



РОСАТОМ

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ГОСУДАРСТВЕННАЯ КОРПОРАЦИЯ ПО АТОМНОЙ ЭНЕРГИИ «РОСАТОМ»

Calculation of Equilibrium Phase Transition Curves by Molecular Dynamics

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Classical Theory of Thermodynamic Equilibrium



Thermodynamic stability

Microcanonical ensemble (NVE)

Entropy **S** is maximal;

Canonical ensemble (NVT)

Helmholtz free energy **F** is minimal;

NPT-ensemble

Gibbs thermodynamic potential **G** is minimal;

None of these quantities can be “measured” directly in a simple CMD simulation (neither in real experiments).

An advanced technique for calculation of “**absolute**” values of free energy of different metastable states – **thermodynamic integration method**

D. Frenkel and A.J.C. Ladd, *J. Chem. Phys.*, v.81, p. 3188 (1984)

D. Frenkel and B. Smit, “Understanding Molecular Simulations. From Algorithms to Applications”, Academic Press, San Diego (2002)





Thermodynamic Integration Method



In classical statistics Helmholtz free energy of canonical ensemble of N equivalent particles is defined as

$$F = -k_B T \ln(Z_N(V, T)) \equiv -k_B T \ln \left(\frac{1}{h^{dN} N!} \int_{\Gamma} d\mathbf{p}^{(N)} d\mathbf{r}^{(N)} \exp \left(-\frac{H(\mathbf{p}^{(N)}, \mathbf{r}^{(N)})}{k_B T} \right) \right)$$

where $Z_N(V, T)$ is statistical integral of the system.

Unfortunately there are too few classical N -particle systems for which one can calculate statistical integral $Z_N(V, T)$ analytically:

1. Ideal gas,
2. Dilute gas of hard spheres,
3. Einstein harmonic crystal in the high temperature limit.

On the other hand one can calculate easily changes of thermodynamic potentials along reversible quasi-equilibrium thermodynamic paths by integration of differential thermodynamic relations of the equilibrium thermodynamics valid along isolines, e.g.:

$$\left(\frac{\partial F}{\partial V} \right)_{N, T} = -P, \quad \left(\frac{\partial(F/T)}{\partial(1/T)} \right)_{N, V} = -E, \quad \left(\frac{\partial G}{\partial T} \right)_{N, P} = S, \quad \left(\frac{\partial H}{\partial S} \right)_{N, P} = T, \quad \left(\frac{\partial G}{\partial P} \right)_{N, T} = V.$$

However, in order to get absolute values of the thermodynamic potentials in the state of interest one needs to know their absolute values at some reference point.





Thermodynamic Integration Method



In Classical Molecular Dynamics we are able to use as thermodynamic variables not only physical measurable in real experiments quantities, but all the parameters of model interatomic interaction potential itself as well.

Consider an artificially constructed potential $U = (1-\lambda)U_I + \lambda U_{II} = U_I + \lambda(U_{II} - U_I)$, where U_I is an atomic interaction potential for which one can somehow (ideally – analytically) obtain free energy value, U_{II} is the potential of interest, and λ is coupling parameter varying in the range from 0 (corresponding to the reference state with known thermodynamic potential values) to 1 (the state of interest).

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda} = \langle U_{II} - U_I \rangle_{\lambda}.$$

$$F(\lambda = 1, V, T) = F(\lambda = 0, V, T) + \int_0^1 d\lambda \langle U_{II} - U_I \rangle_{\lambda}$$

If we could develop a reversible (quasi-equilibrium) thermodynamic path from the reference state ($\lambda = 0$) to the state of interest ($\lambda = 1$) we can do the integration and obtain absolute values of thermodynamic potentials in the state of interest.





Methods to Study Equilibrium Melting Curves



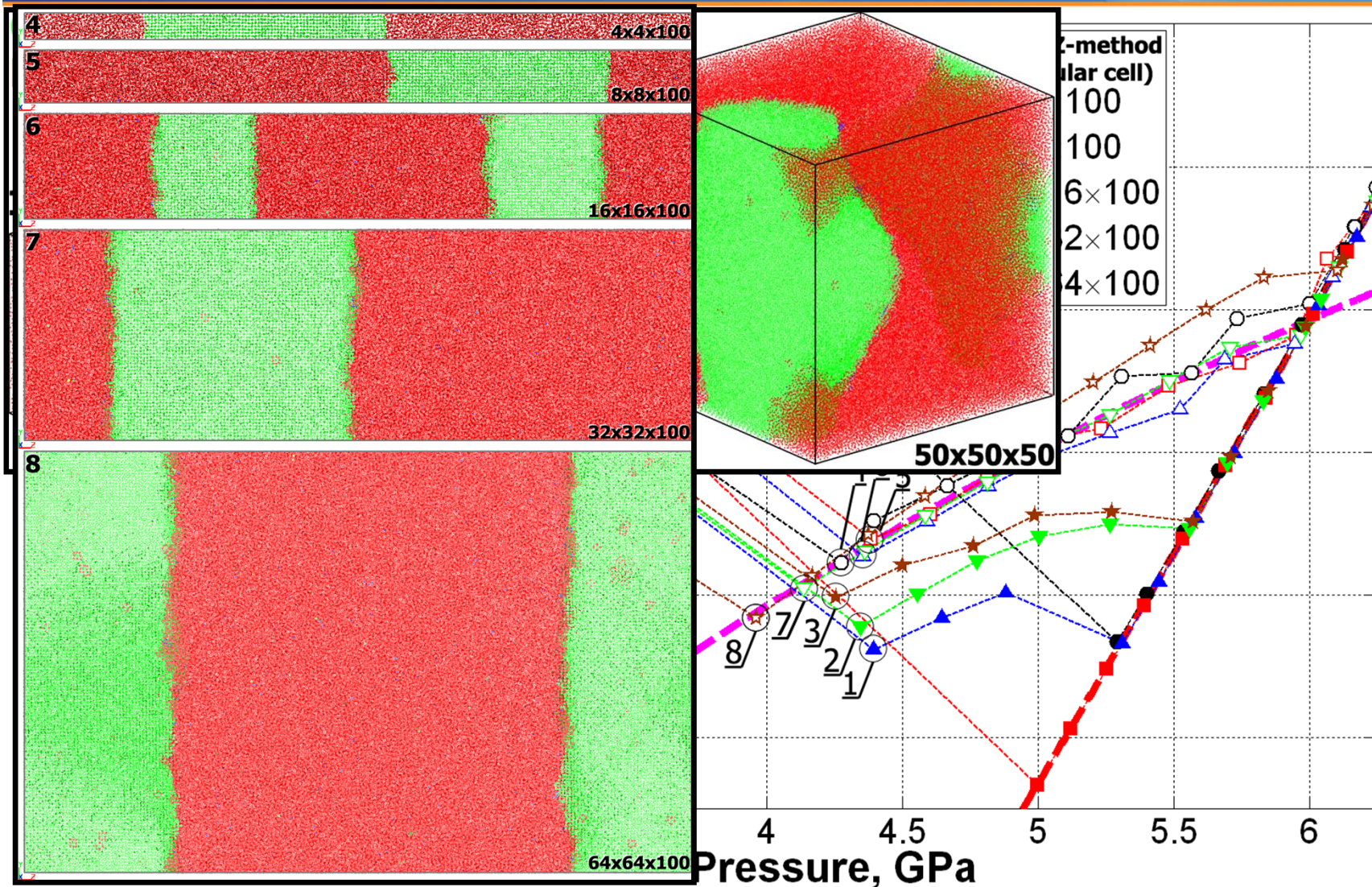
There is a number of methods for evaluation of equilibrium melting curves for a given model of interatomic interaction (empirical classical interatomic potential or *ab-initio* model) in direct MD simulations:

- Heat Until Melts (HUM)
- Hysteresis Method (HM)
- Z-method
- Modified Z-method (by **S. Wang et al., J.Chem.Phys. 138 (2016) 134101**)
- Two Phase Method (TP) or Coexistence Method





Z-method vs Modified Z-method

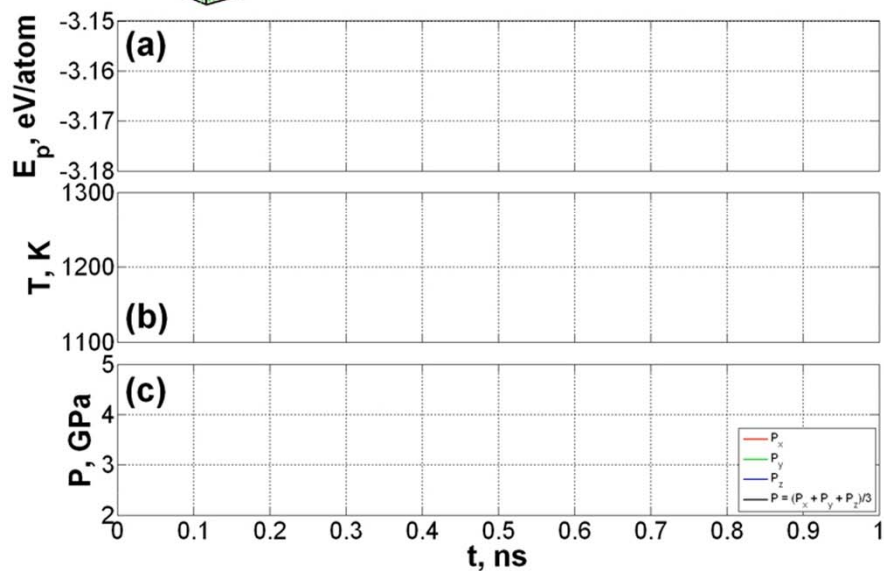
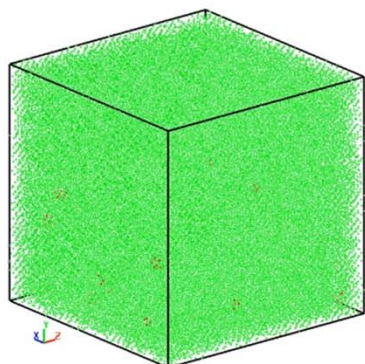




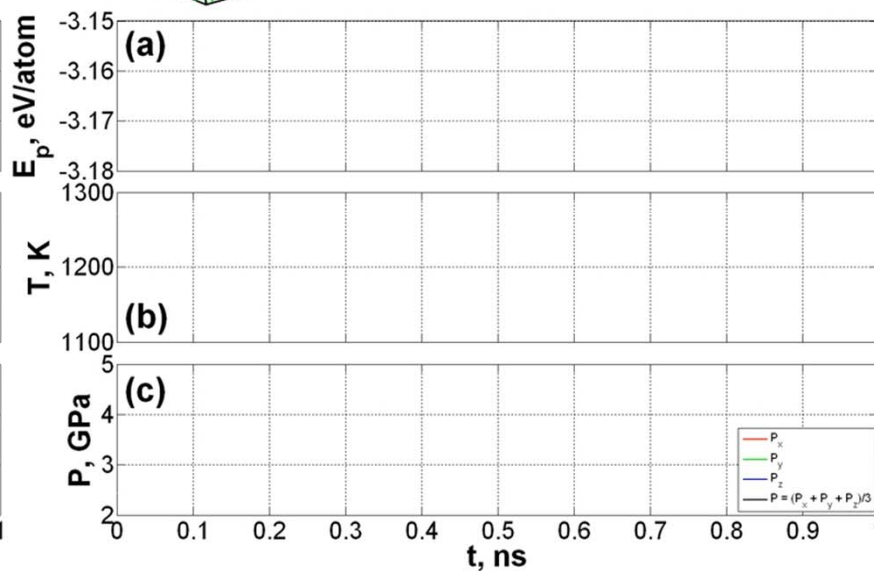
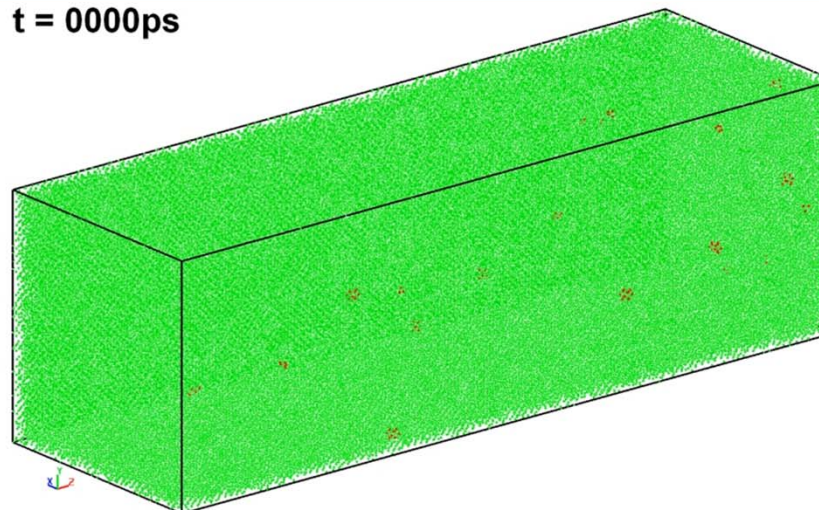
Z-method vs Modified Z-method



t = 0000ps



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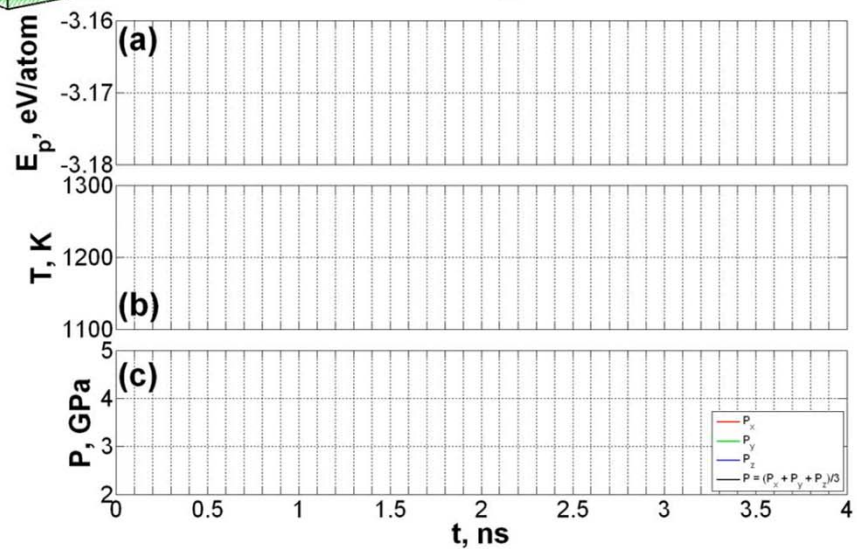
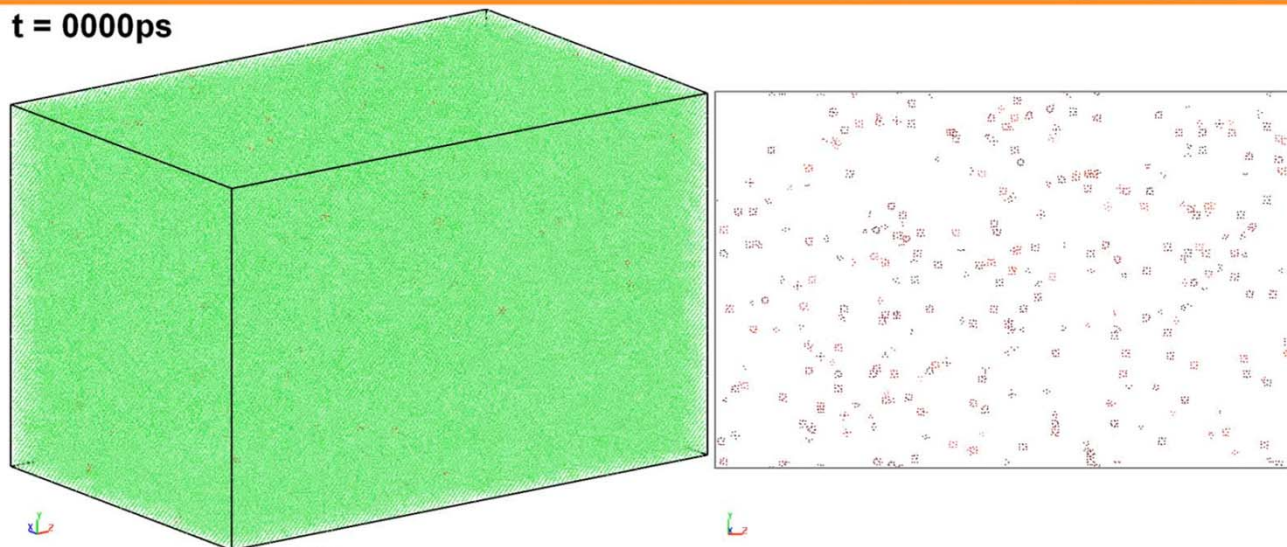




Z-method vs Modified Z-method

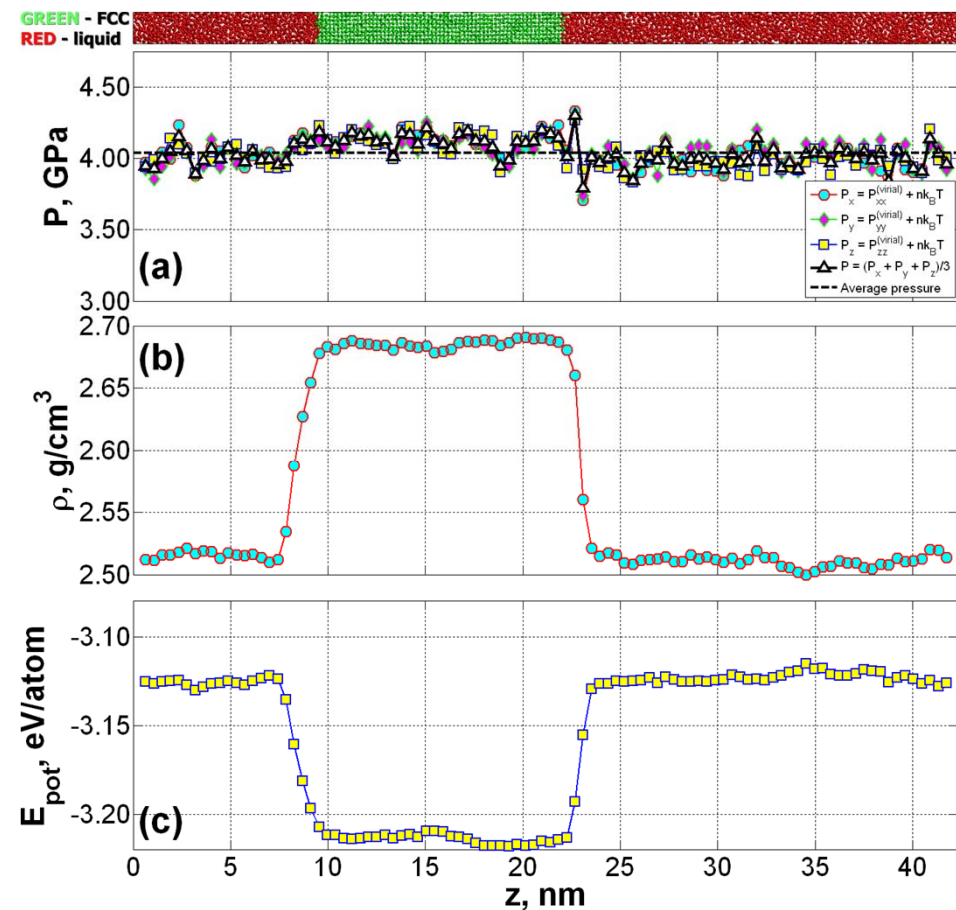
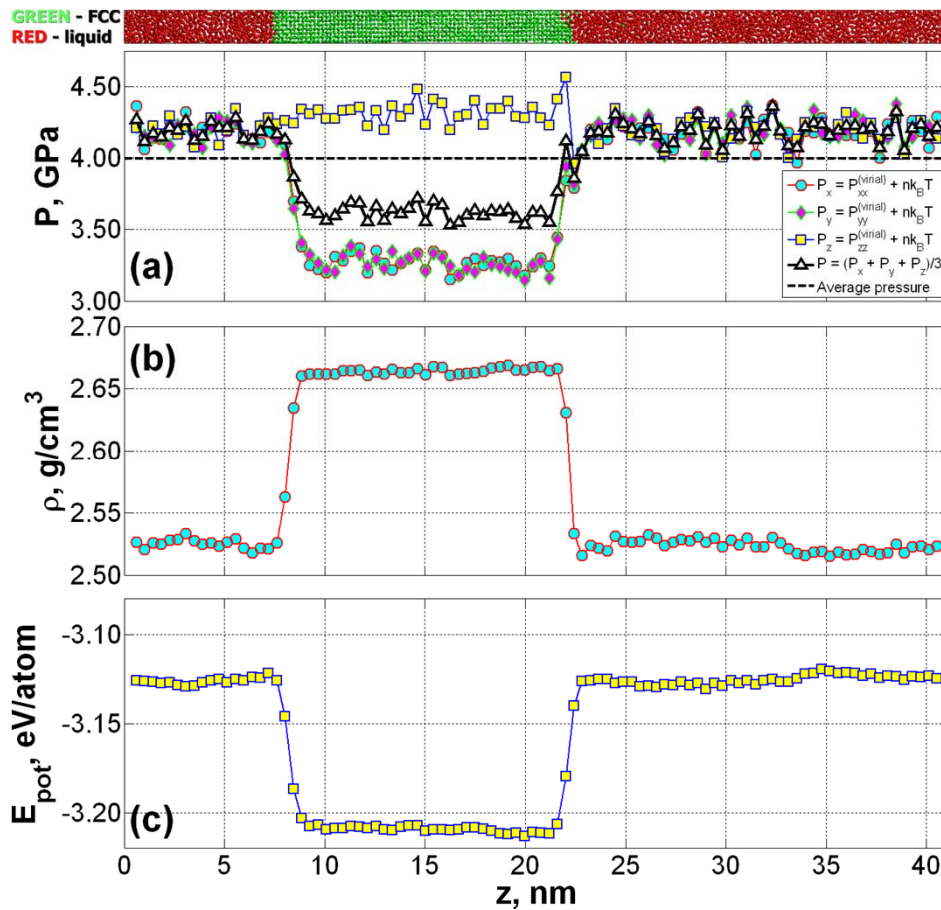


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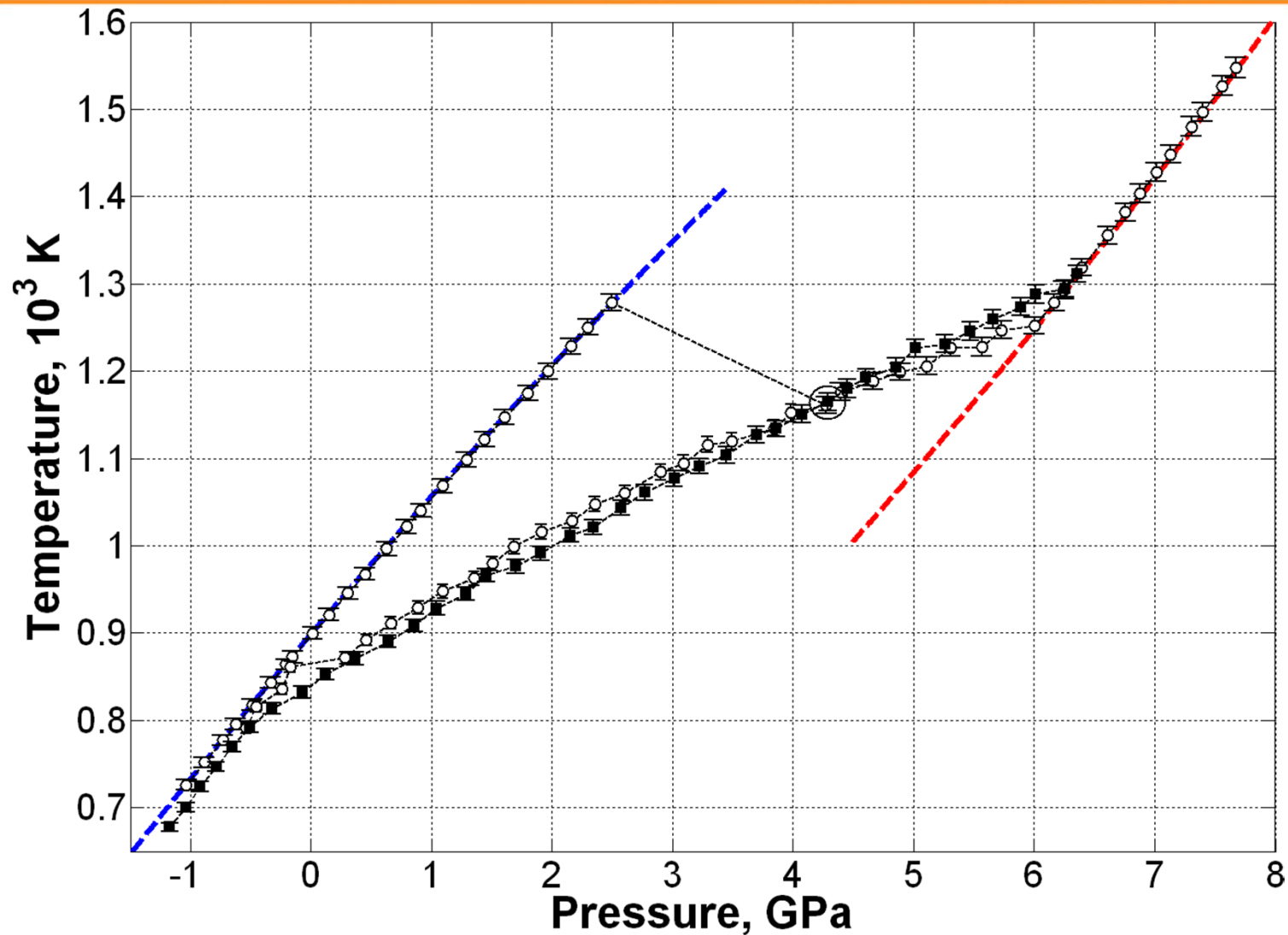


Modified Z-method



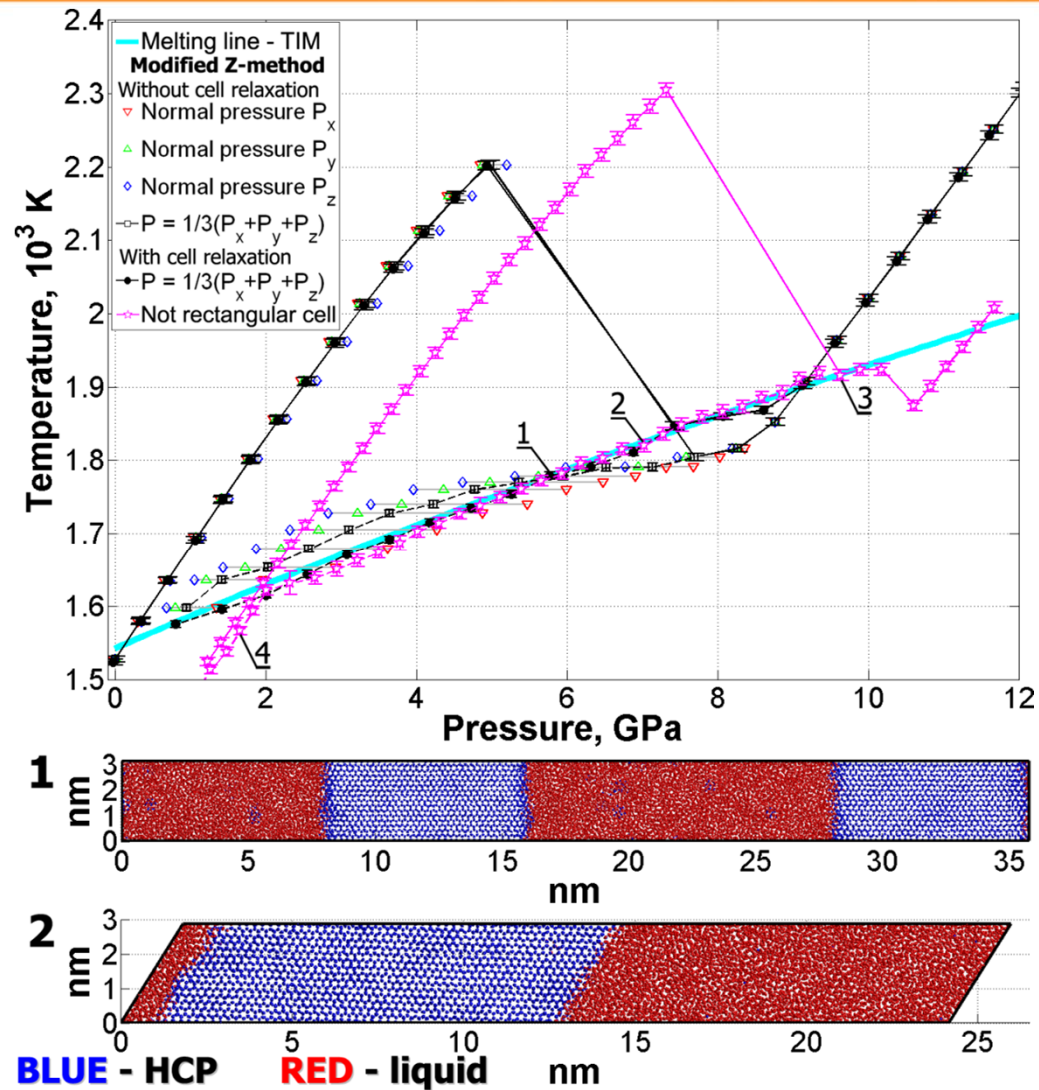


Modified Z-method



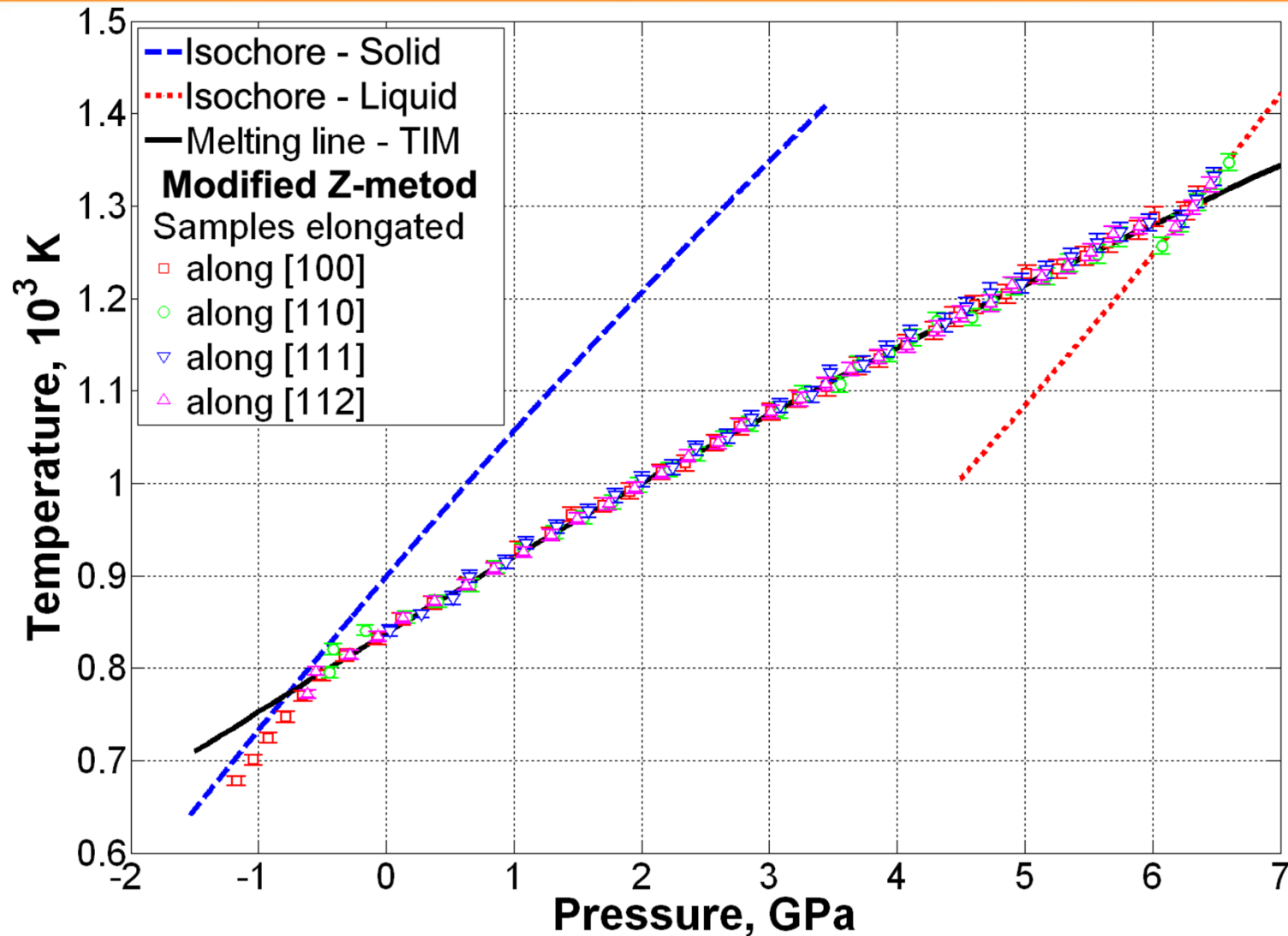


Modified Z-method



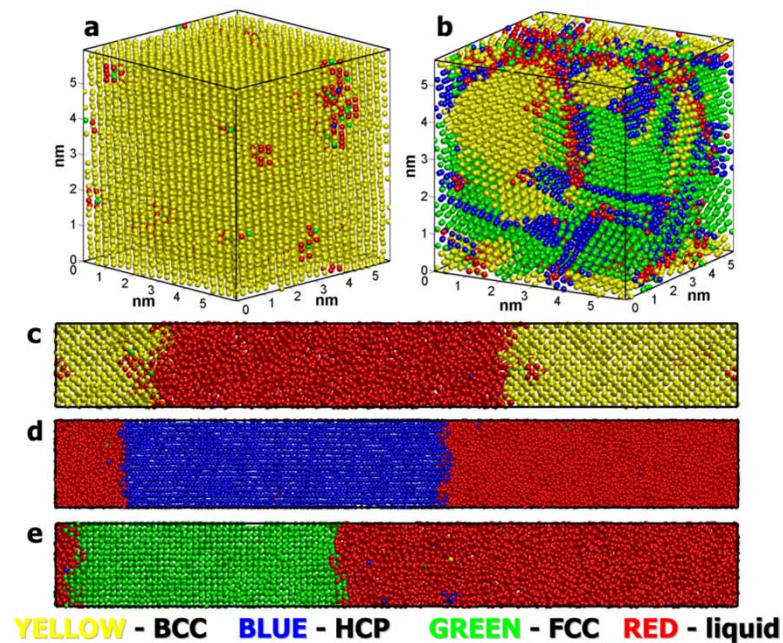
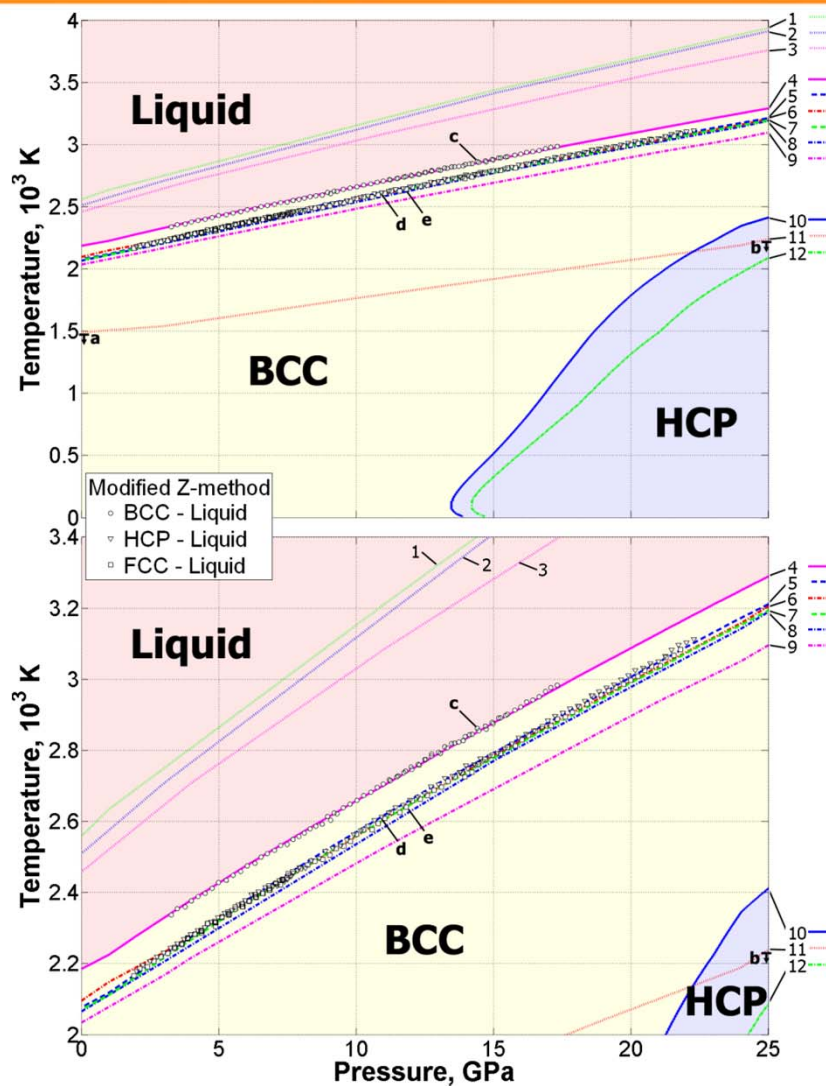


Modified Z-method



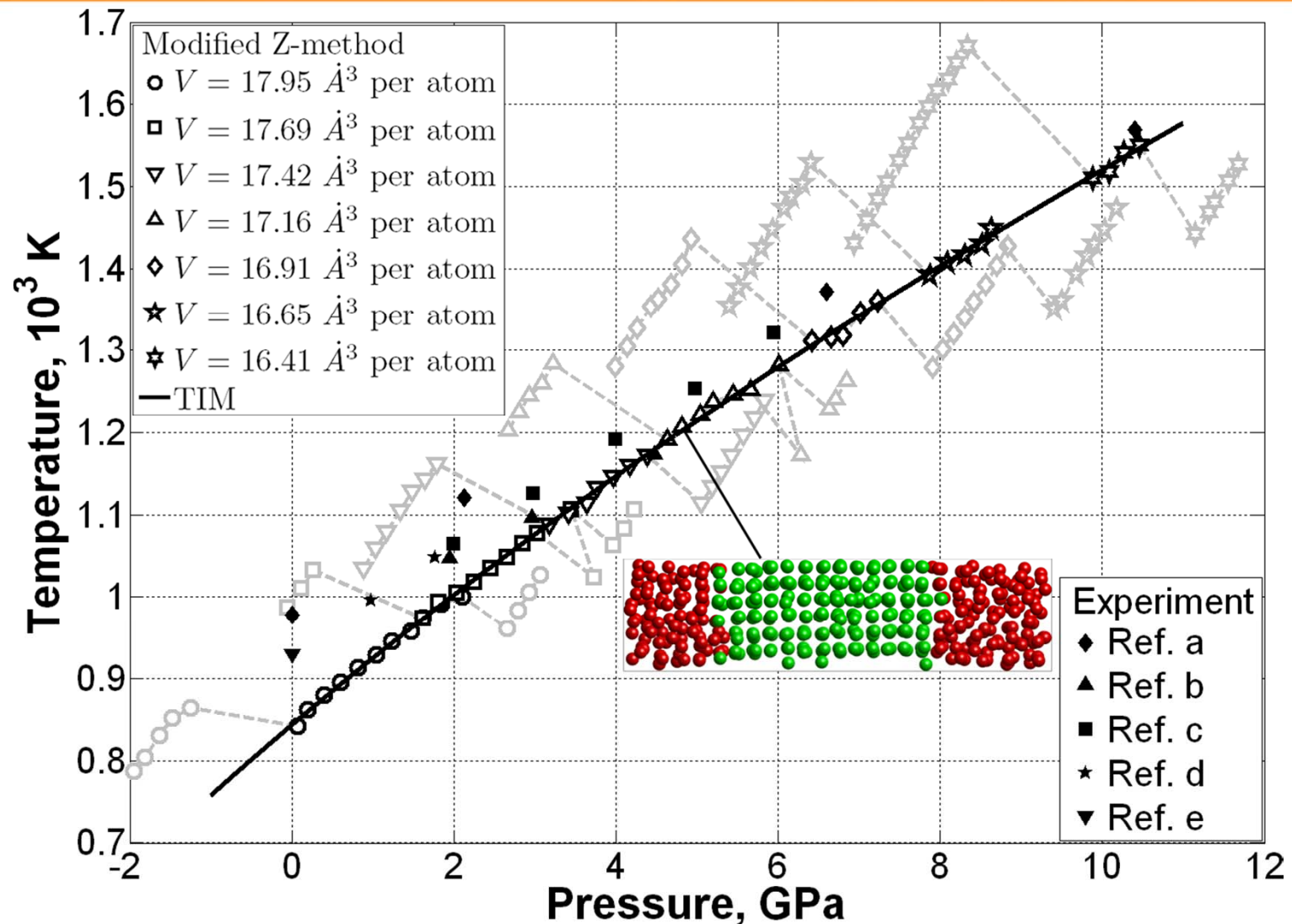


Modified Z-method





Modified Z-method





Solid Entropy Evaluation (SEE) Method



There is a number of methods for evaluation of equilibrium melting curves for a given model of interatomic interaction (empirical classical interatomic potential or *ab-initio* model) in **direct MD simulations**: Heat Until Melts (HUM), Hysteresis Method (HM), Z-method, Modified Z-method, Two Phase Method (TP) or Coexistence Method...

These methods in general are not applicable to the calculation of solid-solid thermodynamic equilibrium curves.

In **the indirect methods** the MD simulations are used to calculate Gibbs thermodynamic potentials $G_{1,2}(P, T)$ of two phases and then to get equilibrium curve $T(P)$ from the equation $G_1(P, T) = G_2(P, T)$.

The indirect method may be subdivided in two groups:

“**Exact**” – for example, Thermodynamic Integration Method (TIM)

“**Model**” – for example, Two Phase Thermodynamics (2PT) method

Solid Entropy Evaluation (SEE) method





Solid Entropy Evaluation (SEE) Method



According to the classical Debye theory of crystals the entropy of a crystal lattice can be calculated as

$$S = Nk_B \left[4D \left(\frac{\theta_D}{T} \right) - 3 \ln \left(1 - \exp \left(-\frac{\theta_D}{T} \right) \right) \right],$$

where θ_D is characteristic Debye temperature which in general is a function of the density and temperature. The characteristic Debye temperature can be calculated in several ways: from the elastic constants of the crystal, from its phonon spectrum, or from the root-mean-square (rms) atomic deviations.

The rms atomic deviations are related to the Debye temperature by

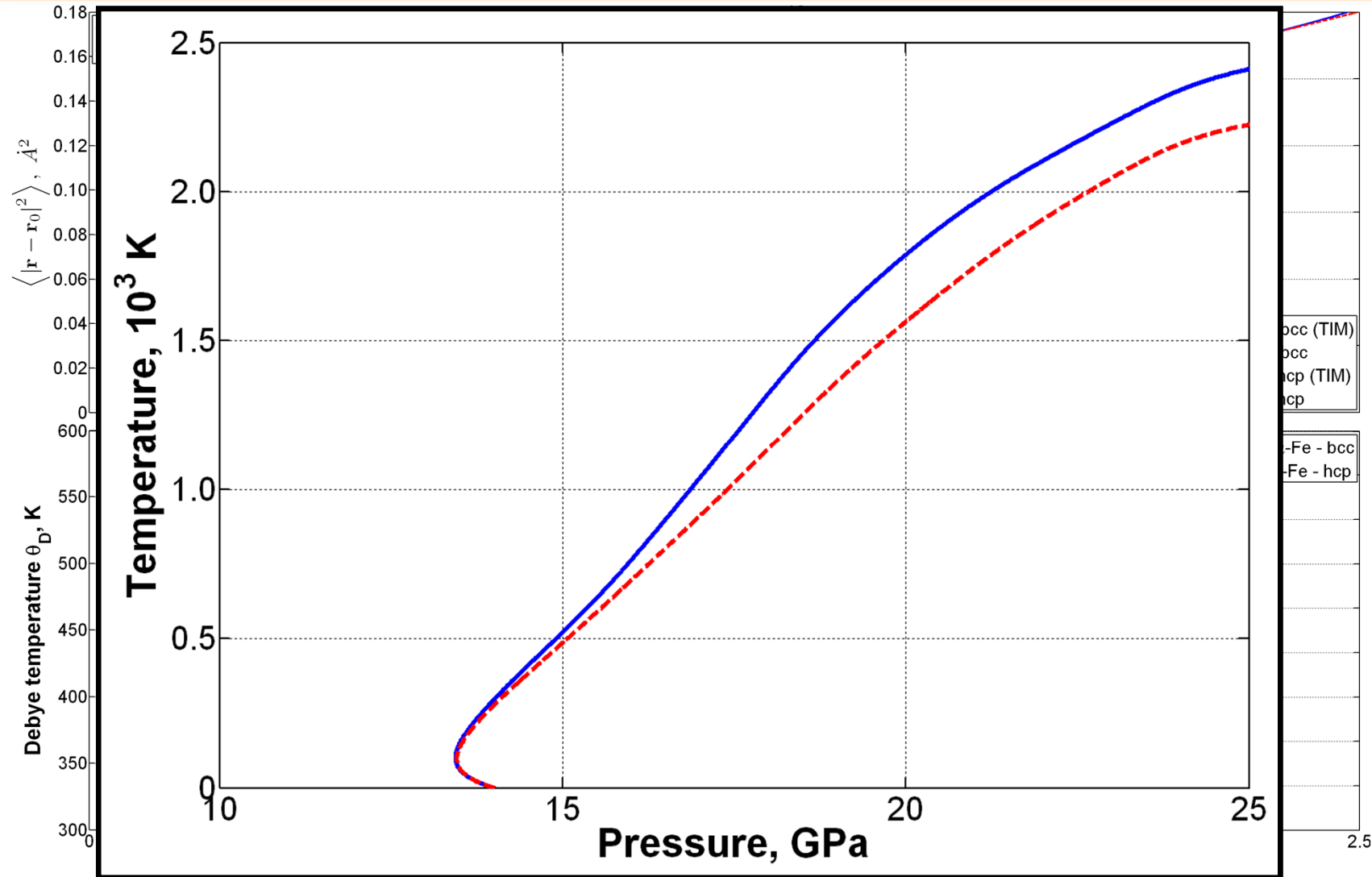
$$\langle u^2 \rangle = \frac{9h^2T}{4\pi^2mk_B\theta_D^2} \left[\frac{\theta_D}{4T} + \Phi \left(\frac{\theta_D}{T} \right) \right].$$

So, performing the rms atomic deviation calculation in simple NVT MD simulation in a state of interest one can estimate entropy and, hence, the thermodynamic potentials.



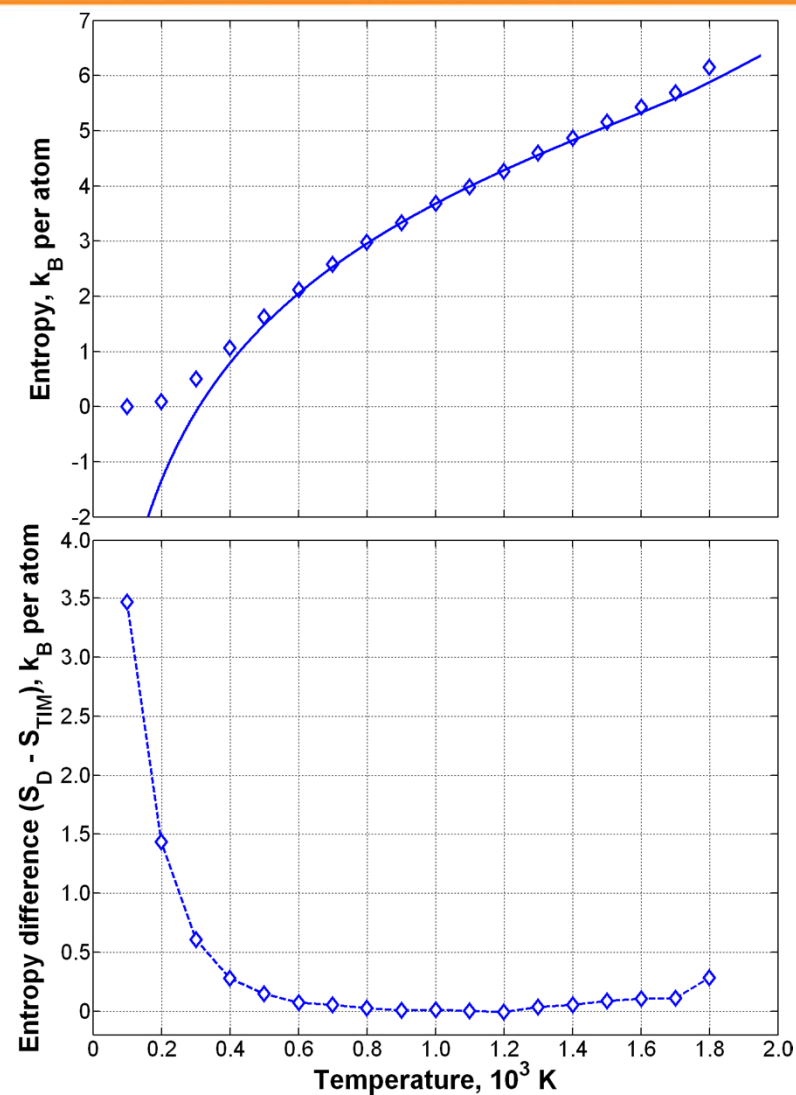
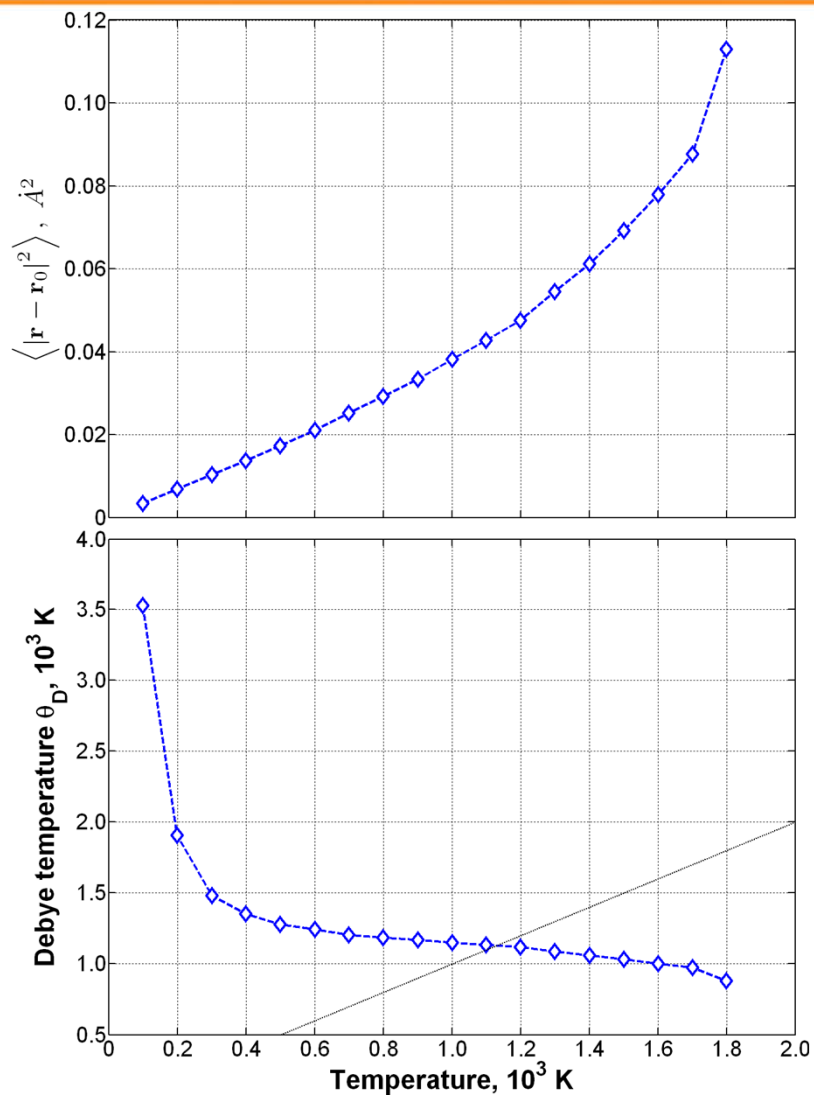


Solid Entropy Evaluation (SEE) Method





Solid Entropy Evaluation (SEE) Method





Conclusion



The capabilities and shortcomings of the modified Z-method (by **S. Wang et al.**, **J. Chem. Phys.** **138 (2016) 134101**) have been investigated. The modified Z-method combines the ease of implementation of the original Z-method with advantages the method of coexistence offers. However, the modified Z-method requires an additional computational procedure. In order to find parameters of the thermodynamic equilibrium of the solid and liquid it is necessary to equalize normal stress components of the sample.

Results of calculations by the modified Z-method with stress equalization are as accurate as those by the thermodynamic integration method but at much lower computational cost and do not depend on the system size.

The elongated calculation cell is not to be necessary shaped as rectangular box. The pressure equalization procedure makes the data independent of the direction of the elongation of the system.

The modified Z-method performs well for the determination of equilibrium melting curves of metastable phases.

A system of $3 \times 3 \times 12$ fcc unit cells (432 atoms) was the smallest for which the calculations were robust.

For details see **A.V. Karavaev et al.**, **Comp. Mater. Sci.**, **124 (2016) 335**.





Conclusion



We proposed a simple and yet accurate method of entropy evaluation for solids in classical MD simulations (Solid Entropy Evaluation (SEE) method). The method is based on the Debye model of crystals. The characteristic Debye temperature is calculated from thermal mean square deviations of atoms from their equilibrium positions.

Our MD simulations demonstrate that rather small samples (couple of hundreds of atoms) are sufficient to provide high accuracy for the calculation of the thermodynamic potentials.

High accuracy of the SEE method is confirmed by the comparison with the results obtained with the thermodynamic integration method.

The applicability of the SEE method is not restricted to semiempirical potentials only. Due to its simplicity the SEE method can be used to calculate ionic contribution to free energy in quantum MD simulations as well.

For details see **A.V. Karavaev and V.V. Dremov, A method of solid-solid phase equilibrium calculation by molecular dynamics, J. Phys.: Condens. Matter 28 (2016) 495201.**

