Soft Matter

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Supplemental Material

Supplemental material for:

"Microphase separation as the cause of structural complexity in 2D liquids"

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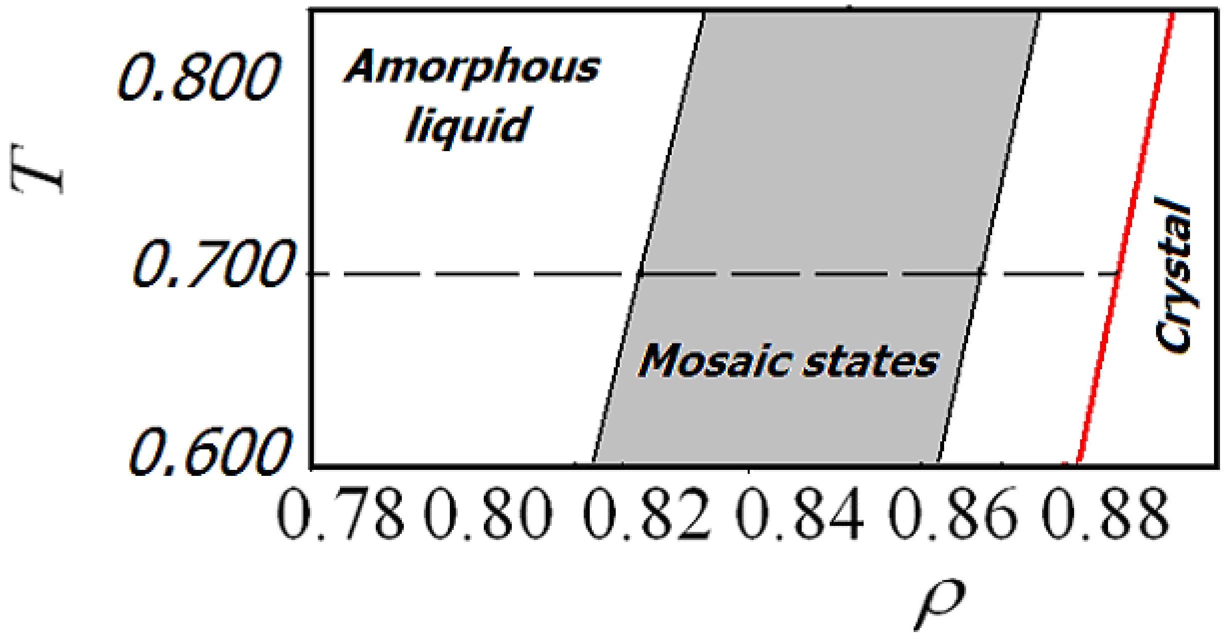

Figure 1S. Mosaic states in the temperature-density thermodynamic plane.

Mosaic states of the *2D* Lennard-Jones liquid are only found [13] in a narrow band of states in the $(T\text{–}\rho)$ thermodynamic plane (see Fig. 1S). The boundaries of this band are approximately parallel to the melting (solidus) line that is close but outside of the band. Isotherms T=const and isochors ρ=const cross the band. Along an isotherm, the crystalline fraction of the liquid monotonously increases with increasing density ρ as described in the main text (Fig. 2 and 3). For T=0.700, the *CL-AL* coarsened mosaics are shown in Fig. 2S. In the uniform liquid at ρ=0.60, small (3-5 particles) clusters of *CL* particles appear as rare and short-living fluctuations. At ρ=0.78, the liquid at any time includes ~10% of *CL* particles (Fig. 3), but the lifetimes of the small *CL* aggregates is of the order of particles vibration period in these aggregates [12,13]. Fig. 2S shows the coarsened *CL-AL* mosaic for T=0.700, ρ=(0.82 – 0.87) , in these pictures *CL* particles are represented by red and *AA* particles by yellow circles. At ρ<0.83, crystallites are spatially separated islands of *CL* particles in a matrix of *AA* particles (Fig. 2S, upper row); with ρ increasing, both the sizes of largest crystallites and the fraction of *CL* particles monotonously increase. Between ρ=0.83 and ρ=0.84 the crystalline (and, correspondingly, the complimentary amorphous) fraction of the *2D* liquid reaches 50%, the percolation threshold for 2D random percolation. [1S]. In a finite system, the percolation point is replaced by a percolation range of densities [1S], so the percolation density ρ_{perc} ~0.83-0.84 is rather a rough approximation. Typical large crystallites and also large amorphous clusters at densities close to-percolation include ~100 particles. At densities ρ>0.84, *CL* particles form a multi-connected crystalline matrix hosting islands of *AA* particles. At ρ=0.90 there are only few very small (less than 10 particles) *AL*-clusters representing vacancies and dislocations in the crystal.

A remarkable feature of the configurations in Fig. 2S is an approximate symmetry with regard to a simultaneous change $CL \leftrightarrows AL$ and $\delta\rho^* \leftrightarrows -\delta\rho^*$, $\delta\rho^*=(\rho^* - \rho^*_{perc}) << \rho^*_{perc}$). The sampled configurations only qualitatively support the assumption of this *CL-AL* symmetry, to prove this assumption one needs to compare probabilities of corresponding configurations – a task not yet performed. The transformation here bears an apparent resemblance to the $m \leftrightarrows -m,\ h \leftrightarrows -h$ transformation for the classical ferromagnetic Ising model (with $m(r)$ =±1 as the local Ising variable and h the magnetic field). However, while in the Ising model the symmetry follows from the form of the Hamiltonian of the model, the $CL \leftrightarrows AL$ symmetry may be only approximate. This situation is generic in the Ising (scalar field φ(r)) universality class of critical behaviour: renormalization of the

Hamiltonian to exclude the molecular-scale degrees-of-freedom (see, for example. [2S]) results in an effective Hamiltonian that parametrically depends on thermodynamic state.

In the mosaic range of densities $\rho = 0.82–0.85$, an isolated cluster of *CL* or *AL* particles includes many tens of particles (see Fig.3). We assume that this size represents the elementary size *R* occupied by either structure. As discussed in the main text, the size of a *CL* cluster is limited by the screening length that is a function of density and temperature. An interesting but open question is long-range correlations between the positions of CL clusters near their percolation. To study these correlations and the percolation-related singularities (for example the expected singularity in the length of the *CL– AL* interface) one needs a system of a size much larger than the one studied here: systems of $N{\sim}10^4$ particles are large enough to allow the measurements of the internal properties of clusters but too small to study long-range correlations between *CL* clusters.

Supplemental References

1S. D. Stauffer, A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis Ltd: London, 1994).

2S. A.Z. Patashinskii, V.L. Pokrovskii, *Fluctuation Theory of Phase Transitions* (Pergamon, Oxford 1979).