

Numerical Studies of Melting in Infinite Crystalline Solids

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Abstract

We present preliminary results on numerical studies of melting in two and three-dimensional infinite crystalline solids. We used a Lennard-Jones 12-6 interatomic potential in a Molecular Dynamic simulation that reproduces Isothermal Isobaric Ensembles. Enthalpy, pair distribution function, orientational correlation function, elastic constants and other quantities are computed in systems with periodic boundary conditions and up to 702,464 particles. Comparisons of our results with Kosterlitz, Thouless, Halperin, Nelson and Young's theoretical prediction of an intermediate Hexatic Phase in 2D are provided. In addition we discuss and compare previous numerical and theoretical results on melting- superheating in two and three-dimensional systems.

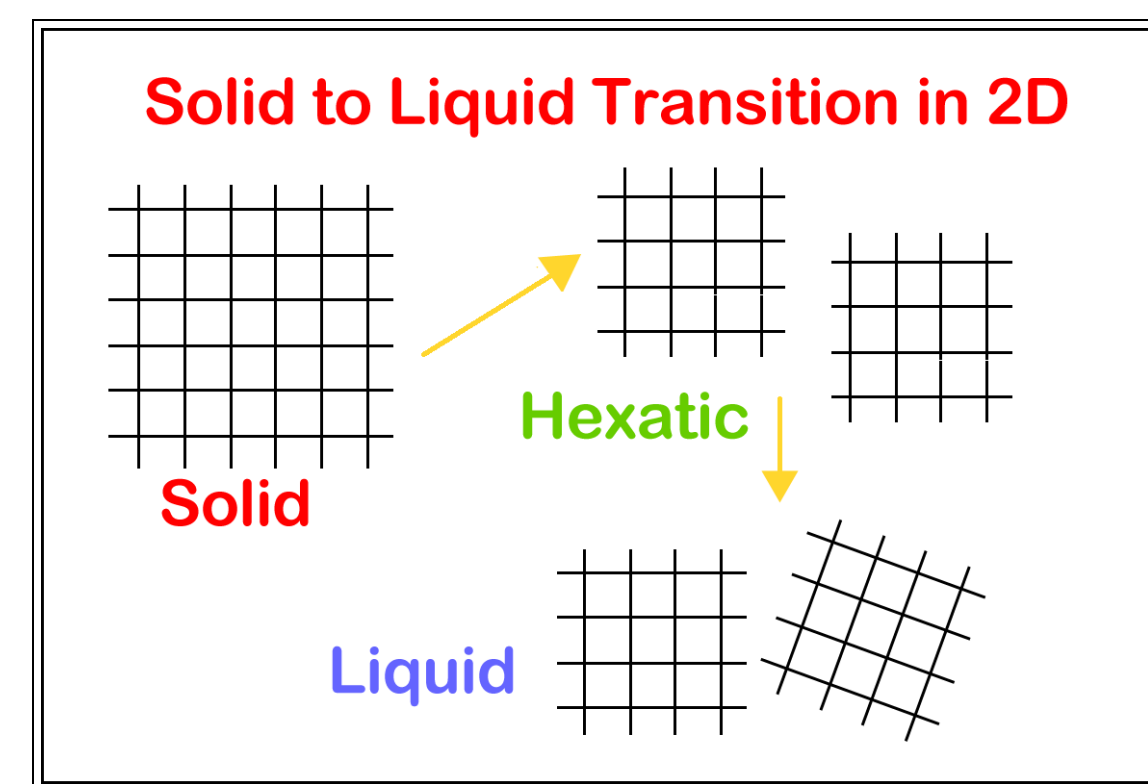
Introduction

Solid to liquid transition is one of the most common phenomena in nature. However, a detailed description of this process under different conditions is still unknown. In the past several years it has become clear that thermodynamic melting begins at the surface of the solid. If the surface is suppressed, for instance, by coating a specimen with a different material of higher melting temperature, superheating can be achieved. It has been proposed that an upper limit to the metastability of a superheated solid would be provided by a sudden proliferation of thermally excited dislocations.

In 2D, a defect-mediated melting theory by KTHNY⁽¹⁾ predicts that thermally excited dislocations and disclinations do indeed drive two continuous phase transitions from a solid, to a new hexatic phase, and finally to a liquid.

In 3D, different theories have been proposed and a hierarchy of stability limits has been established⁽⁵⁾. In particular, a theoretical work by Arias and Lund⁽²⁾ (using an approach similar to that used by KTHNY) predicts a continuous phase transition where the shear modulus vanishes as a power function of temperature.

In the present work we compare our results from molecular dynamics simulations with these theoretical predictions. We have first reobtained, using different equations of motion, results presented by Chen et al.⁽⁴⁾ in 2D. In addition we computed elastic constants and have studied 3D systems with up to 702,464 particles.



Method

We have developed a parallel molecular dynamic code that solves the modified Newton's equations using a Lennard-Jones Potential. In order to reproduce the isothermal isobaric ensemble (to avoid coexistence of different phases) the system is extended in such a way that when integration over extra variables is carried out, the microcanonical partition function of the extended system becomes the isothermal-isobaric partition function in the real system⁽³⁾.

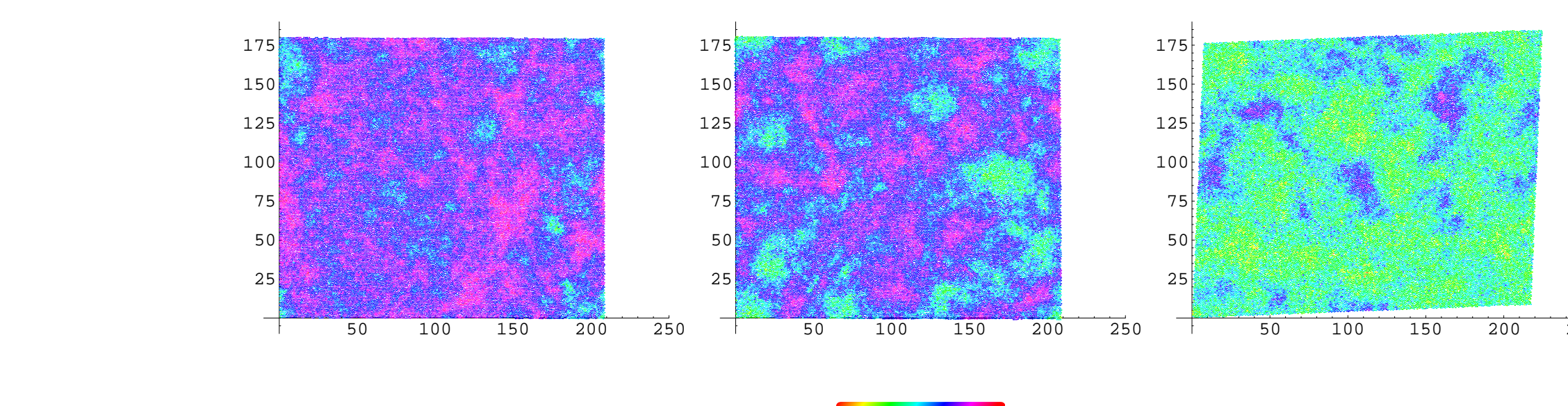
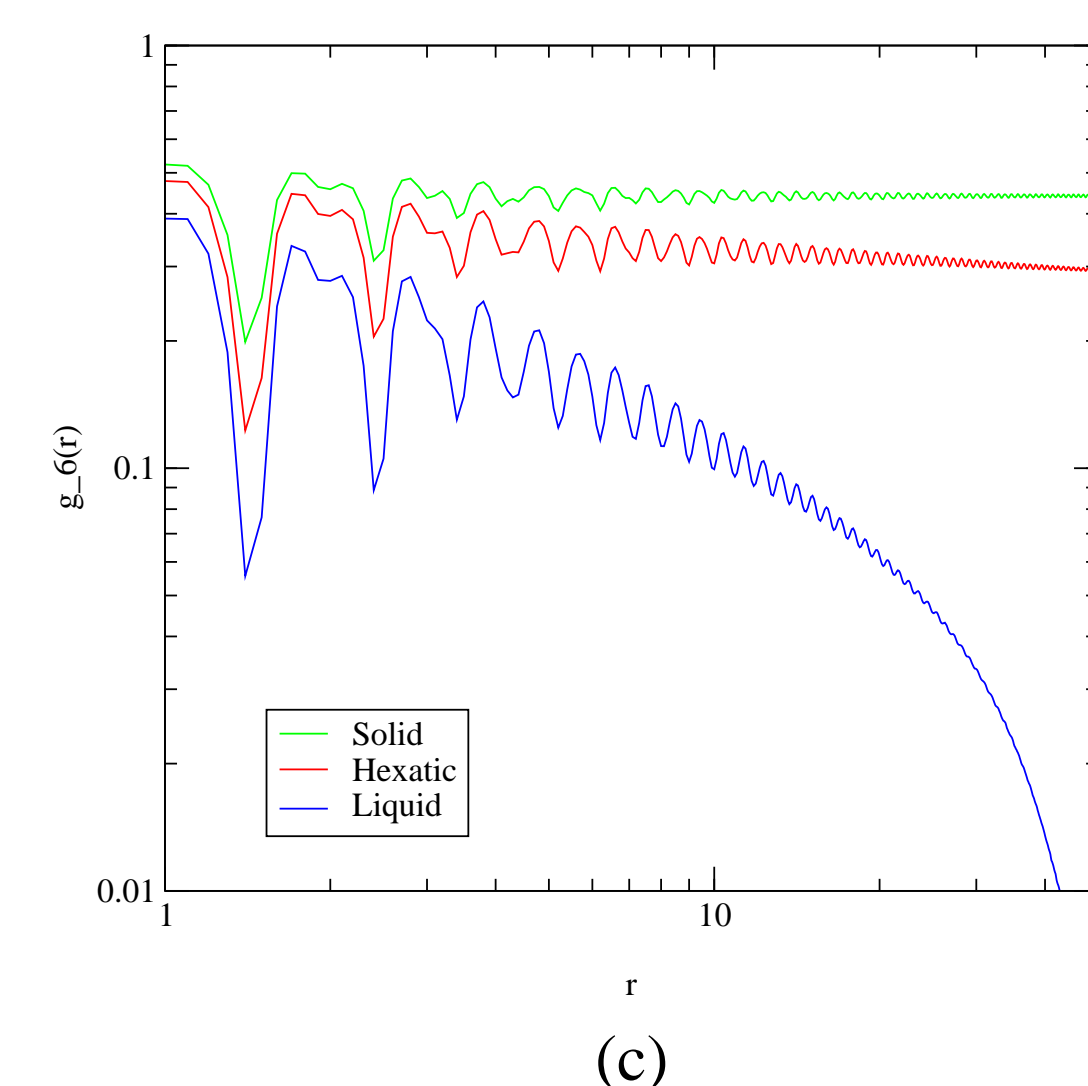
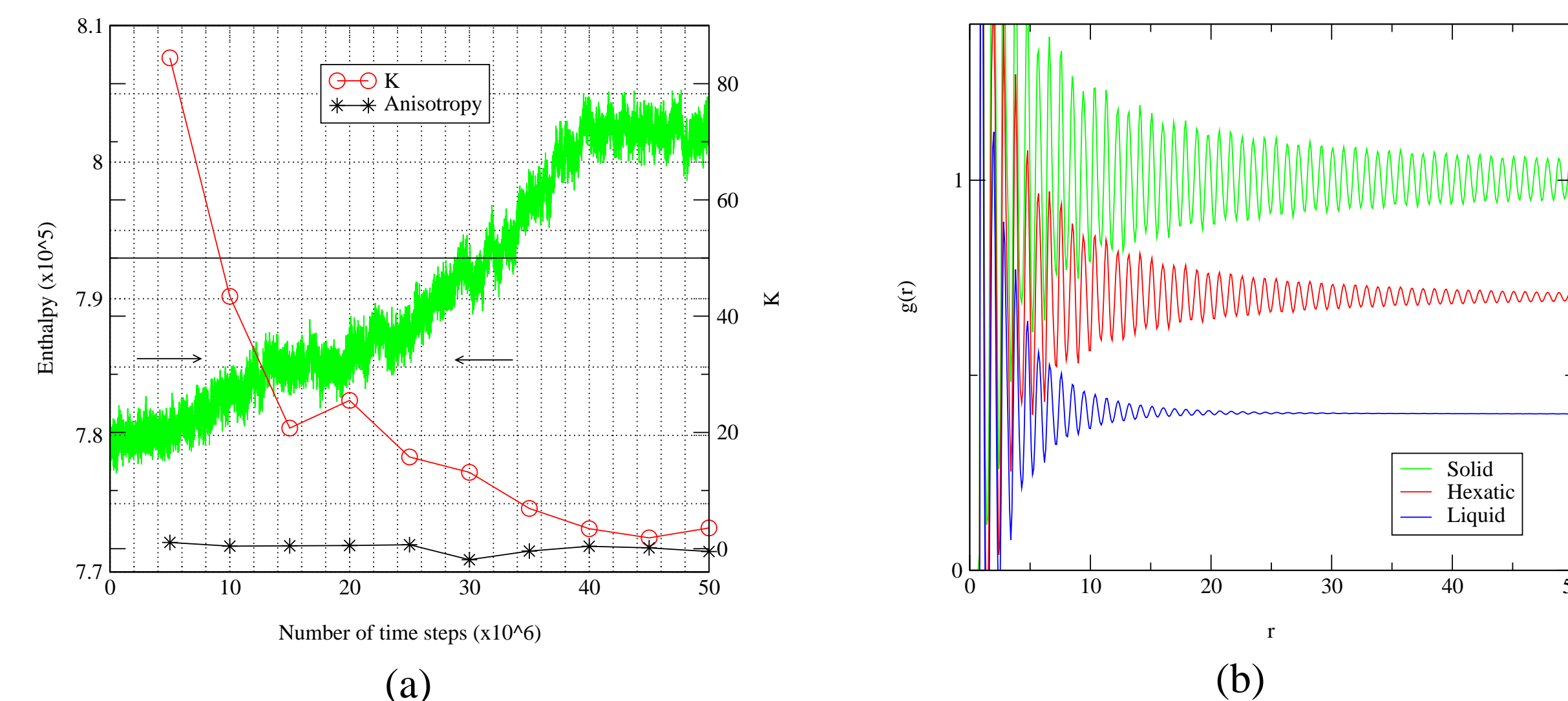
The modified equations of motion are solved using a standard 5 value Gear predictor corrector algorithm with periodic boundary conditions in a shape-varying box. We also employ a cutoff for our potential that permits the use of a Verlet neighbour list created using a cell structure in a parallel configuration. Our results are expressed in the following units (Argon): a unit of temperature ~ 120.6 K; a unit of energy ~ 0.0104 eV; a time step ~ 34 fms; a unit of pressure ~ 42 MPa; a unit of length ~ 3.4 Å.

Equations of Motion

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + \frac{\mathbf{p}_{90}}{W_{90}} \mathbf{r}_i + \frac{p_\epsilon}{W} \mathbf{r}_i \\ \dot{\mathbf{p}}_i &= \mathbf{f}_i - \frac{\mathbf{p}_{90}}{W_{90}} \mathbf{p}_i - \left(1 + \frac{D}{DN}\right) \frac{p_\epsilon}{W} \mathbf{p}_i - \frac{p_\xi}{Q} \mathbf{p}_i \\ \dot{V} &= \frac{D V p_\epsilon}{W} \\ \dot{p}_\epsilon &= DV(P_{\text{int}} - P_{\text{ext}}) + \frac{D}{DN} \sum_{i=1}^N \frac{p_i^2}{m_i} - \frac{p_\xi}{Q} p_\epsilon \\ \dot{\mathbf{h}}_0 &= \frac{\mathbf{p}_{90} \mathbf{h}_0}{W_{90}} \\ \dot{\mathbf{p}}_{90} &= V(\mathbf{P}_{\text{int}} - \mathbf{I} P_{\text{ext}}) - \frac{V}{D} \text{Tr} \left[\mathbf{P}_{\text{int}}^{\leftrightarrow} - \mathbf{I} P_{\text{ext}} \right] \mathbf{I} - \frac{p_\xi}{Q} \mathbf{p}_{90} \\ \dot{\xi} &= \frac{p_\xi}{Q} \\ \dot{p}_\xi &= \sum_{i=1}^N \frac{p_i^2}{m_i} + \frac{p_\epsilon^2}{W} + \frac{1}{W_{90}} \text{Tr} \left[\mathbf{P}_{90}^{\leftrightarrow} \mathbf{p}_{90} \right] - (DN_f + D^2) kT \end{aligned}$$

Two Dimensions

In order to identify the hexatic phase predicted by KTHNY we measured the enthalpy of the system. We also computed the pair distribution function and the orientational correlation function at three different stages of a simulation of 36,864 atoms in 2D. We followed a procedure similar to that used by Chen et al.⁽⁴⁾ and obtained the same results using different equations of motion. In addition, we computed elastic constants and the average potential energy per particle. The initial condition was a thermalized hexagonal lattice. **Pressure was set at $P = 20$ and temperature at $T = 2.16$. The cutoff radius was $r_c = 4$.**



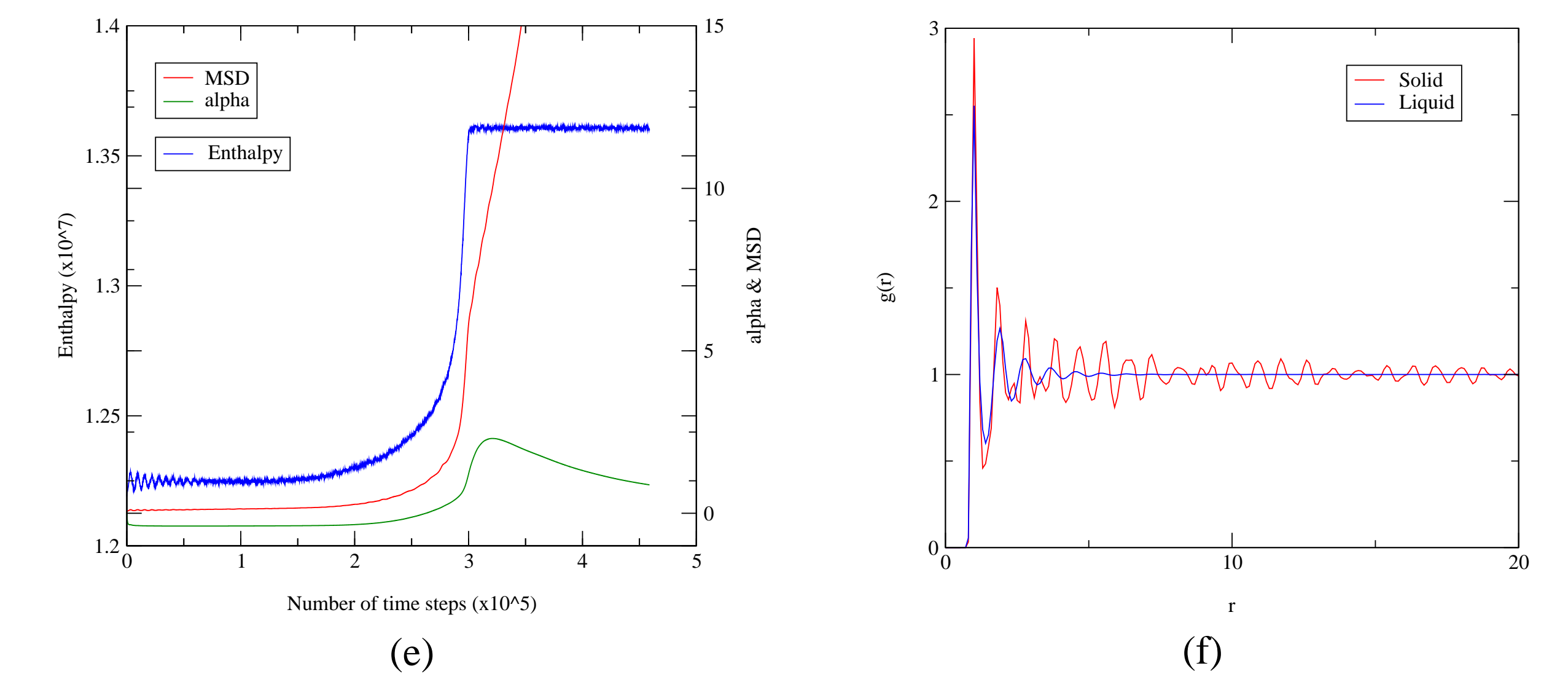
(d) Average potential per particle at three different stages (at 2×10^5 , 16×10^5 and 48×10^5 time steps). Color code: -0.45 left of the bar, -0.81 right of the bar. The appearance of defects in the lattice can be observed as the system evolves to a liquid phase.

Preliminary Results

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Three Dimensions

In three dimensions we have computed the enthalpy, the non-gaussian parameter and the mean square deviation in systems with up to 702,464 particles. Using the pair distribution function we identified each phase. Our results seem to agree with those presented in⁽⁵⁾.



(e) The transition between a solid and a liquid in 3D is detected by a sudden change in the enthalpy (blue) and the slope of MSD (red). Non-gaussian parameter ($\alpha = \frac{D \langle \Delta r^4 \rangle}{(D+2) \langle \Delta r^2 \rangle^2} - 1$) behaves in agreement with (5). (f) The pair distribution function confirms the nature of each phase.

(a) A metastable state can be observed in the enthalpy (green, for about $\sim 5 \times 10^6$ time steps). The parameter $K = 4\mu(\mu + \lambda)/(2\mu + \lambda)$ ⁽⁶⁾ was calculated using a fluctuation formula for the elastic constants⁽⁷⁾: $c_{ijkl}^{-1} = \beta V_0 (\langle \epsilon_{ij} \epsilon_{lk} \rangle - \langle \epsilon_{ij} \rangle \langle \epsilon_{lk} \rangle)$. The anisotropy factor was calculated using $2C_{44}/(C_{11} - C_{12})$. The horizontal line corresponds to K predicted by KTHNY.

(b) & (c) The pair distribution function and orientational correlation function for three different stages of the simulation. Typical behavior of solid, hexatic and liquid phases is observed

Discussion and Future Work

We have presented preliminary evidence of a hexatic phase in 2D solid to liquid transition. The behaviour of elastic constants seems to contradict theoretical predictions. However, more studies concerning the role of pressure are needed in order to get a definitive answer⁽⁸⁾.

In three dimensions, our results seems to favor a first order phase transition scenario. However, computation of the Gibbs free energy and use of a larger system is required in order to compare our results with theory.

References and Acknowledgments

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