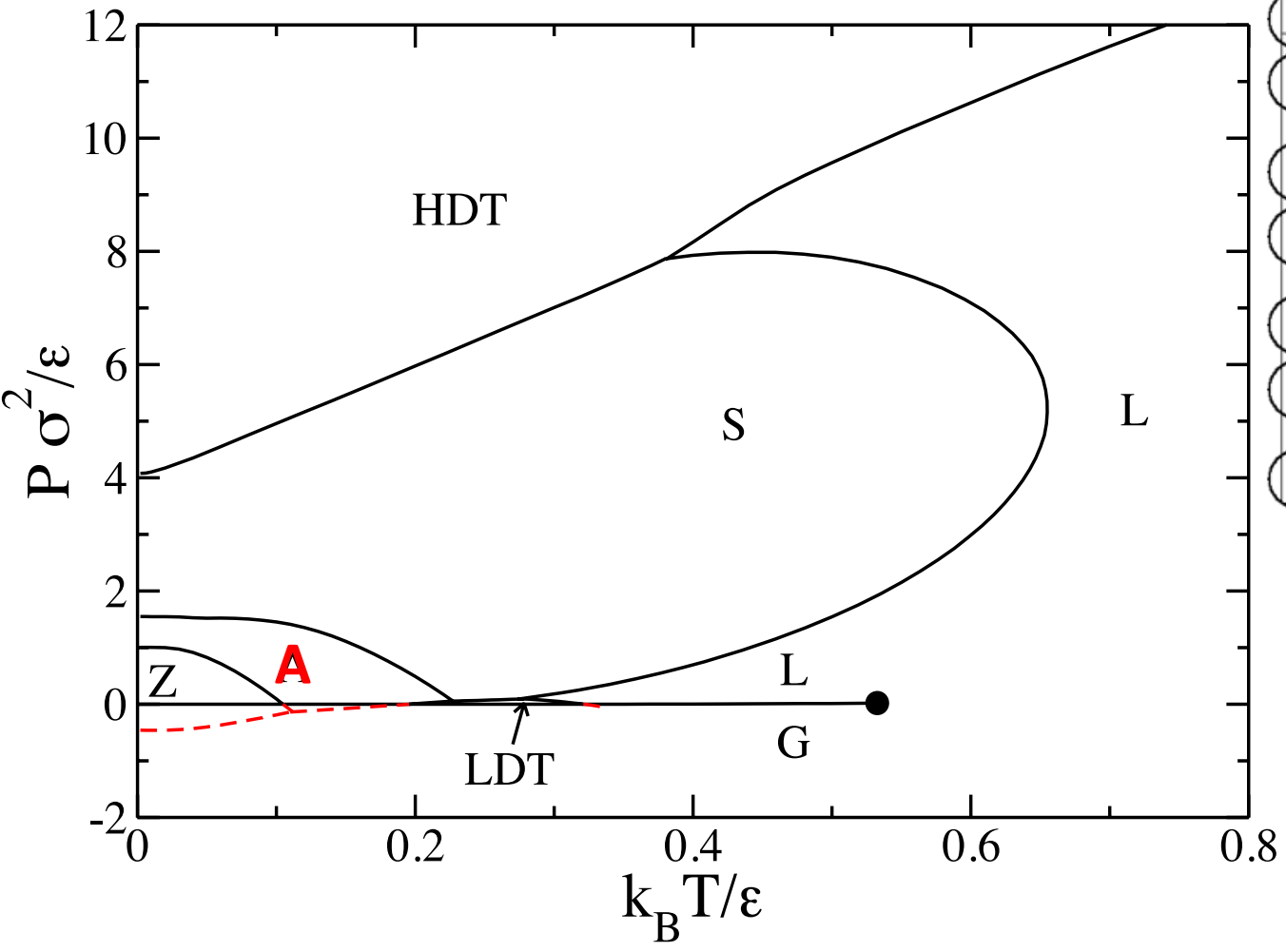

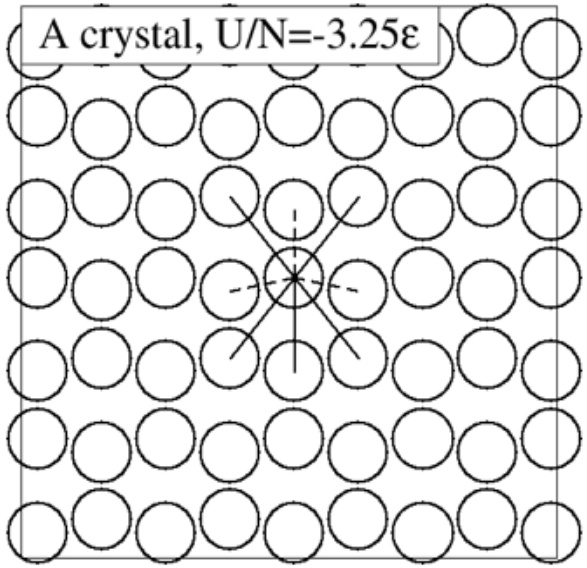

(not previously reported)

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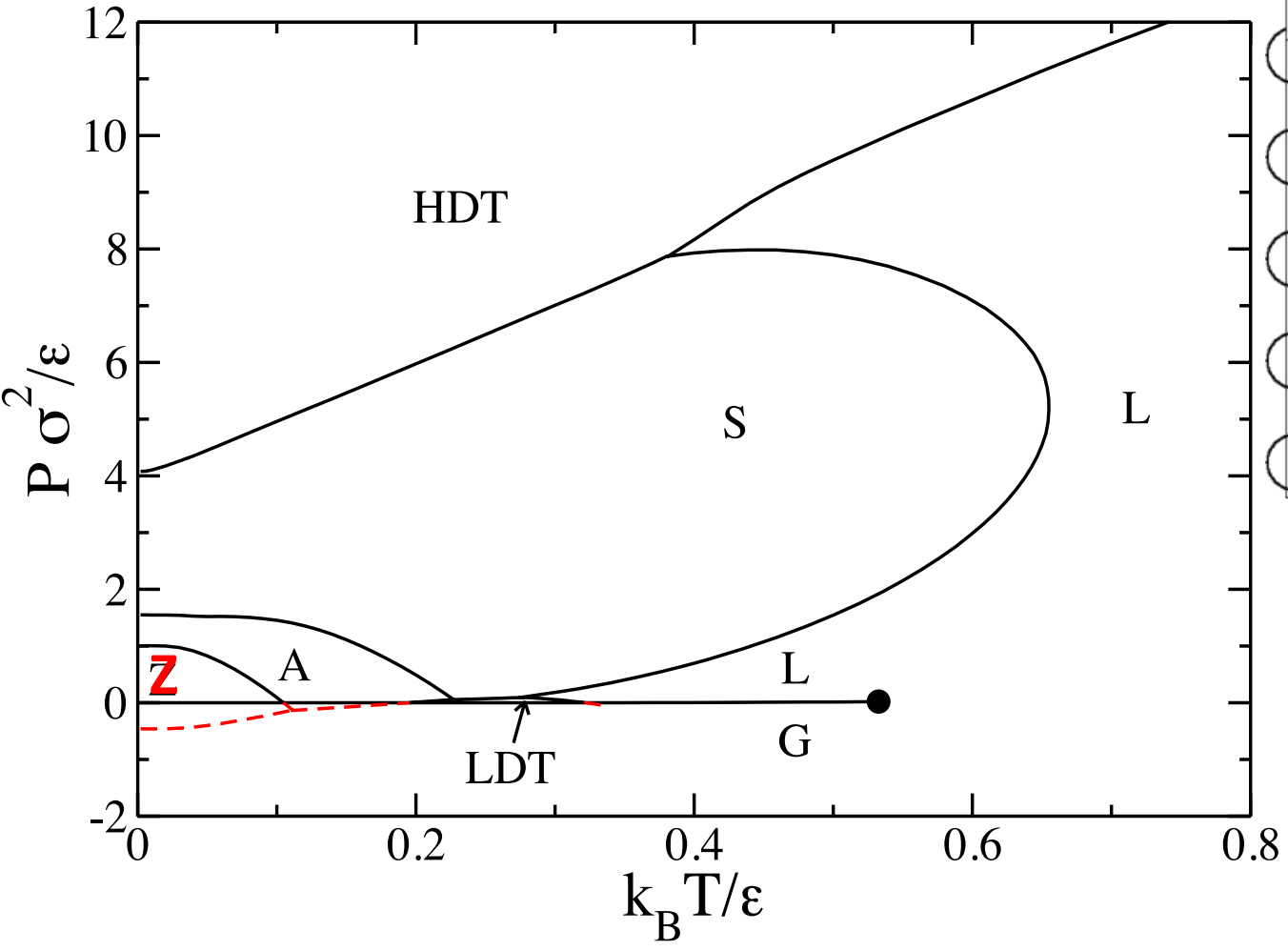

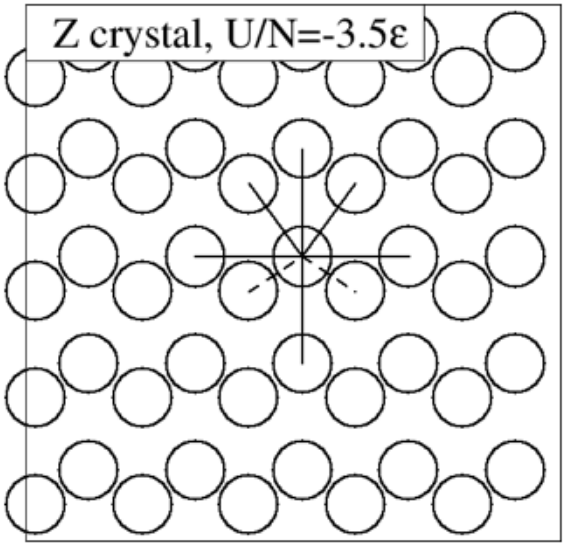

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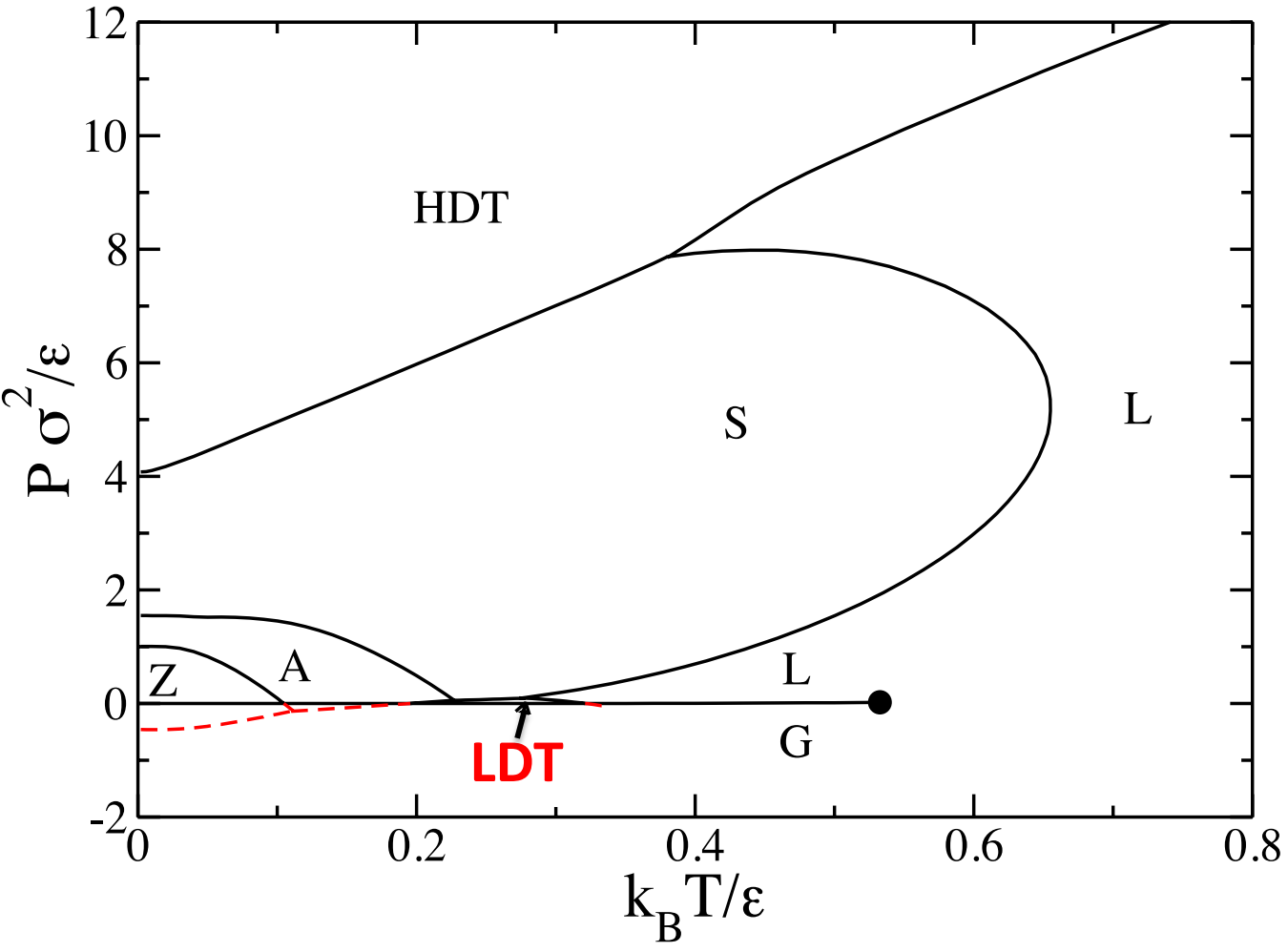

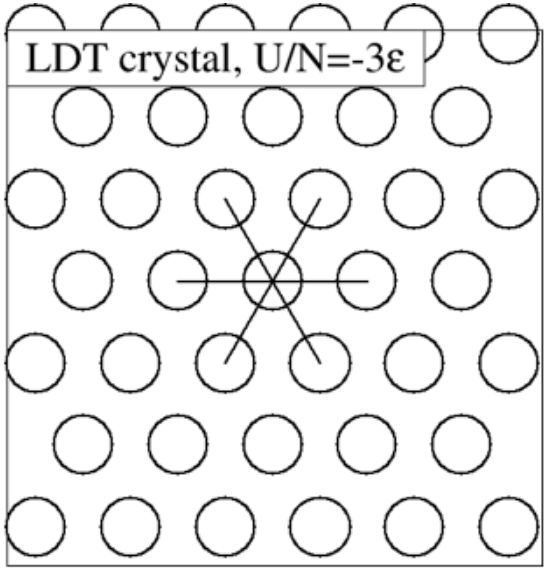

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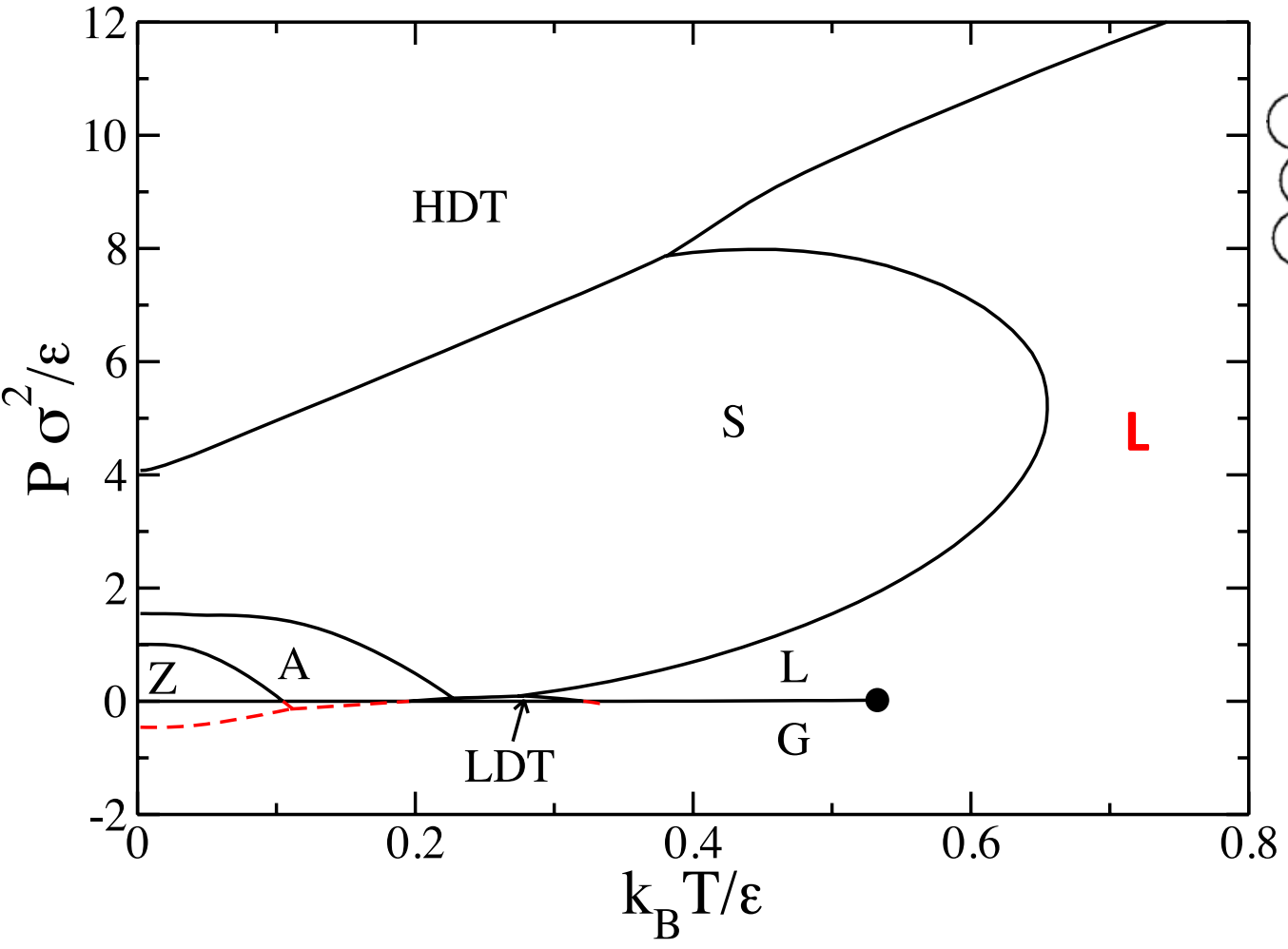

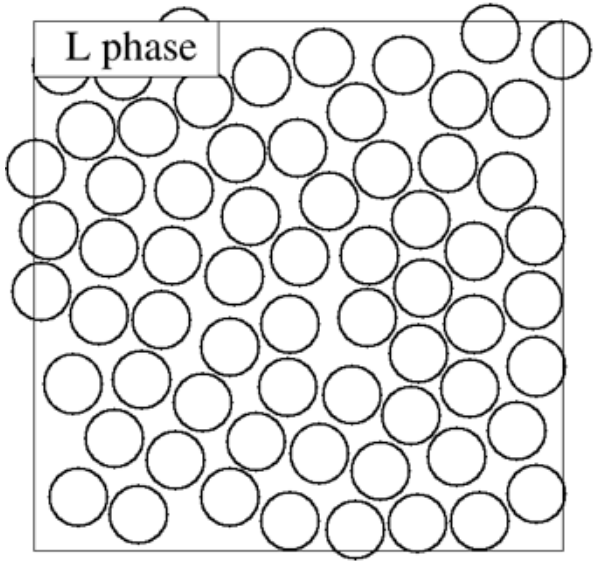

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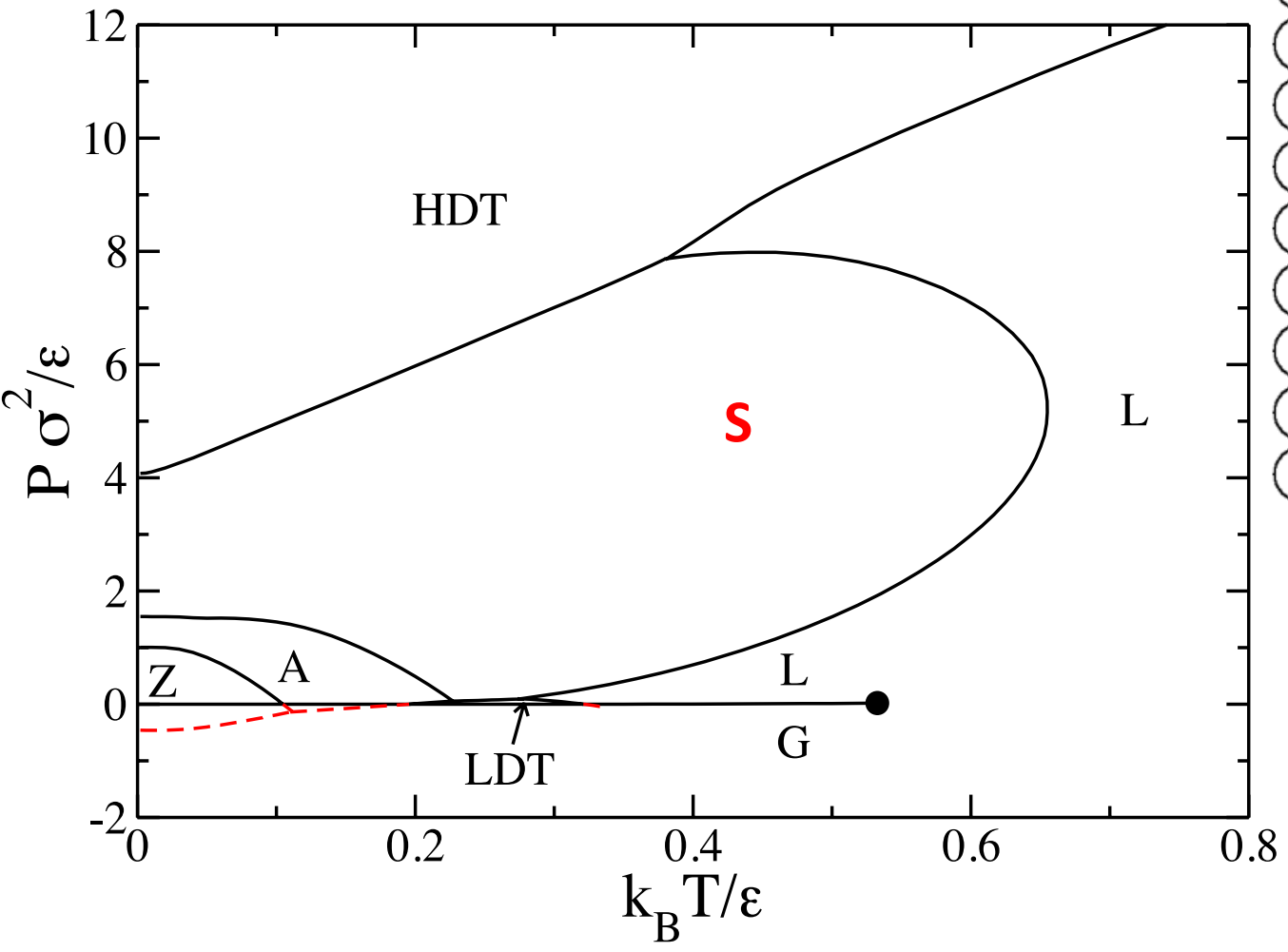
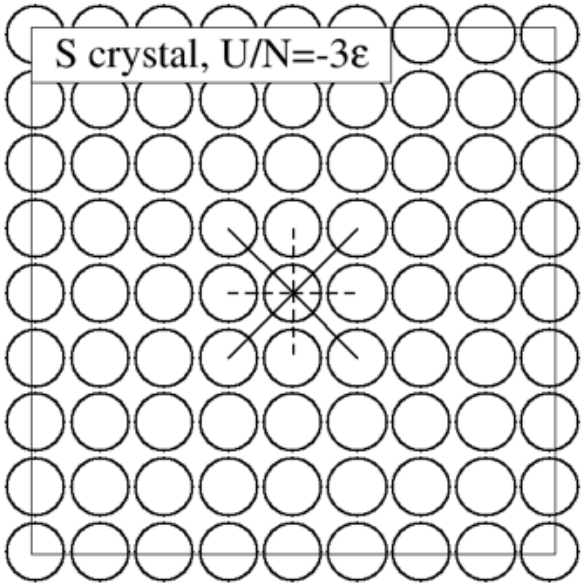
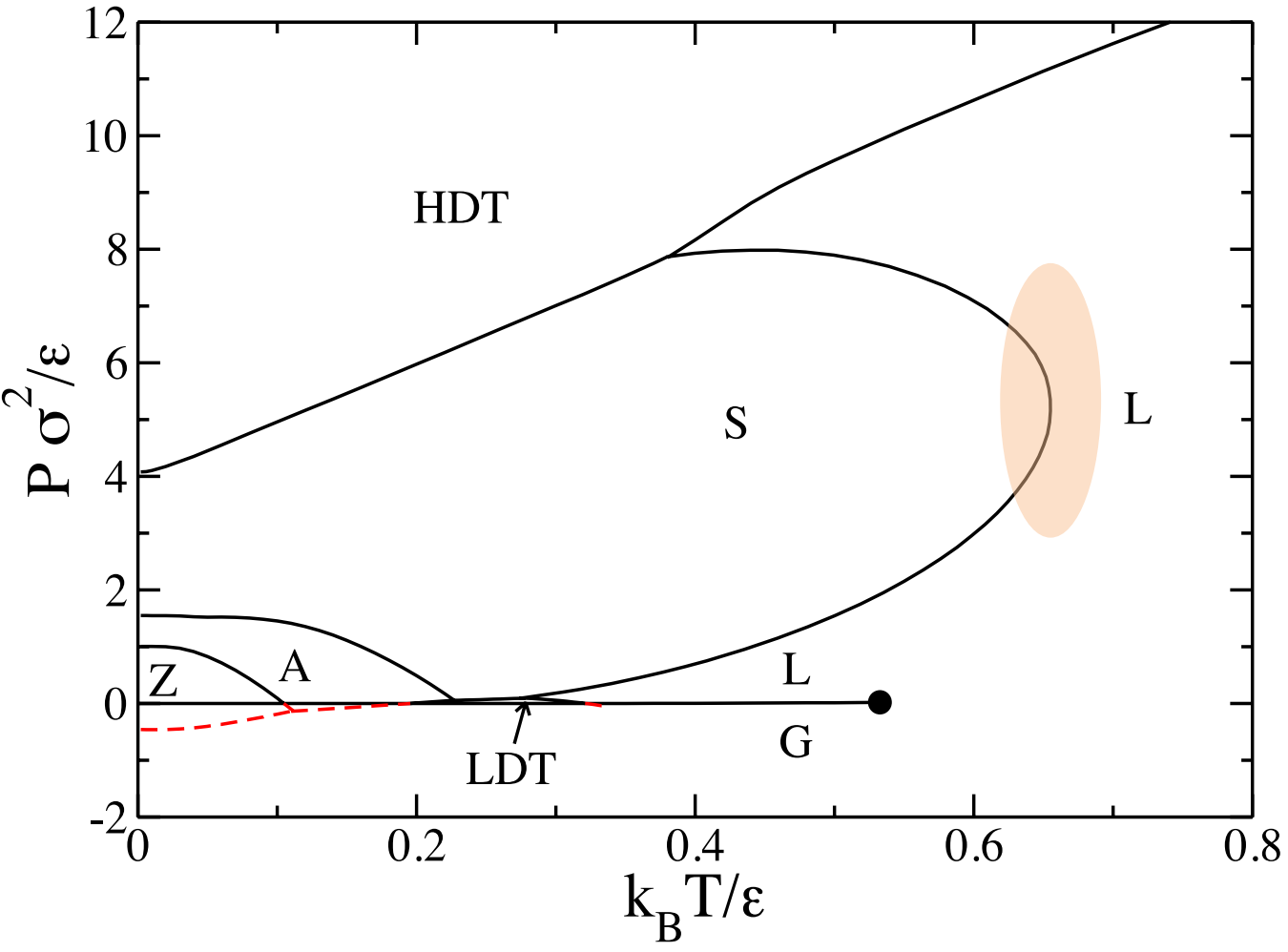


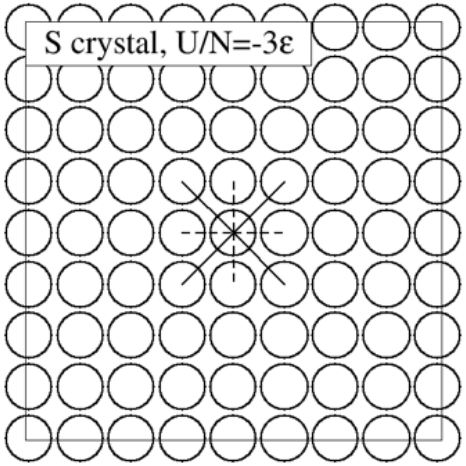


A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 137, 034507 (2012).

Maximum melting temperature



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



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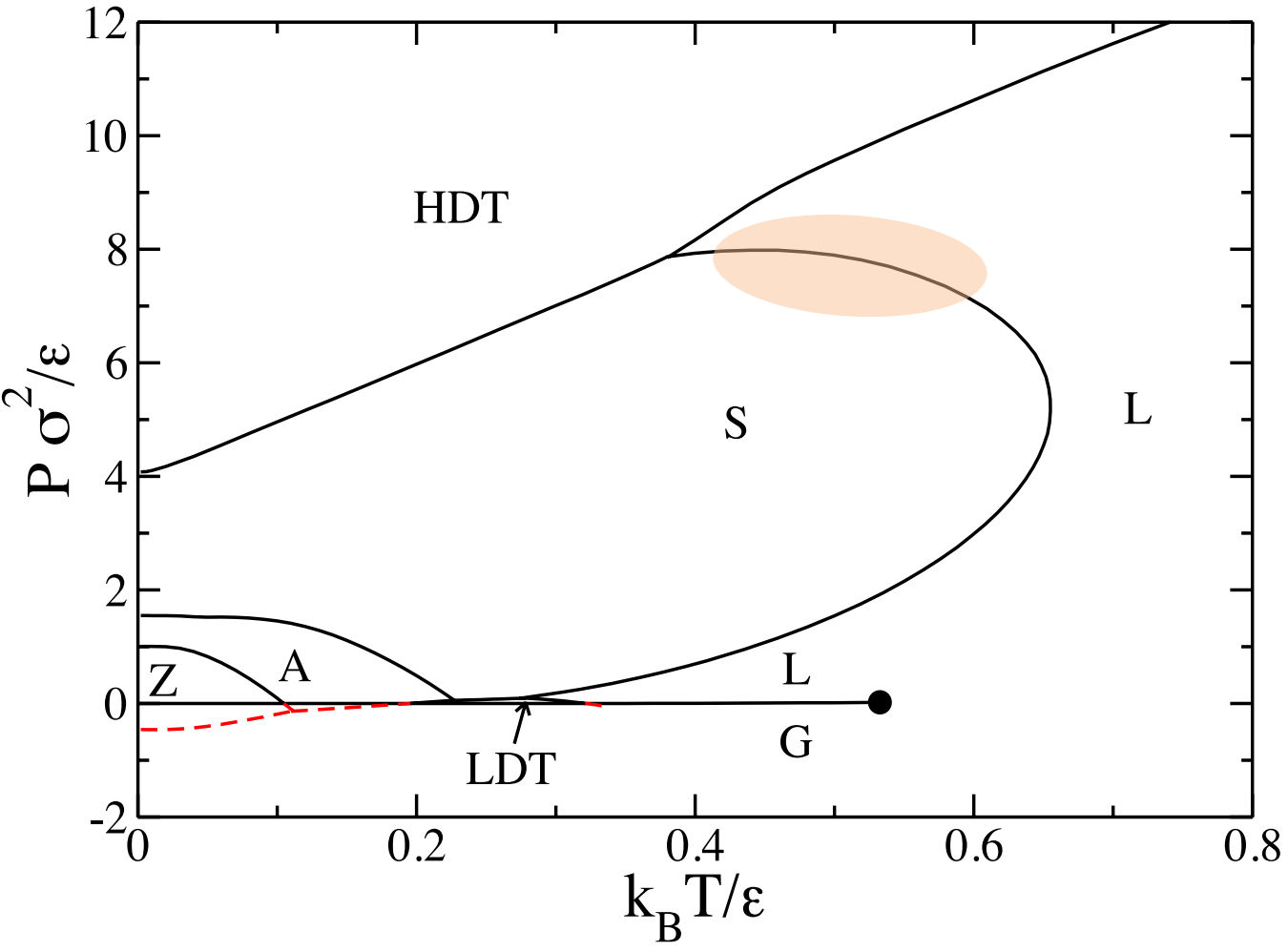
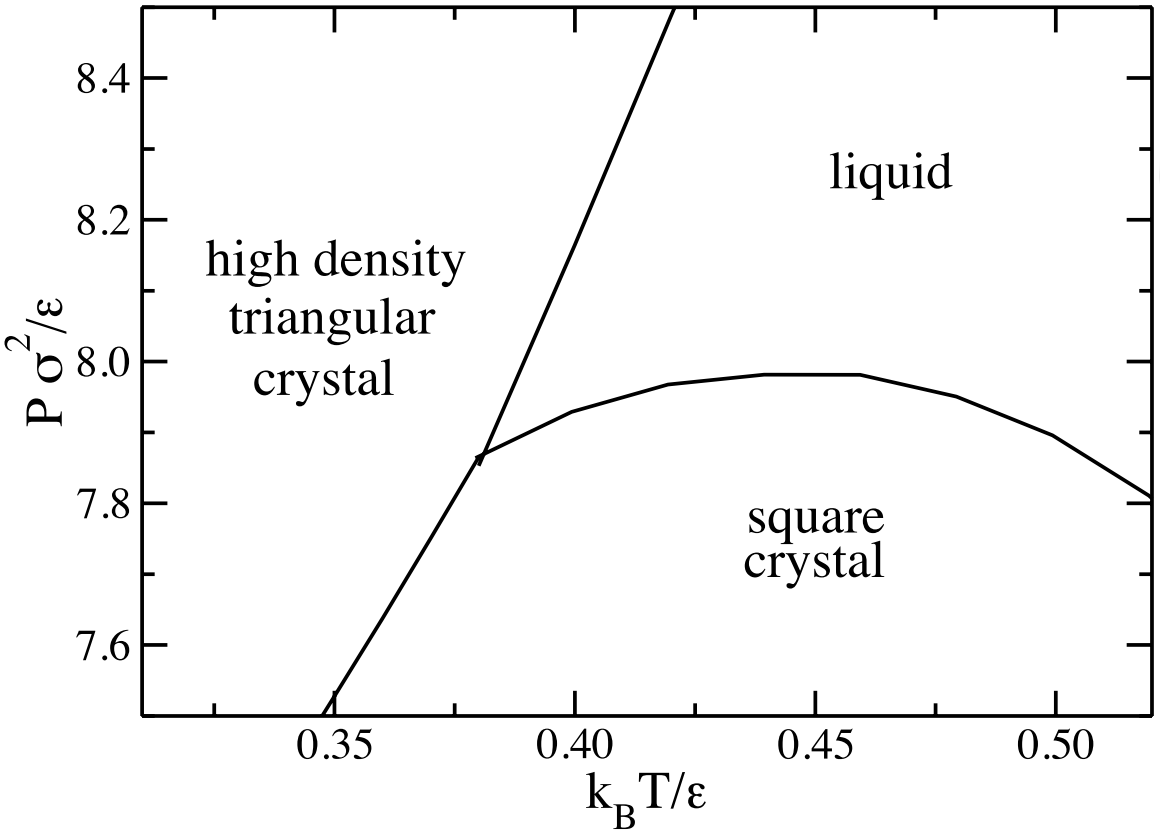
Maximum melting pressure

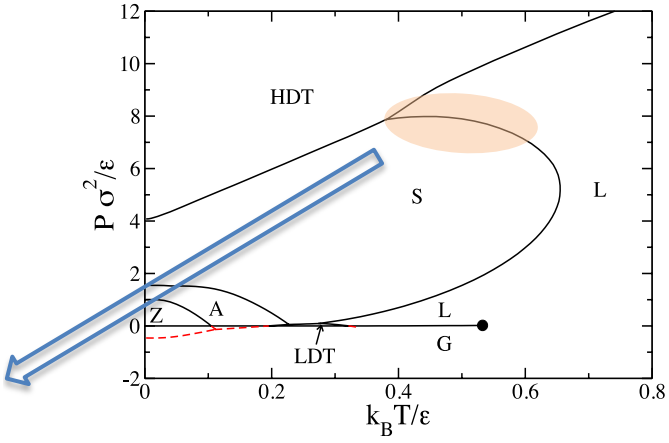


Also it exhibits a maximum pressure, indicating that the inverse melting occurs in a small range of pressure

A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 137, 034507 (2012).

Inverse melting

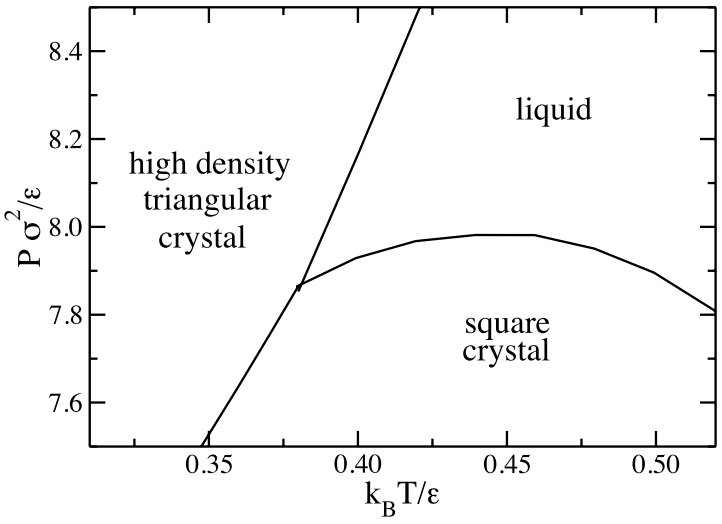




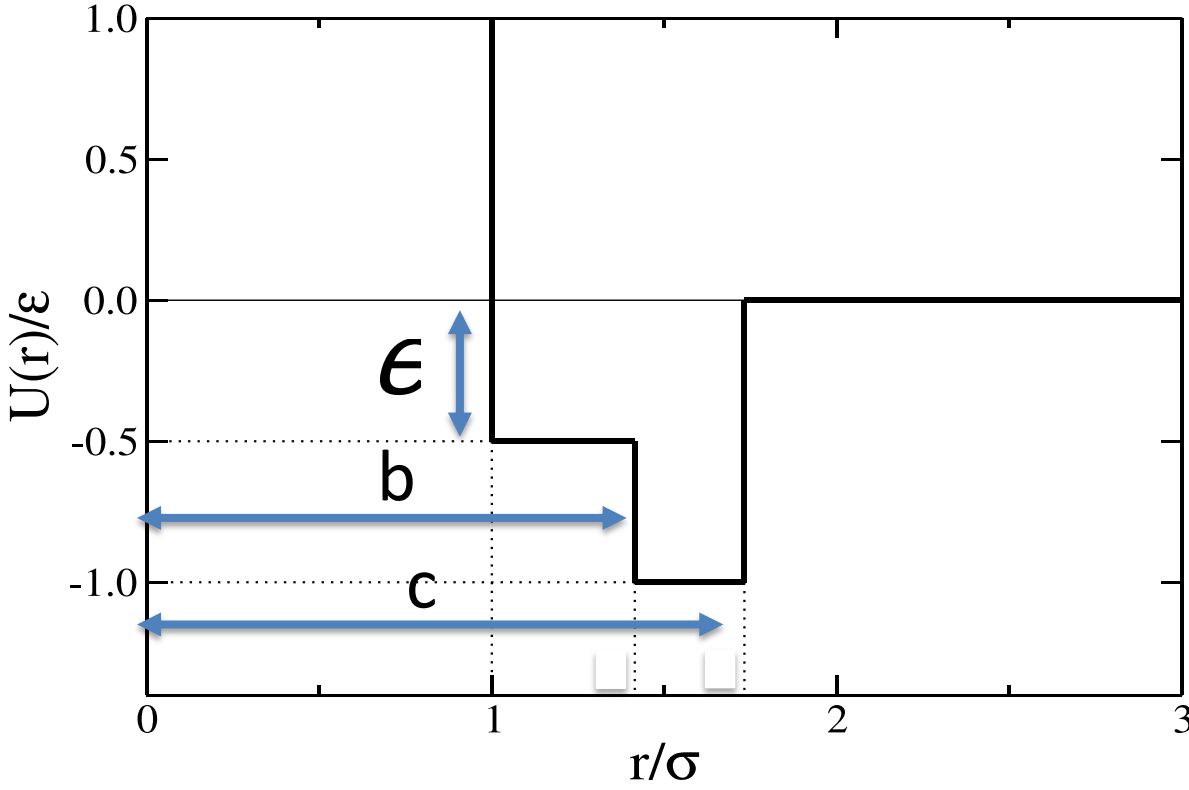
Inverse melting is a rare phenomenon and confirming it for a simple model will allow for deeper exploration into the basic physics surrounding it.

A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 137, 034507 (2012).

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?

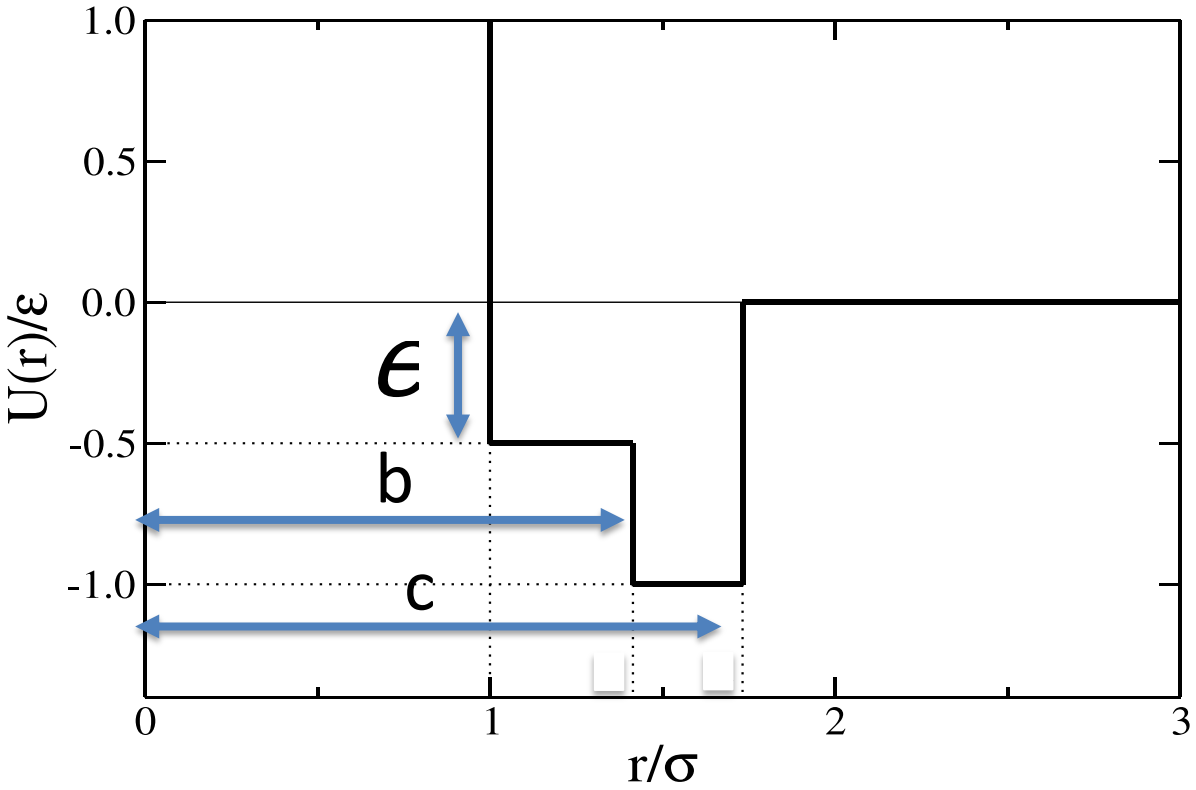


Hamiltonian Gibbs-Duhem Integration

- This technique allows one to obtain a phase diagram of a new model u_2 starting from the known phase diagram (for u_1).

$$u=(1-\lambda)u_1+\lambda u_2$$

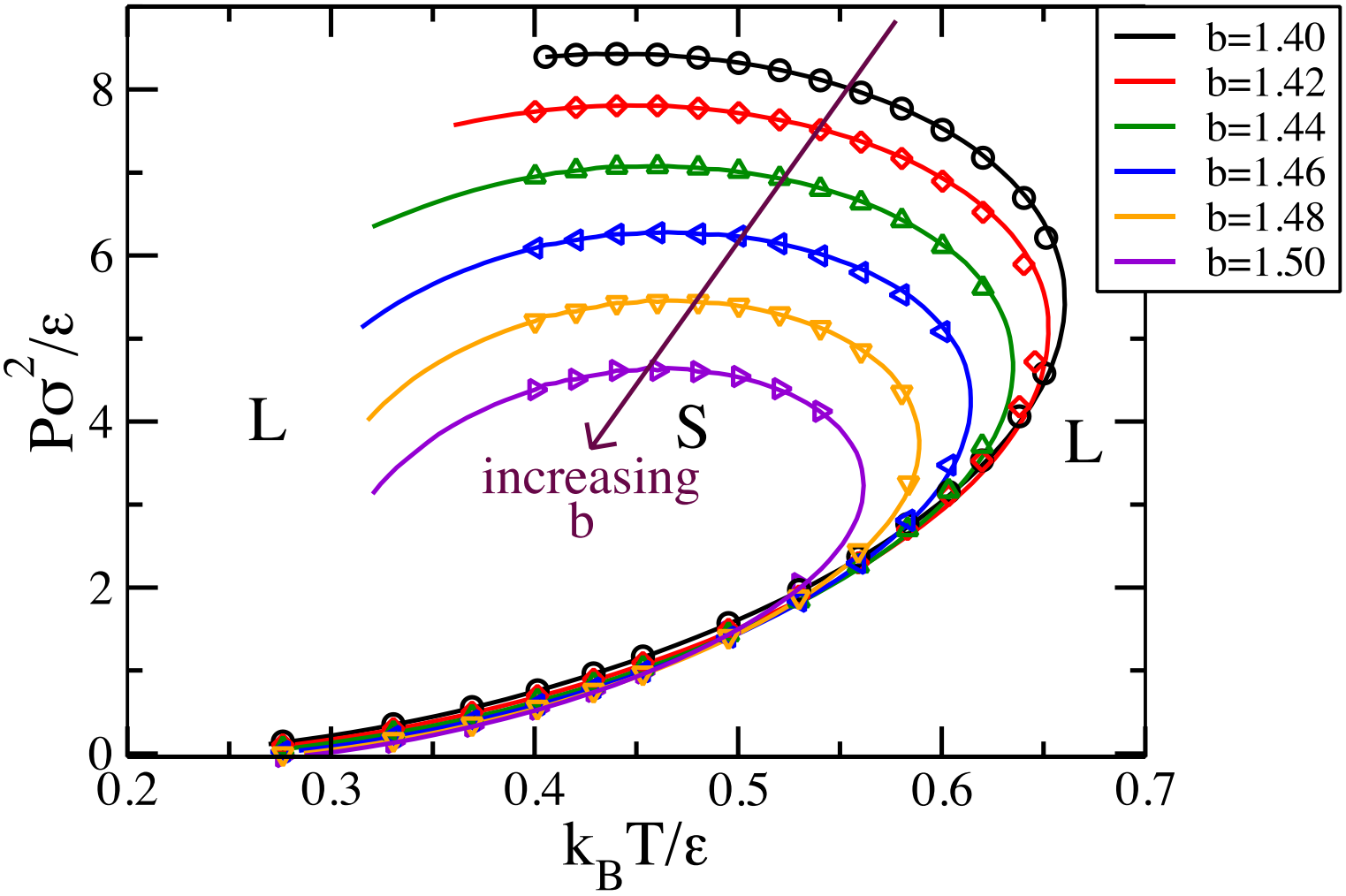
- At λ=0 we recover the original potential and at λ=1 we transform the potential to the new one.



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

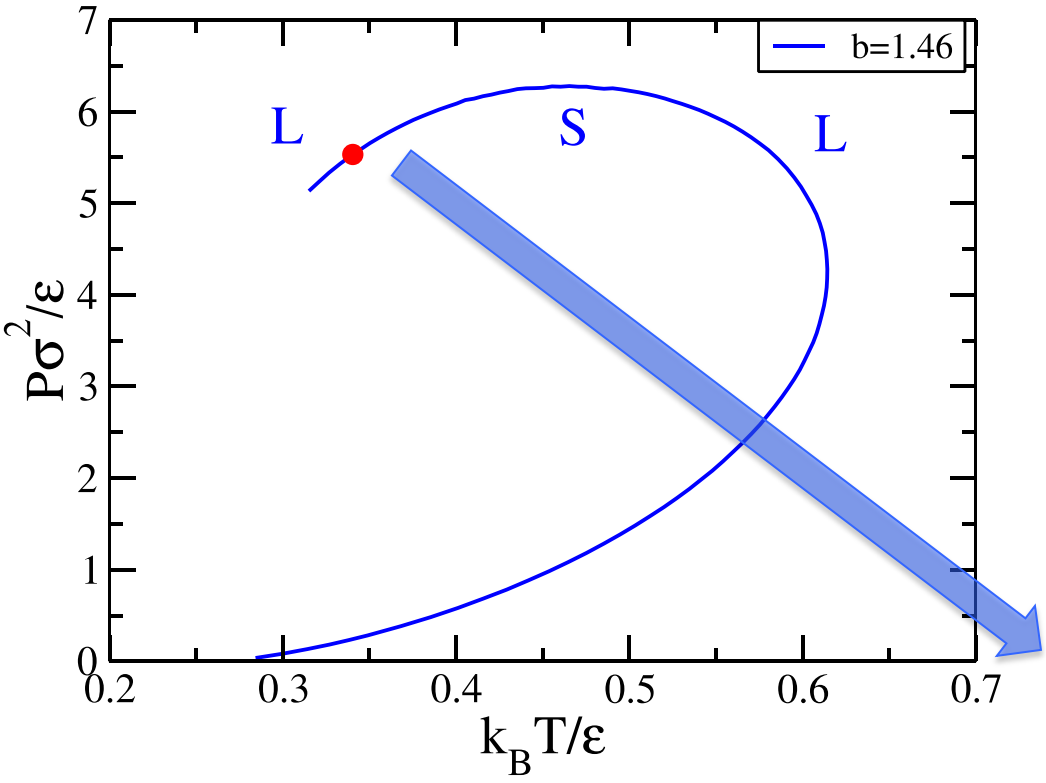
Parameters to be changed are ϵ, b and c.

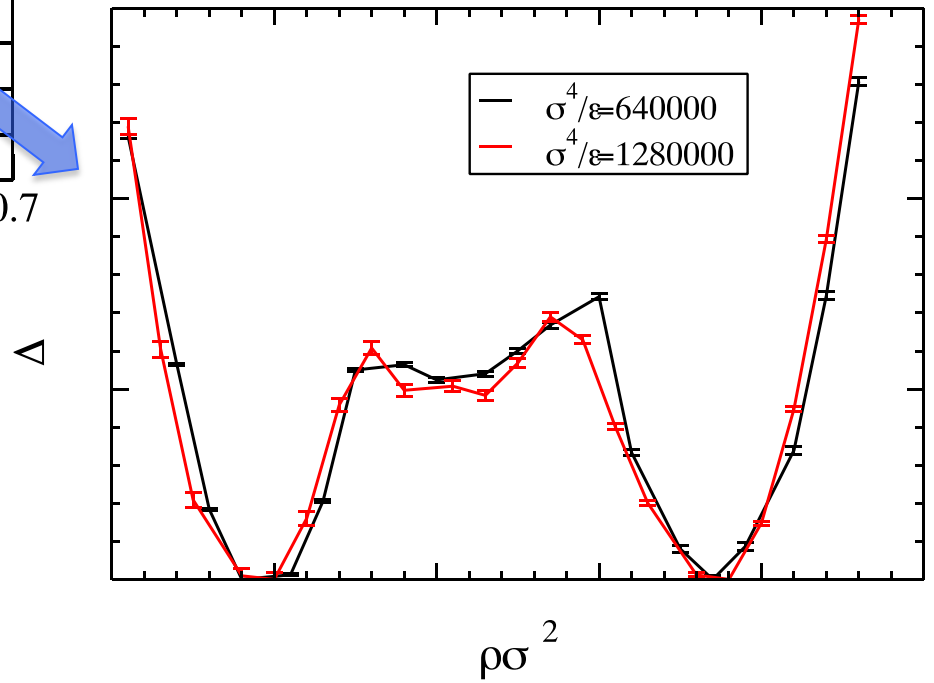
Inverse melting becomes more obvious



A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 140, 144505 (2014).

Pick b=1.46 and confirm transition

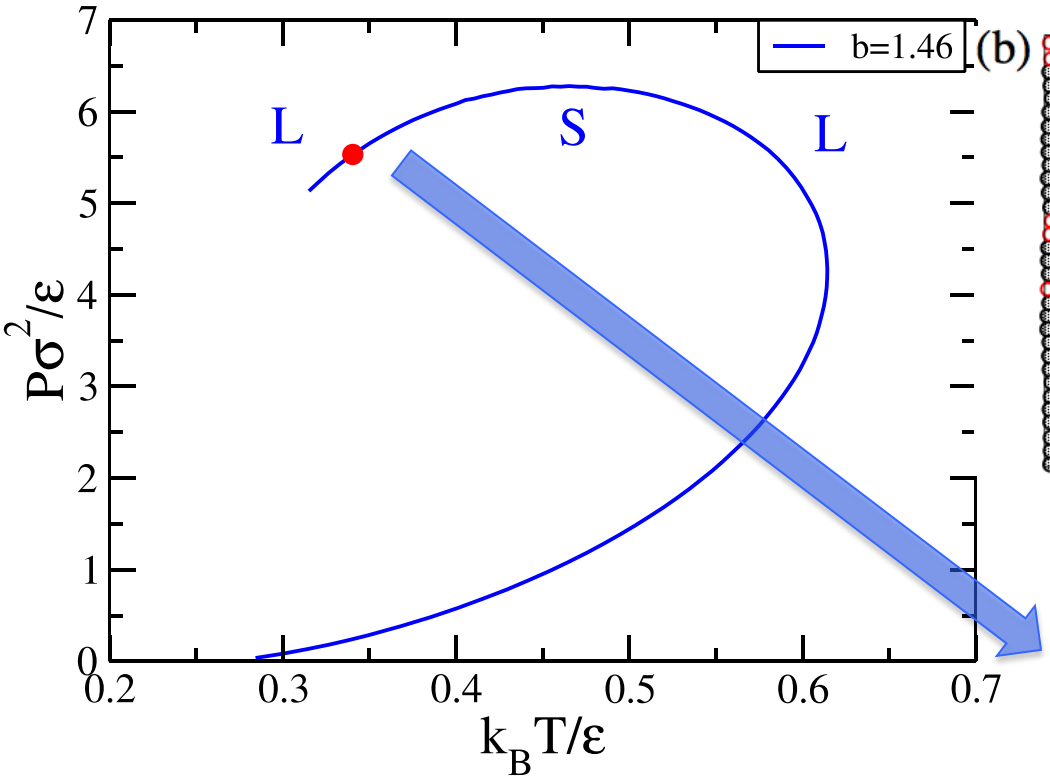


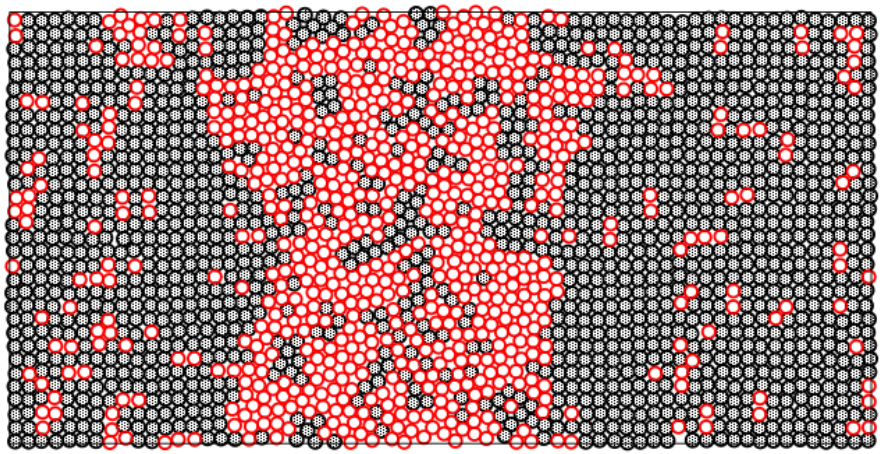


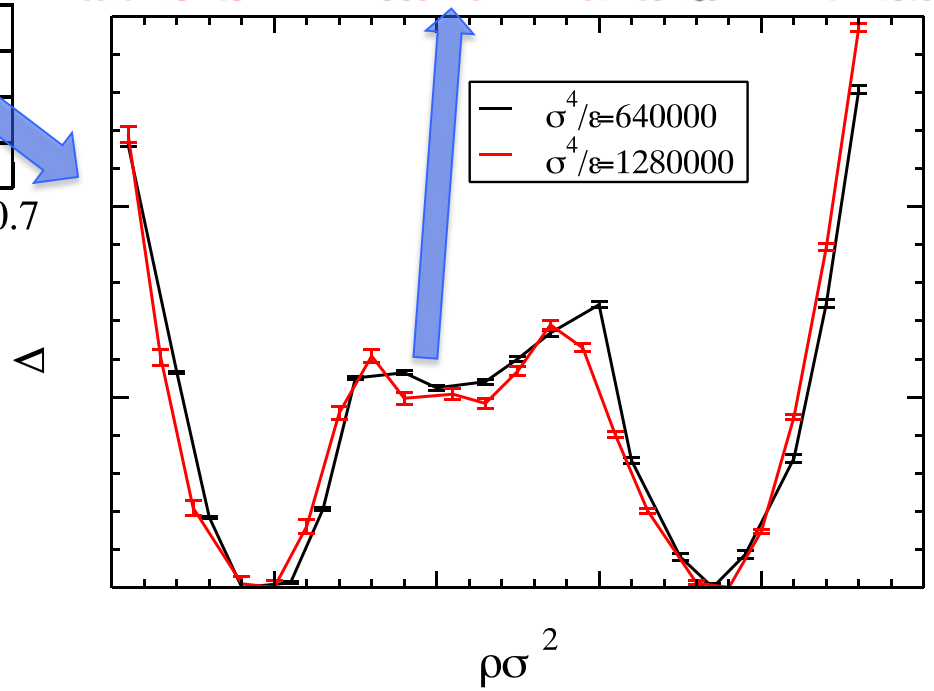
Carry out umbrella sampling Monte Carlo to calculate the free energy as a function of density at constant T and P, which are taken to be on the coexistence line.

A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 140, 144505 (2014).

Confirming transition







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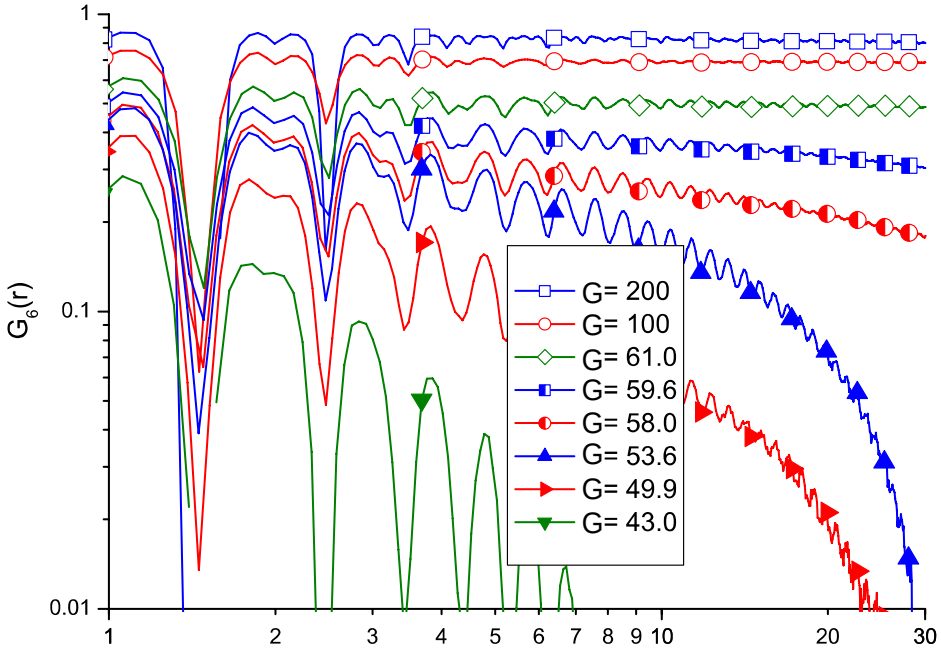
Hexatic Phase: Colloidal Experiment



PHYSICAL REVIEW E **75**, 031402 (2007)

Frank's constant in the hexatic phase

P. Keim,[1] G. Maret,[2] and H. H. von Grünberg[1]

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

$$\psi(\vec{r}) = \psi_k = \frac{1}{N_j}\Sigma_j e^{i6\theta_{jk}}.$$

KTNHY Theory

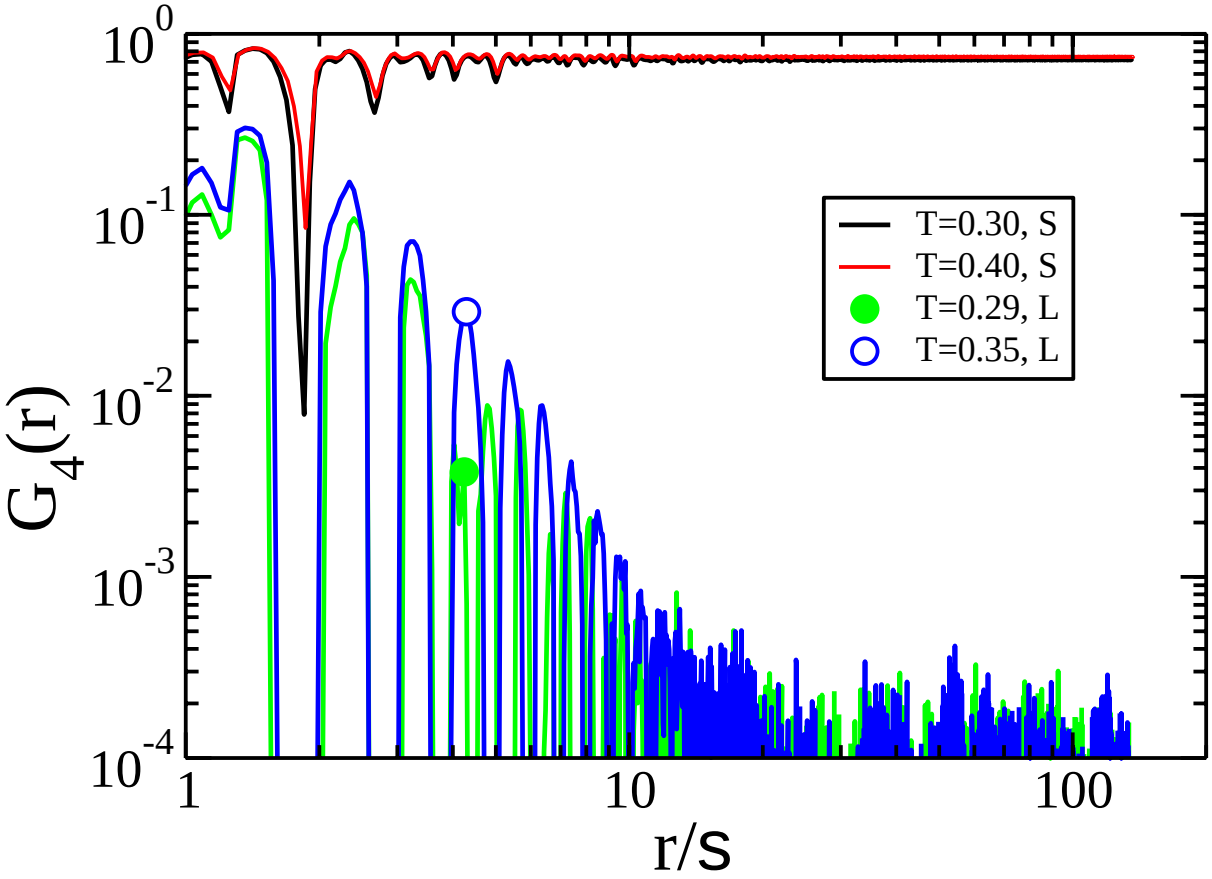
Kosterlitz, Thouless, Halperin, Nelson and Young

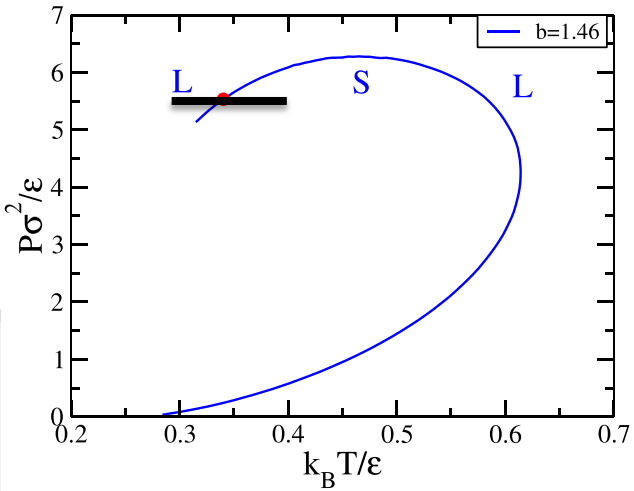
$\lim_{r\to\infty} G_6(r) \neq 0$ crystal: long-range order,

$G_6(r) \sim r^{-\eta_6}$ hexatic: quasi-long-range order, $\eta_6 < 1/4$

$G_6(r) \sim e^{-r/\xi_6}$ isotropic: short-range order.

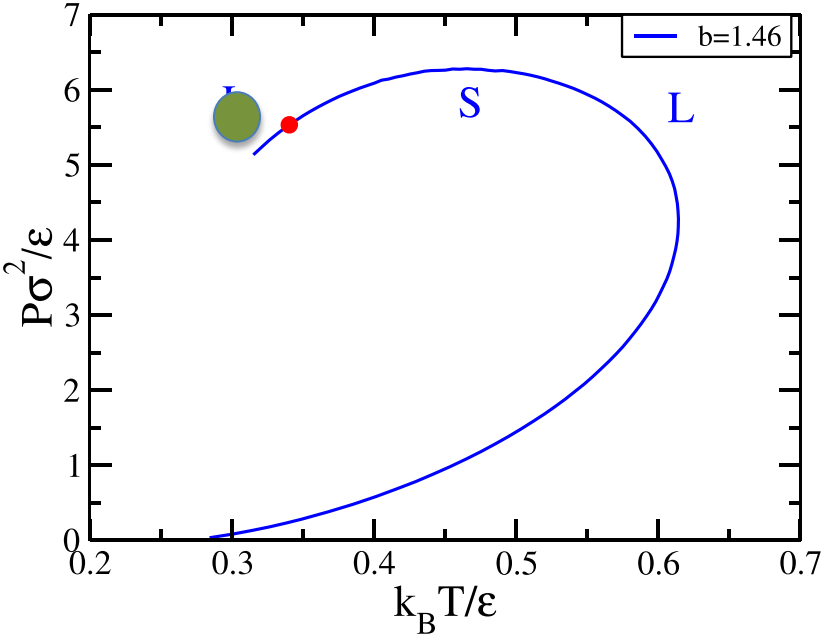
Checking for hexatic phase, N=65536, P=5.6

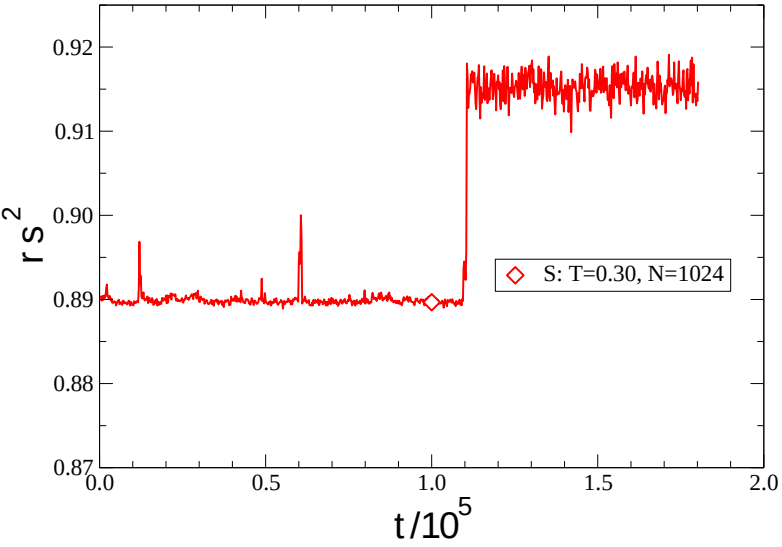




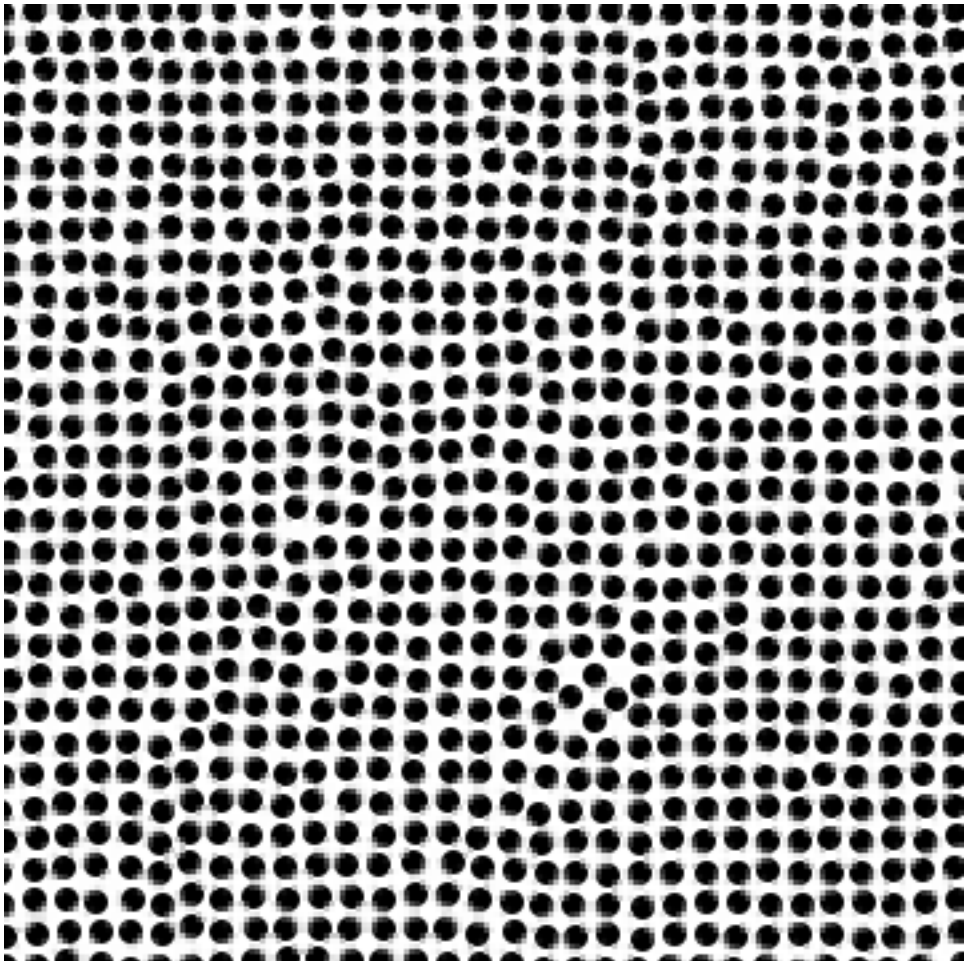
A. M. Almudallal, S. V. Buldyrev and I. Saika-Voivod, J. Chem. Phys. 140, 144505 (2014).

Direct Confirming with MD



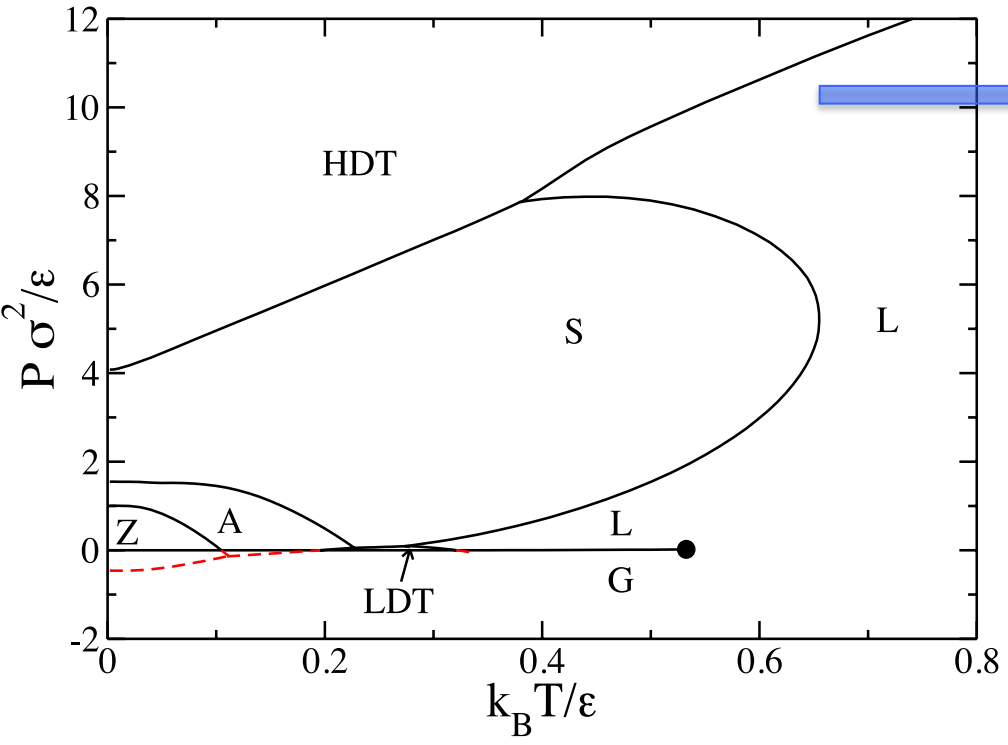


Start with S crystal at P=5.6, T=0.30 and see what happens.



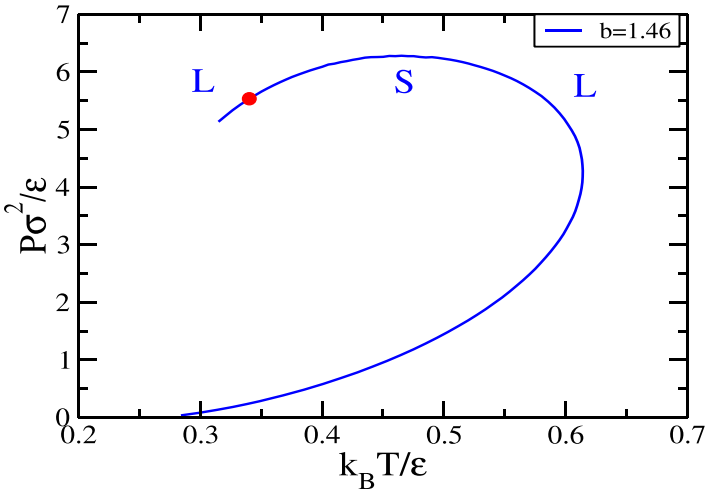
What about the rest of the phase diagram?

$b = \sqrt{2} \approx 1.414$

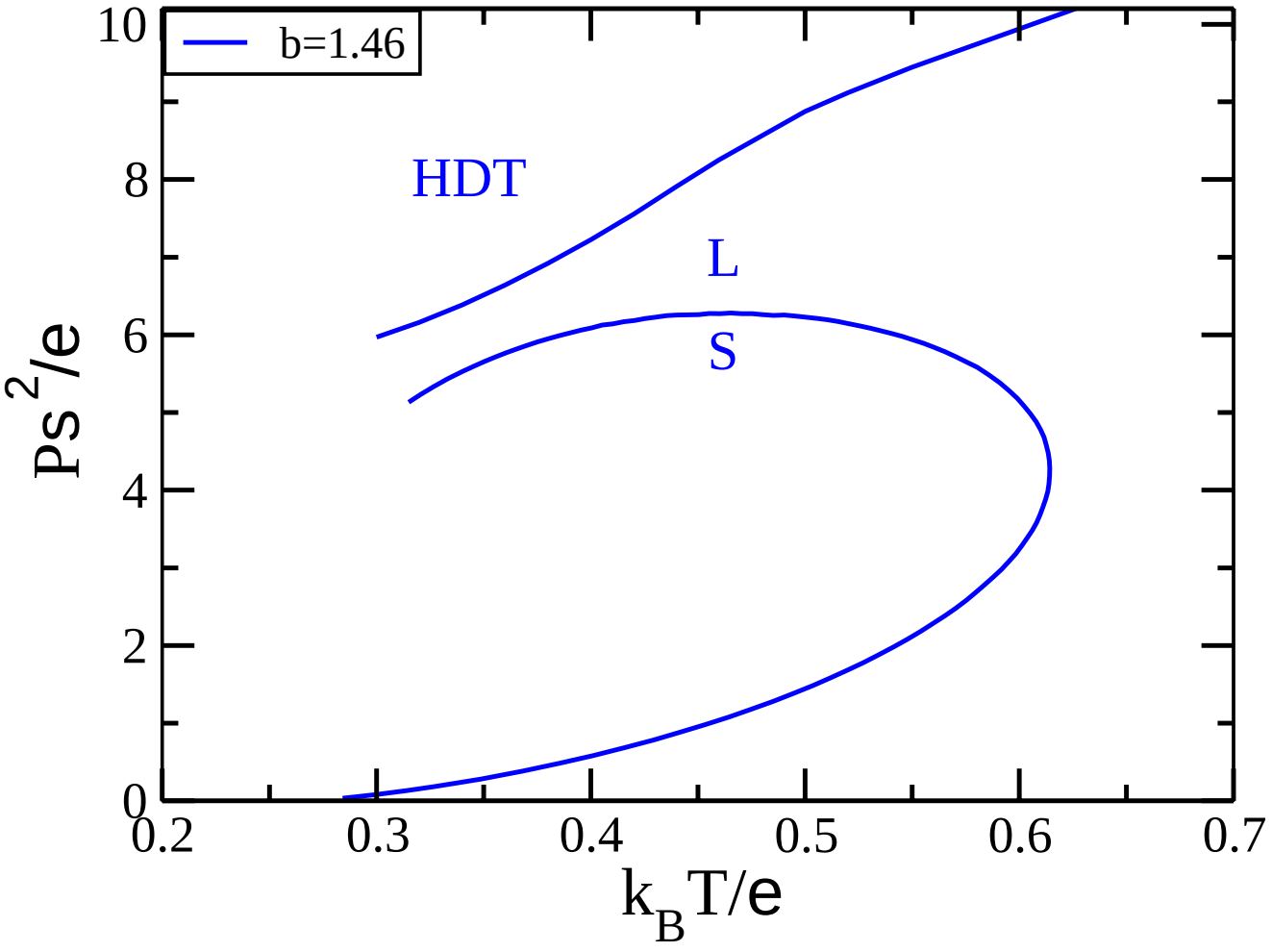


$b = 1.46$

HDT melting line would need to curve a lot.



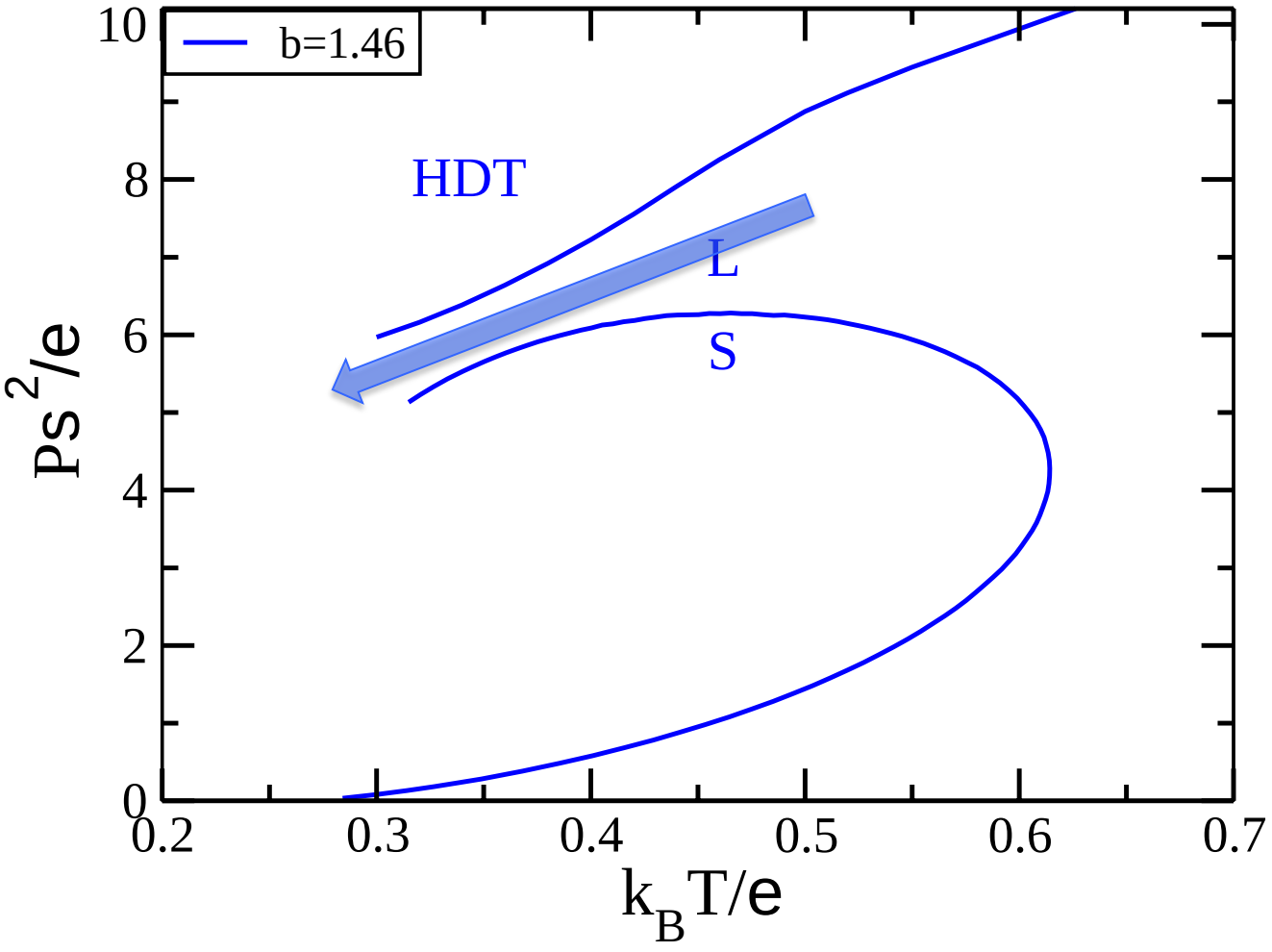
Add HDT-L Coexistence Curve



HDT-S-L triple point disappears

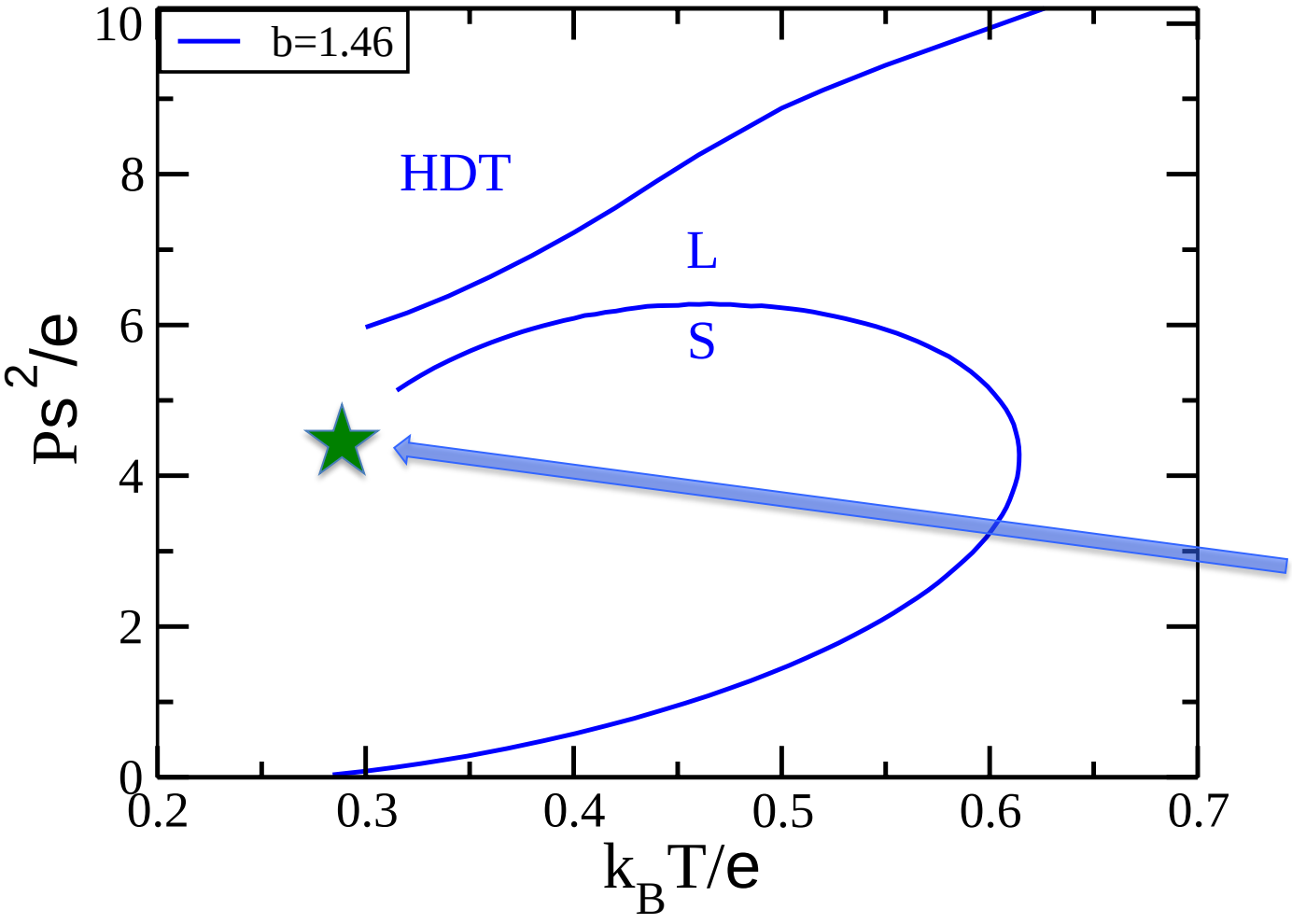
HDT-L line inflects (?!)

Add HDT-L Coexistence Curve



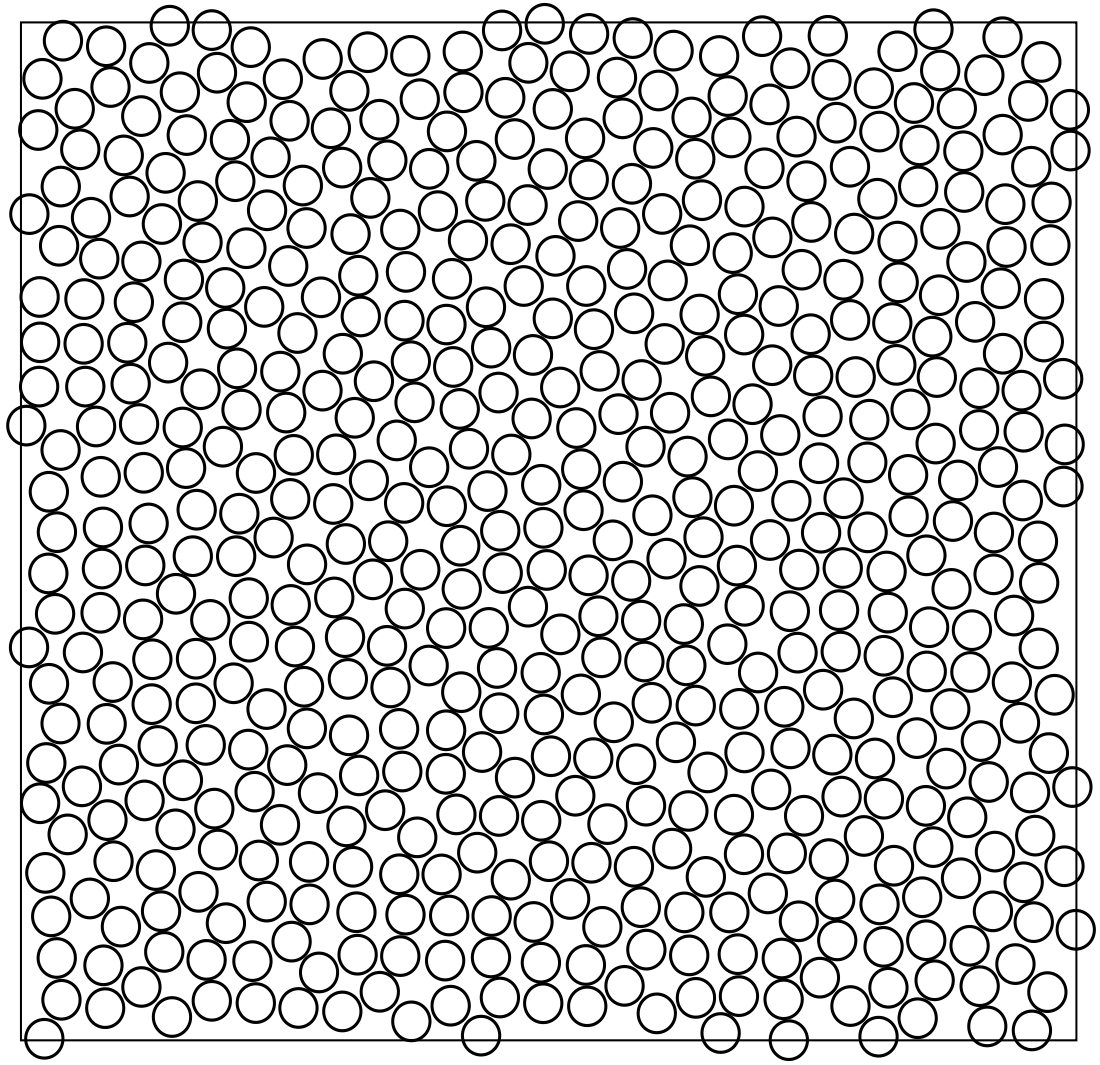
Is this a channel of liquid super stability with no crystals in the way?

Add HDT-L Coexistence Curve

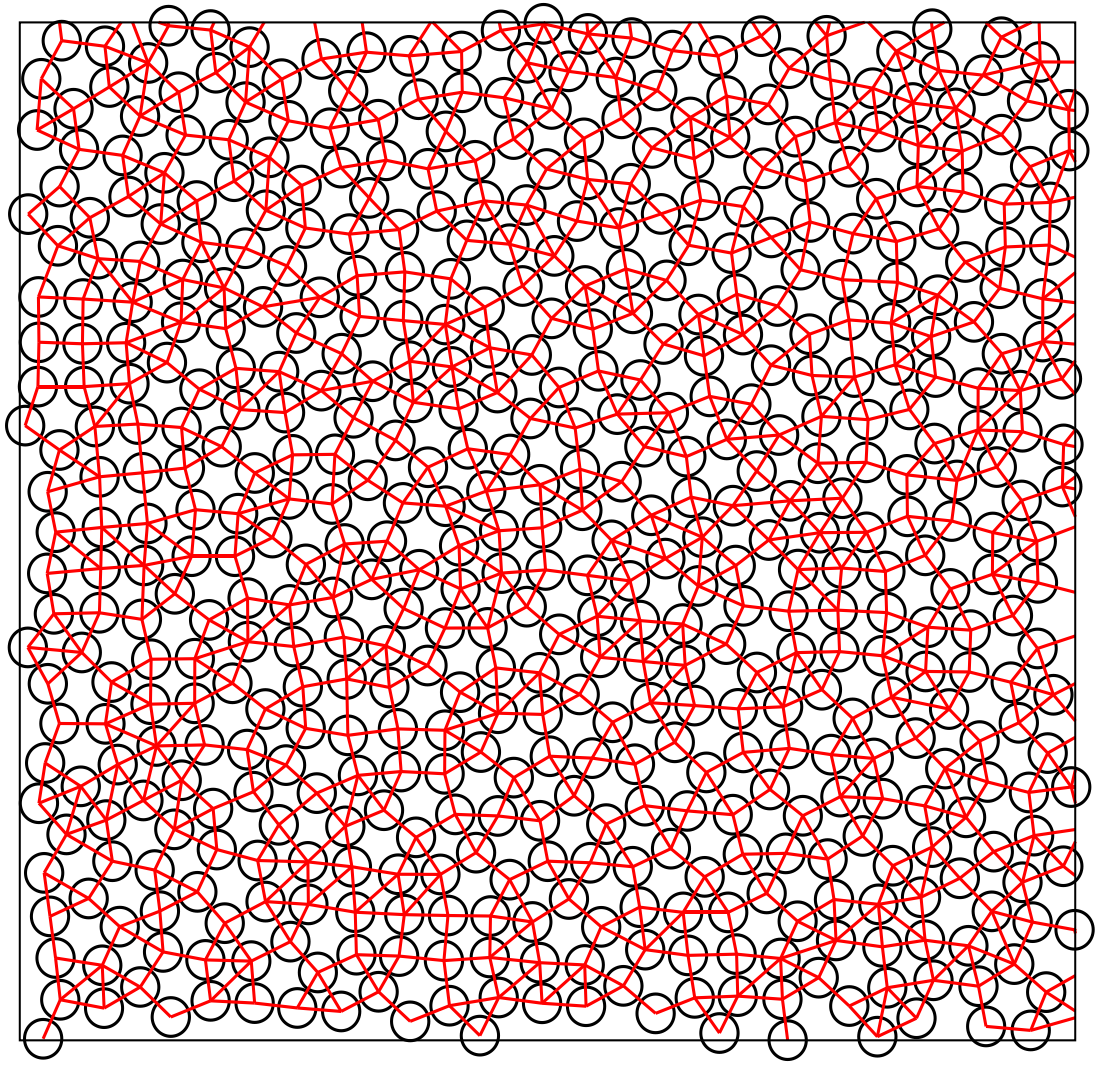


Let's take a look at the liquid here.

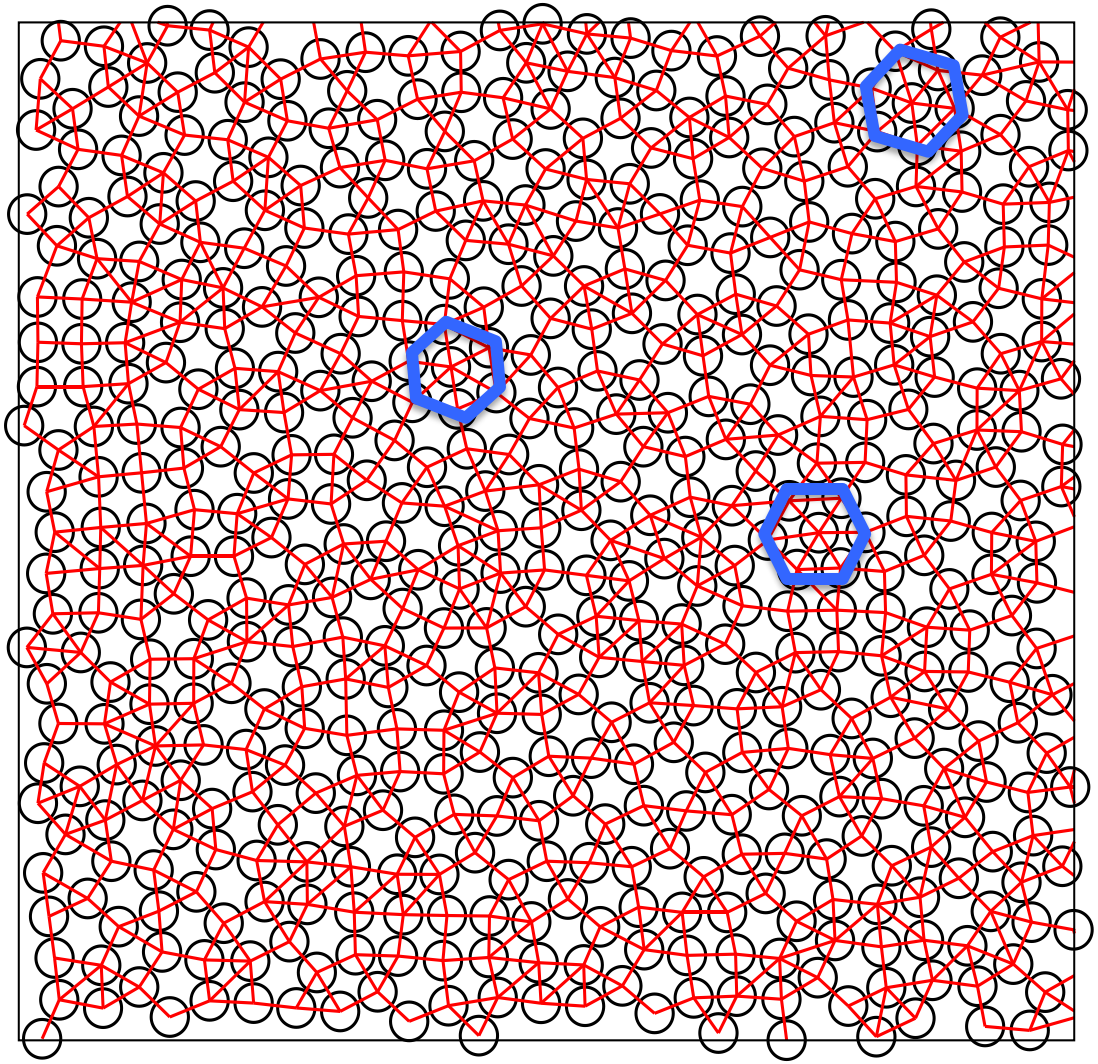
Liquid at ★



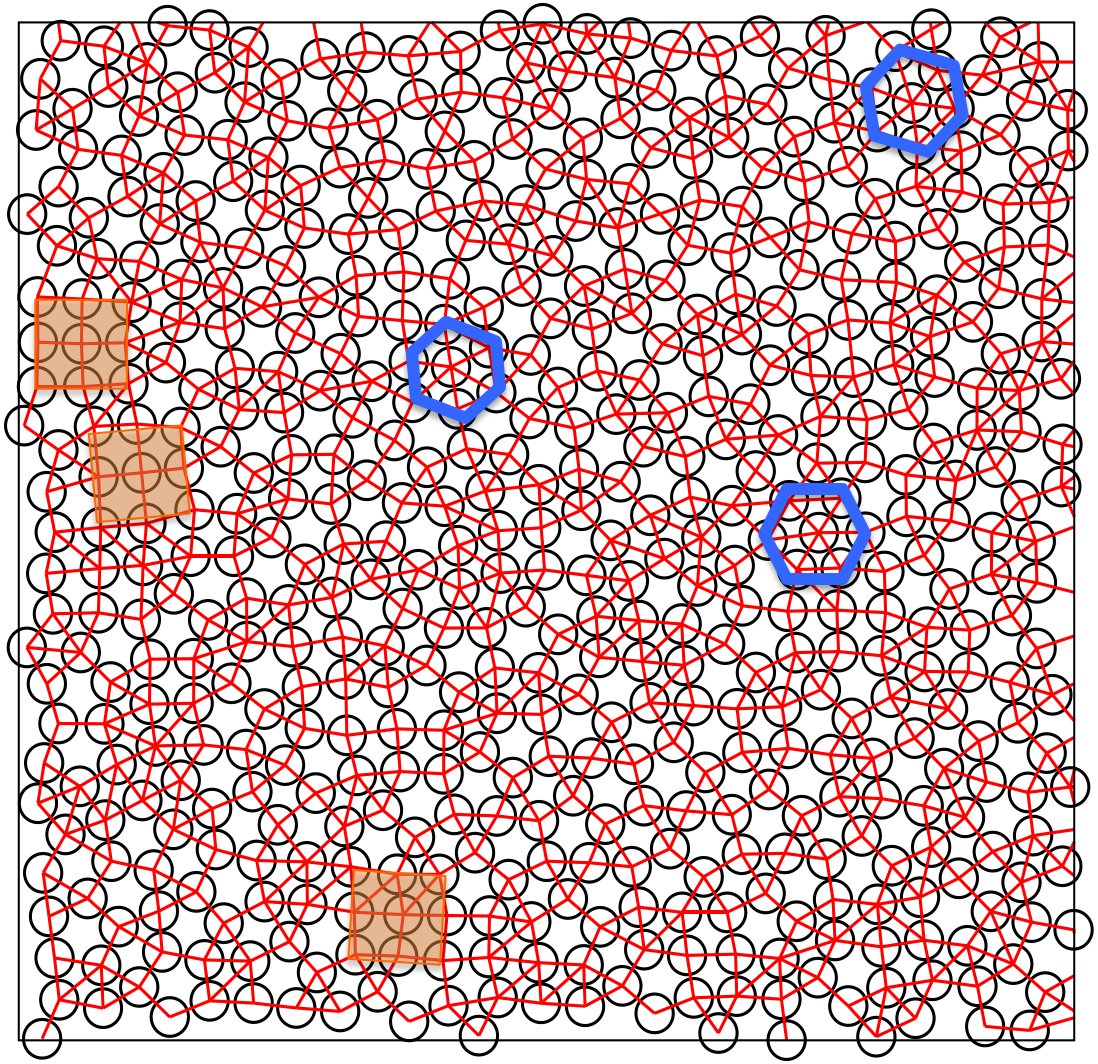
It has various local environments



Close-packed

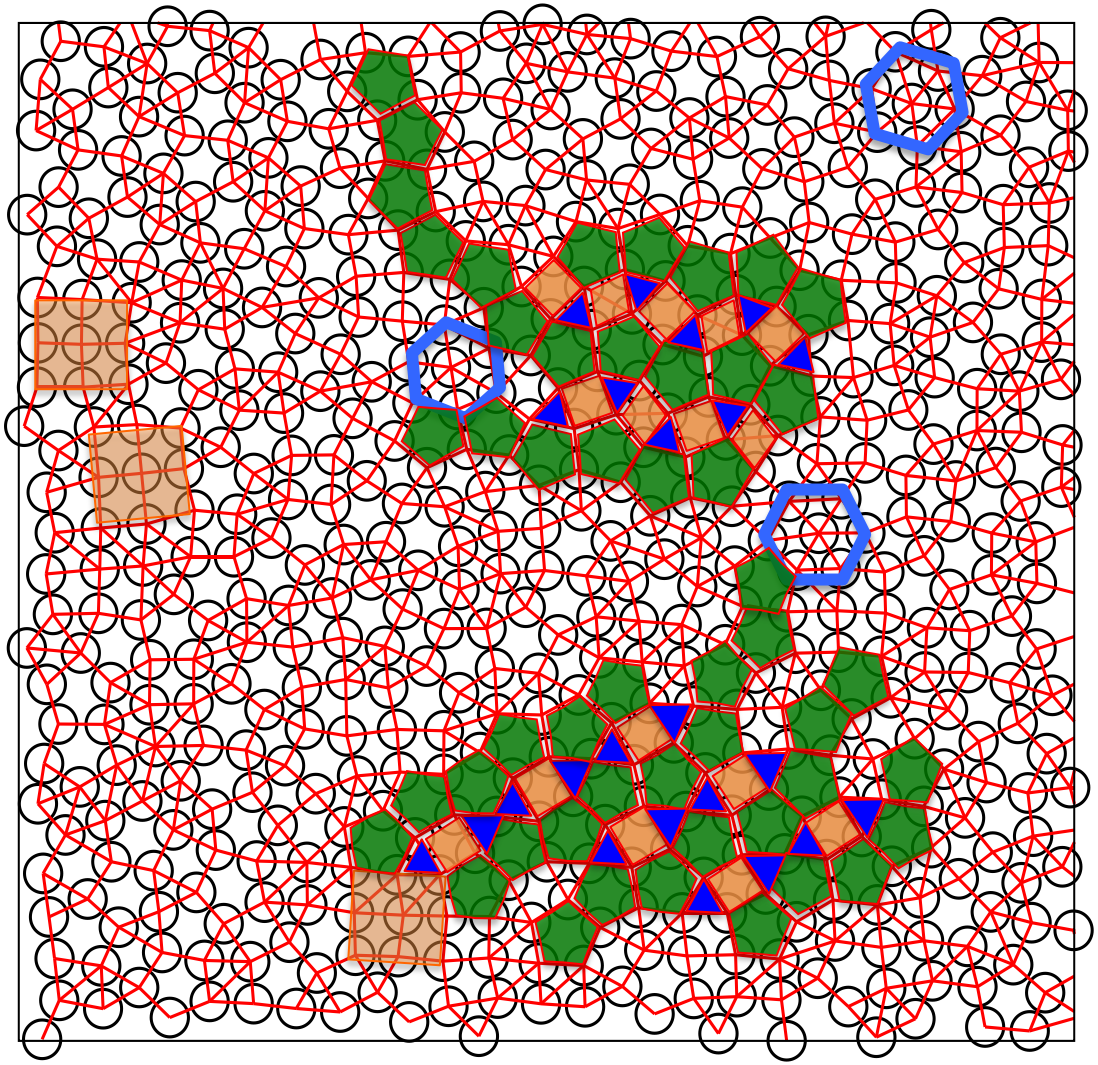


Squares



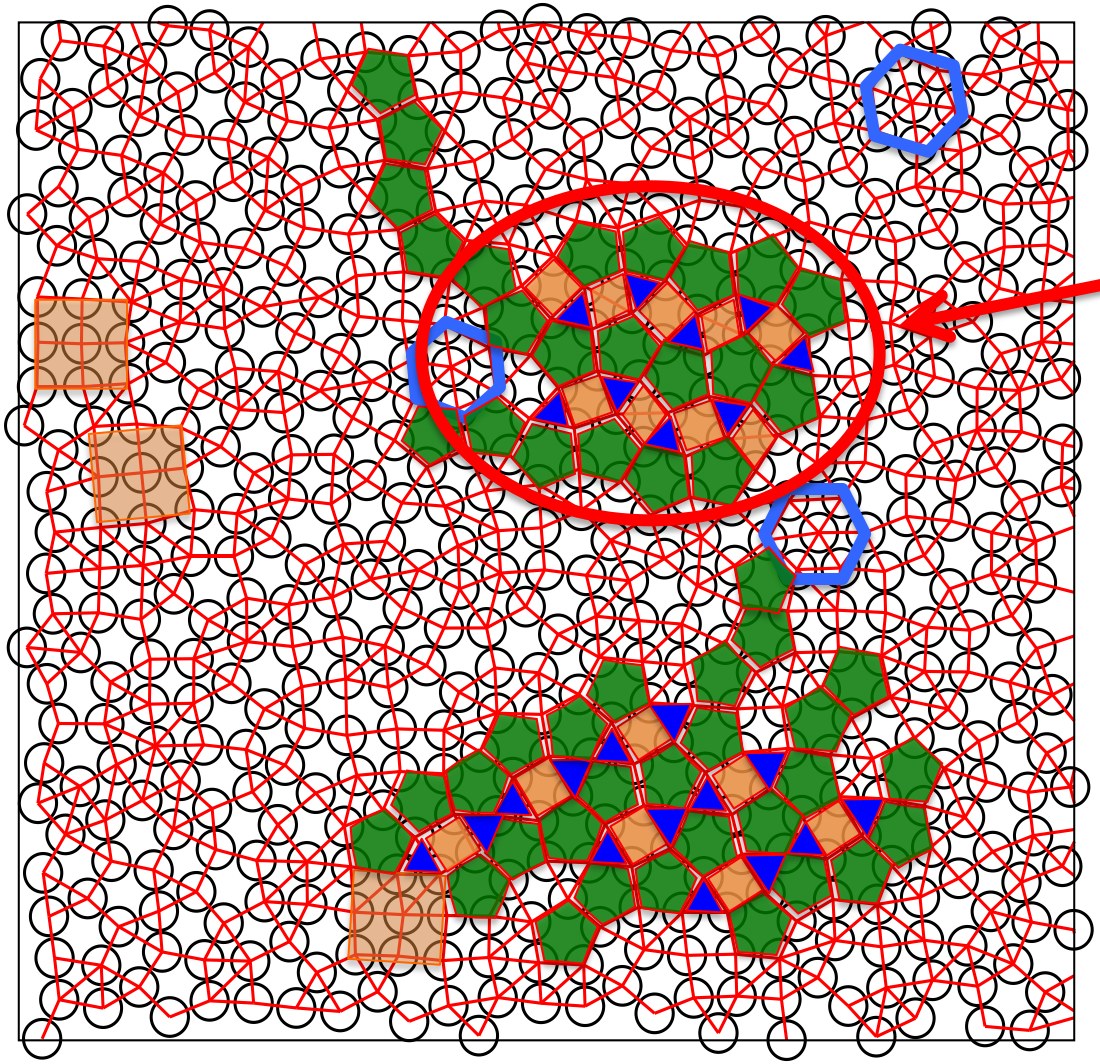
And pentagons

(surrounded by triangles and little squares or rhombuses)



And pentagons

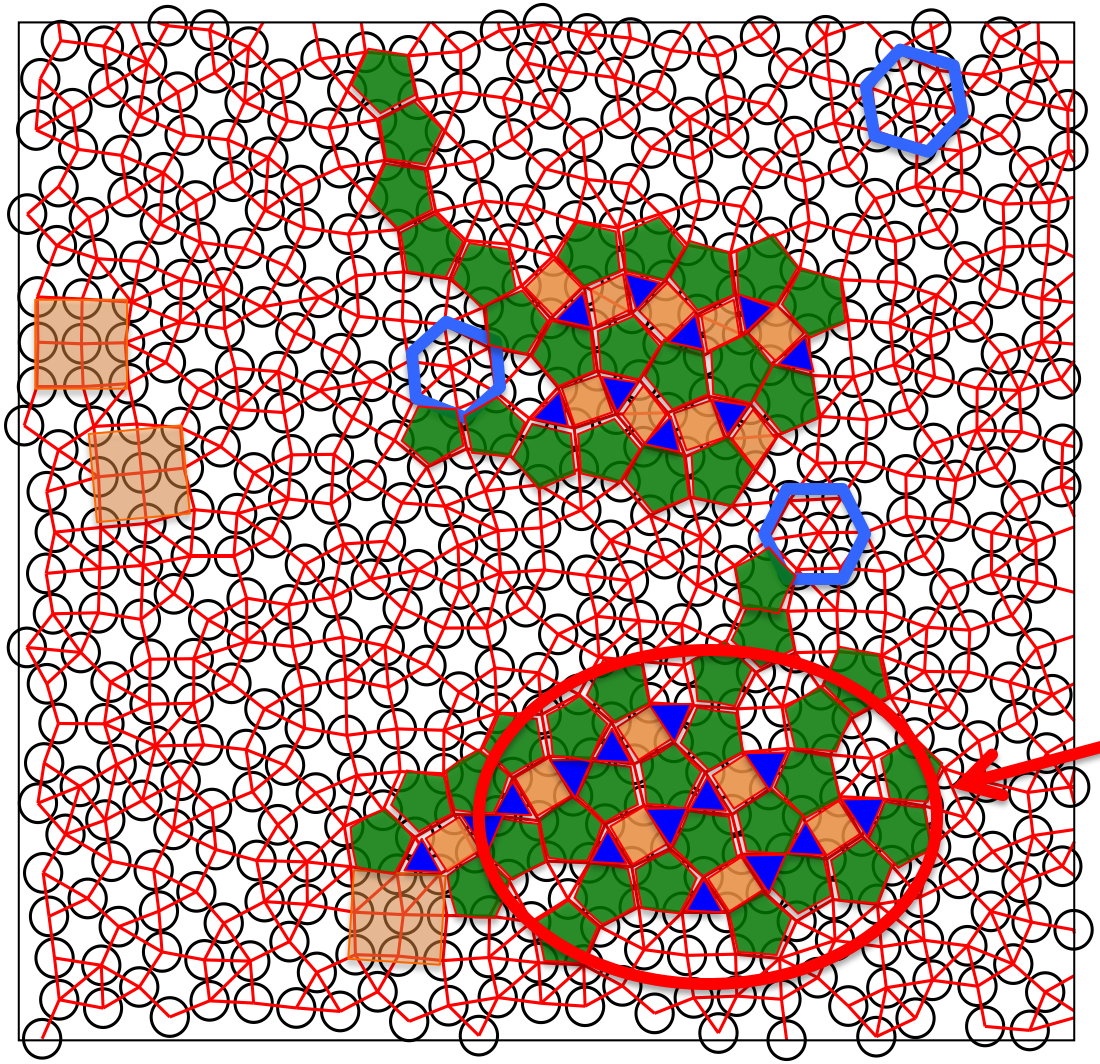
(surrounded by triangles and little squares or rhombuses)



O-phase
(Outphase?
… still looking
for a name)

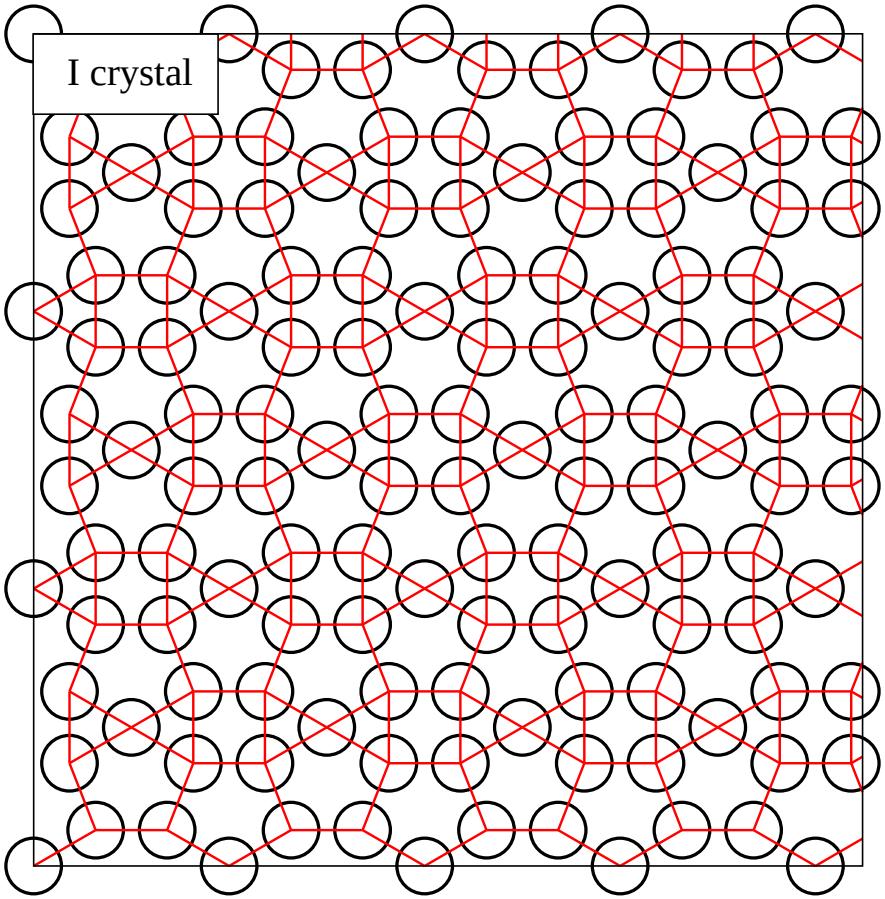
And pentagons

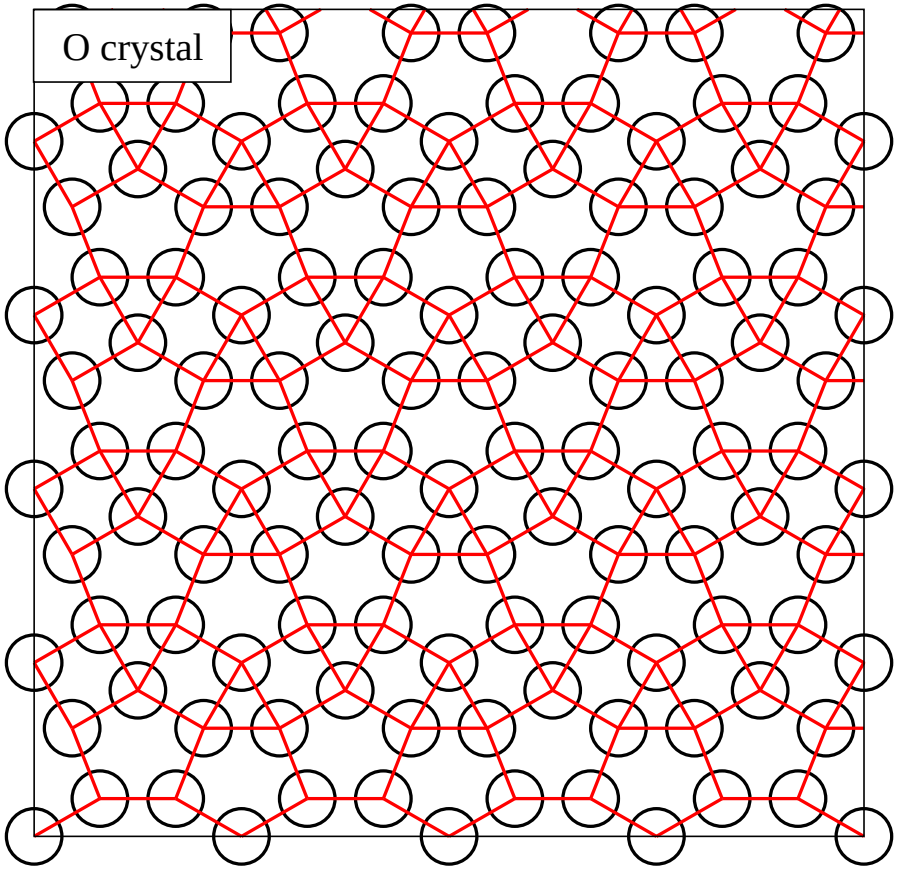
(surrounded by triangles and little squares or rhombuses)



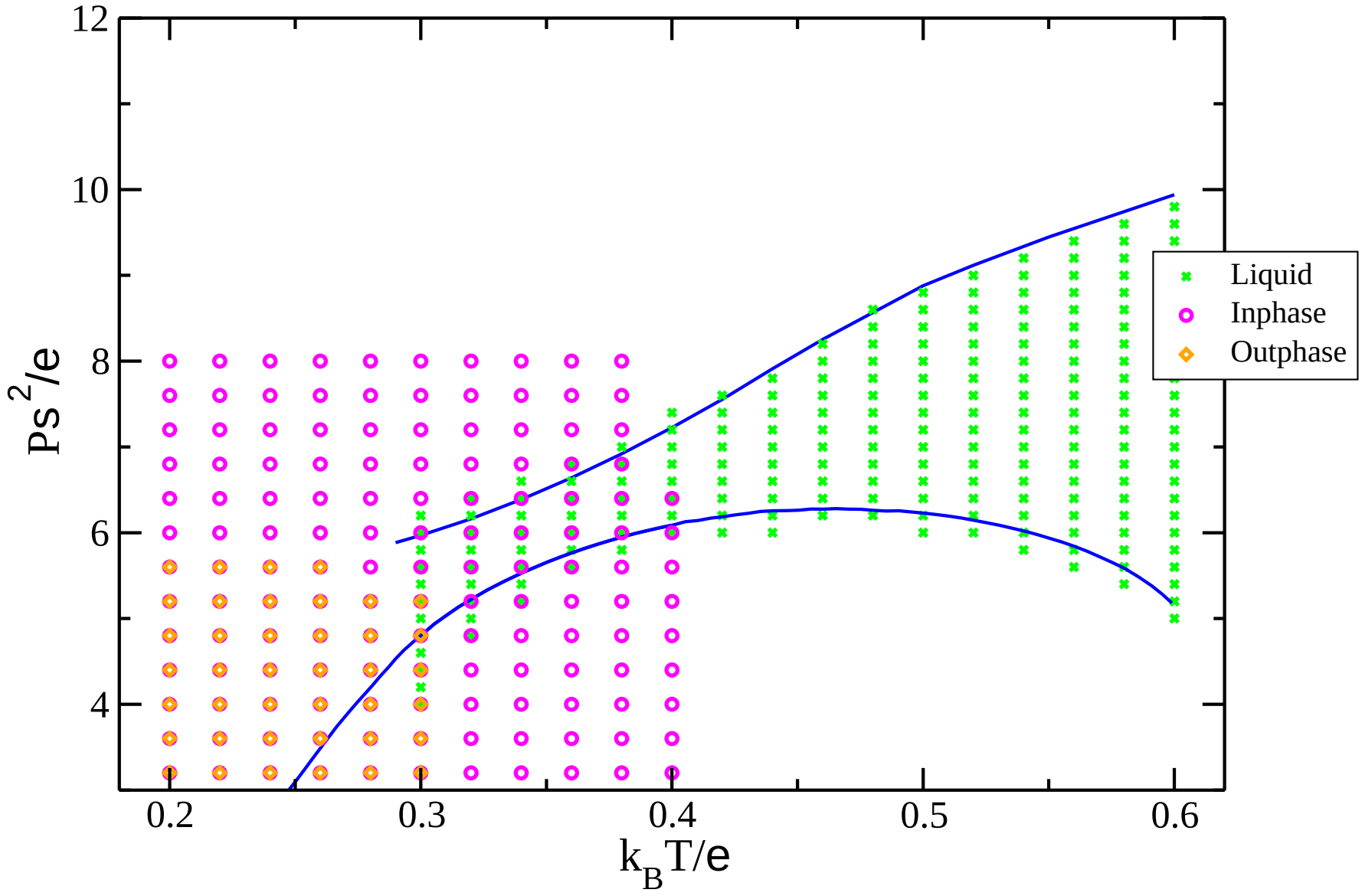
I-phase
(Inline phase?
… still looking
for a name)

New Phases



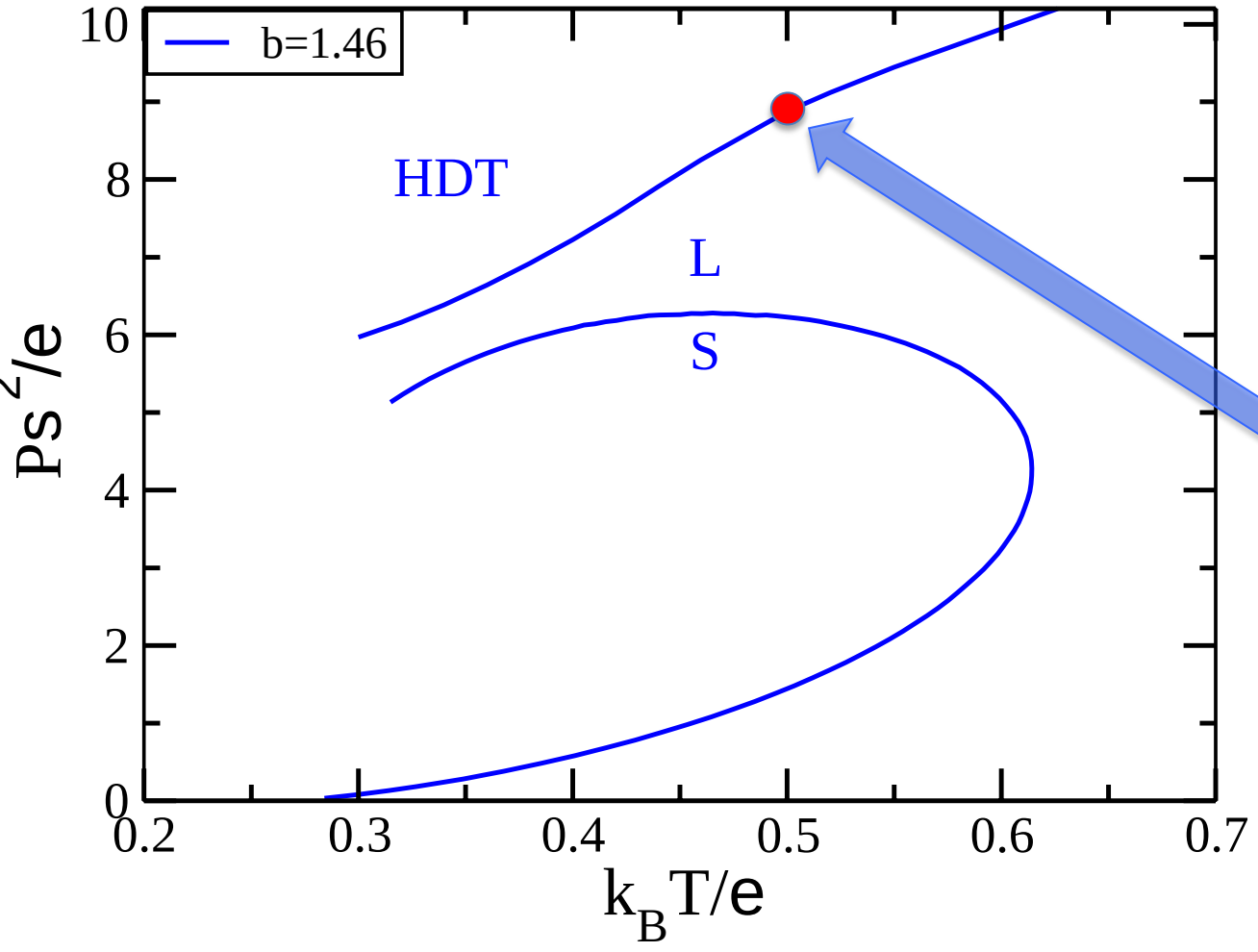


A look at metastability



I-phase not stable above T=0.4

HDT-L Coexistence Curve

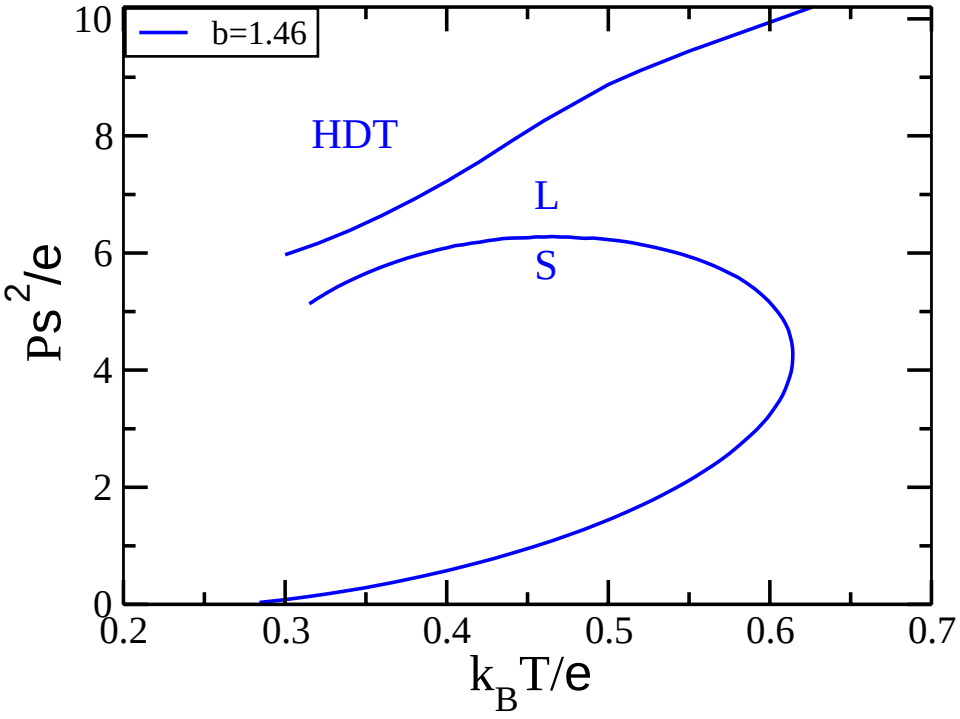


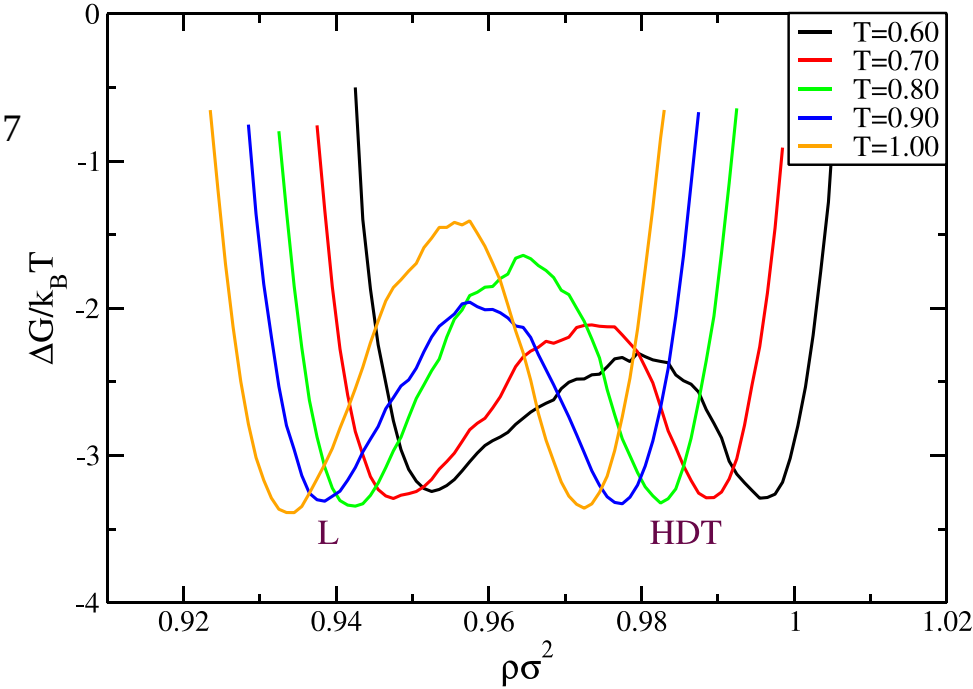
HDT-S-L triple point disappears

HDT-L line inflects (?!)

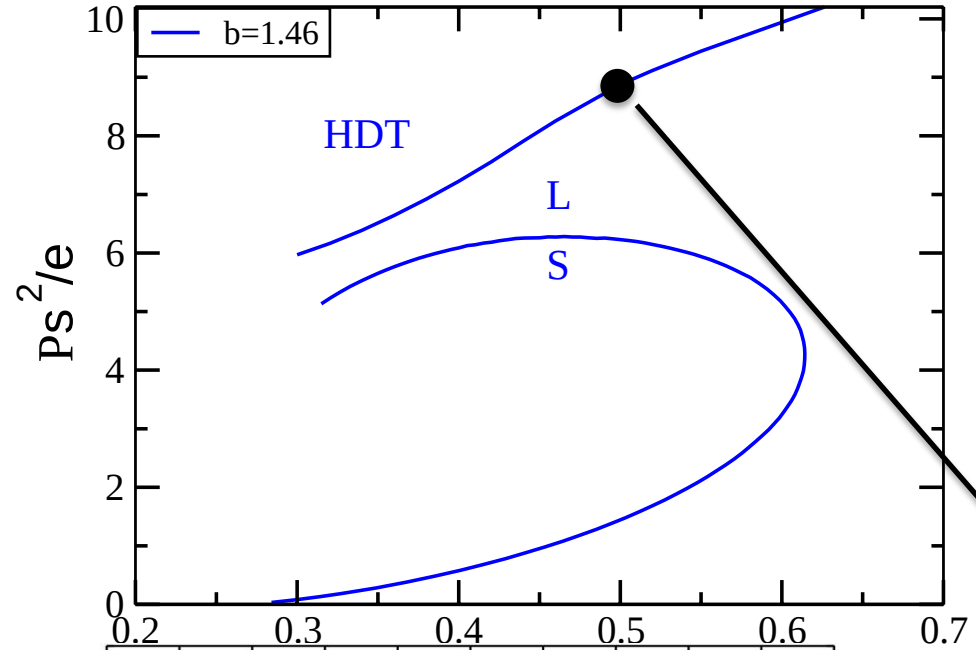
This is a very strange point, as we shall later see.

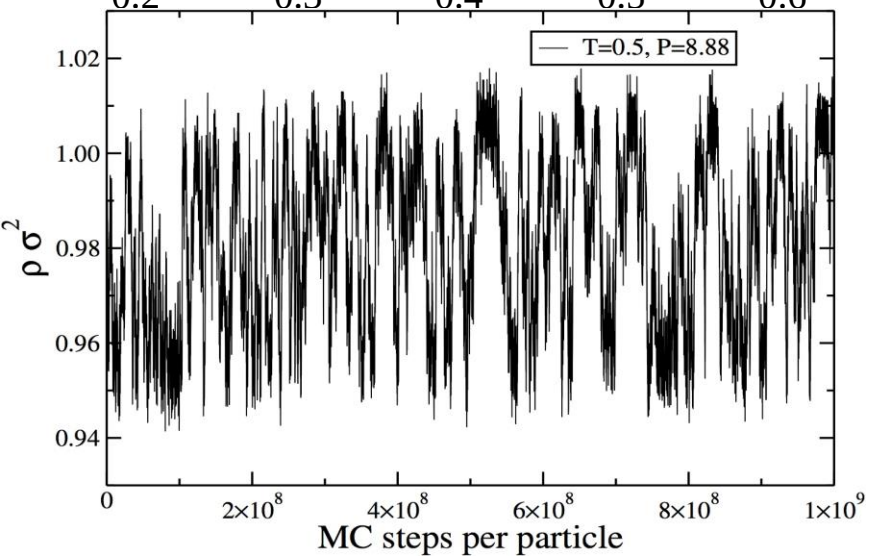
HDT-L Coexistence Curve



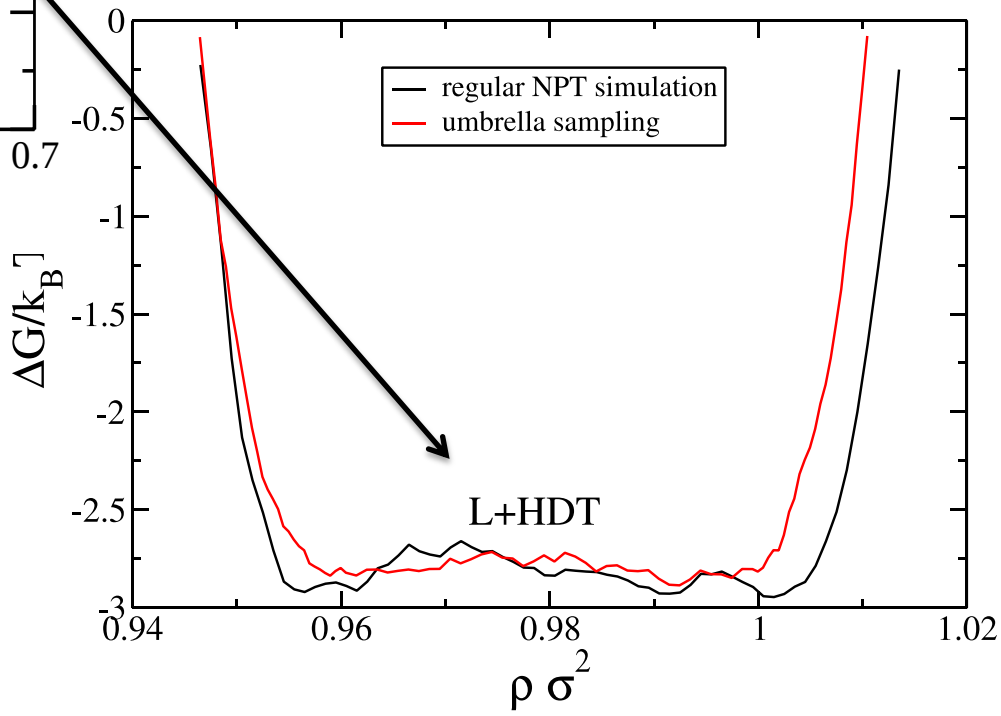


HDT-L Coexistence Curve

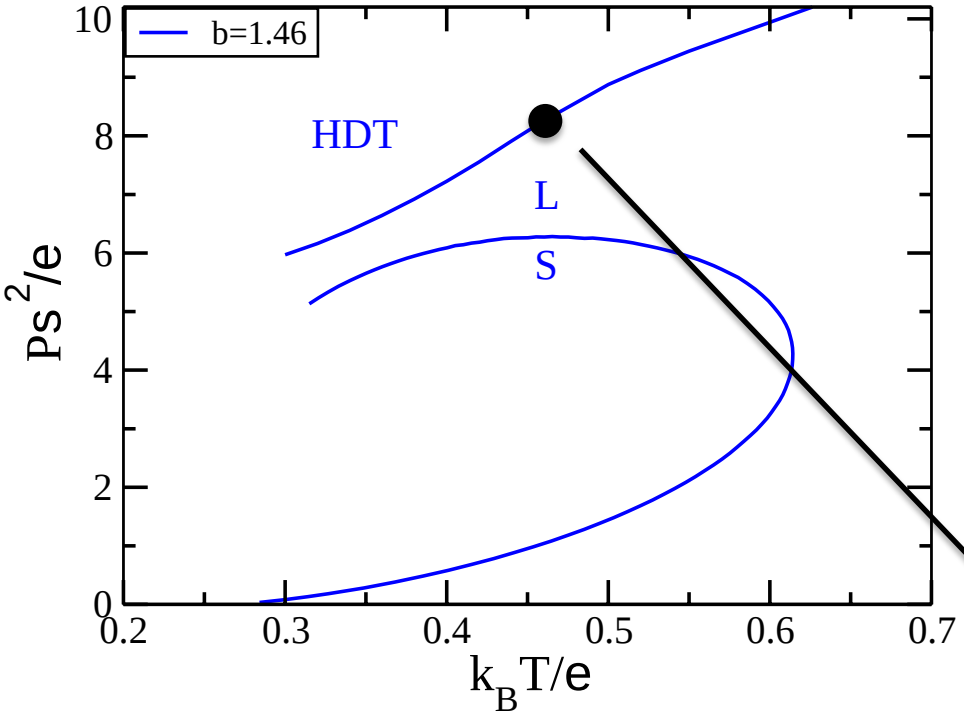




T=0.5

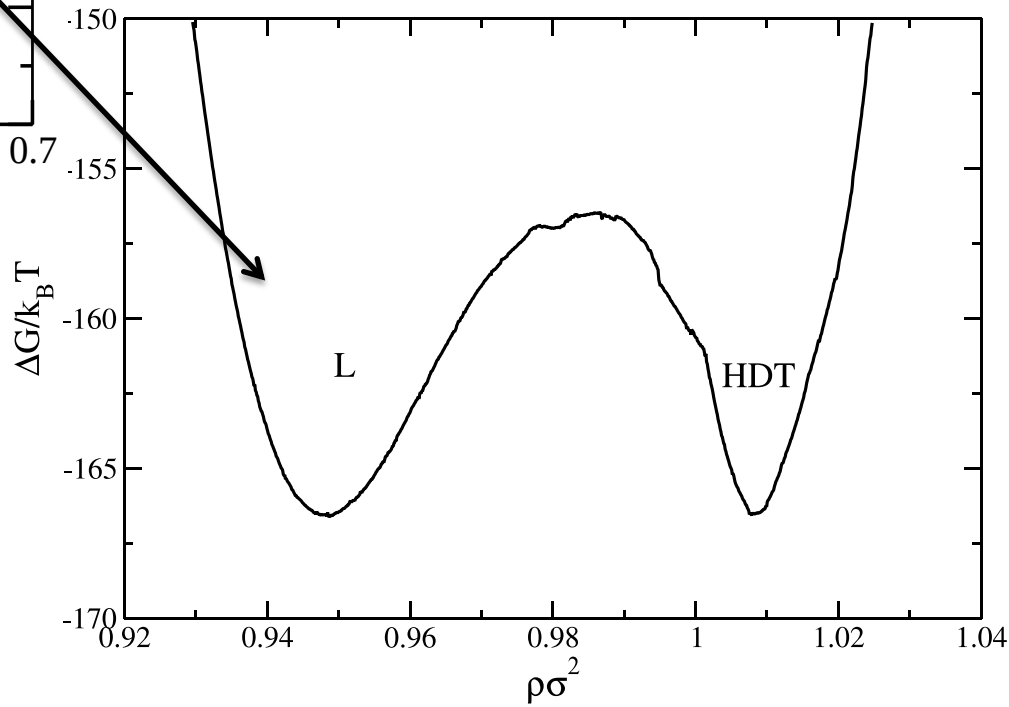


HDT-L Coexistence Curve



T=0.46

(umbrella sampling)



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

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