# FLUCTUATIONS AND LOCAL STRUCTURE IN TWO-DIMENSIONAL LENNARD–JONES LIQUID*

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We quantify the concept of ensembles of atoms' fluctuations for 2D liquids close to and in the two-phase coexistence region, using a probabilistic method of local structure analysis. Two ensembles are studied: gas-like independent gaussian fluctuations (IGF) A.C. Mituś, A.Z. Patashinski, A. Patrykiejew, S. Sokolowski, *Phys. Rev.* **B66**, 184202 (2002) and a truly solid-like fluctuations (SF) characteristic for a two-dimensional (2D) triangular solid. For a 2D Lennard–Jones (LJ) system simulated using Monte Carlo and molecular dynamics methods those ensembles yield a statistically reliable description of local solid-like structures in the two-phase region. Both ensembles undergo a spectacular breakdown as the density changes. A hypothetical relation of this breakdown to the behaviour of the heat capacity in the two-phase region is proposed.

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## 1. Outline of the problem

The main object of our study are the fluctuations of the atoms in a two-dimensional (2D) Lennard–Jones (LJ) liquid. For historical reasons we interpret the occurring phenomena using the terms of liquidus, solidus and coexistence region, typical for melting taking place via I-order phase transitions [2]. This by no way excludes the possibility of KTHNY scenario [3–7], in particular in light of recent simulations of a liquid of hard disks [8].

In a recent paper [1] we have quantified the concept of a sudden crossover between solid-like and non-solid-like ensembles of the fluctuations of the solid-like atoms (see below) in a liquid of hard disks and in the 2D liquid of atoms interacting via LJ potential. Local structure analysis, based on probabilistic concepts and mathematical statistics methods, has lead to an interesting physical picture of various 2D liquids (LJ [1,9], hard disks [1,10], liquid with quantum degrees of freedom [11]) as locally solid-like ordered systems. Namely, in a liquid close to the coexistence region, some of 7-atom clusters display structural properties similar to those in a fluctuating 2D triangular lattice; the central atoms of those clusters are called solid-like. The concentration of solid-like atoms close to the liquidus line constitutes approximately 0.5. More details can be found in a review paper [12].

The local solid-like structure of 2D LJ liquid and of a liquid of hard disks was successfully described using an ensemble of independent gaussian fluctuations (see Section 2.2) in wide temperature/density intervals on the liquid side of the coexistence regime [1]. Inside the coexistence regime, a spectacular breakdown of the IGF ensemble occurred: statistically independent fluctuations gave way to more collective fluctuations. However, no further speculations about the character of those fluctuations were made.

The aim of this paper is to present some preliminary results supporting a hypothesis that the fluctuations of solid-like atoms in the coexistence regime of 2D liquids are truly solid-like in nature.

## 2. Local structure analysis (LSA)

### *2.1. Probabilistic formalism of structural invariants*

Local order in a 2D system in the neighborhood of an atom located at the point $\vec{r}$ is described by 2D local version of bond-order parameter of Nelson *et al.* [9,13,14]:

$$Q_{6m}(\vec{r}) = \frac{1}{N_0} \sum_{i=1}^{N_0} Y_{6m}(\pi/2, \phi_i)\,, \tag{1}$$

where $Y_{6m}(\theta, \phi)\,(m = -6, \ldots, 6)$ denotes the spherical harmonic function, the sum is taken over the $N_0$ nearest–neighbors of the atom located at the

point $\vec{r}$ and the pair of polar and azimuthal angles, $(\theta_i, \phi_i)$, describes the direction between the central atom $\vec{r}$ and its $i$-th nearest neighbor. The invariant $Q(\vec{r})$ for $(N_0 + 1)$-atom cluster with central atom at $\vec{r}$ is defined as [9, 14]:

$$Q^2(\vec{r}) = \frac{4\pi}{13} \sum_{m=-6}^{6} |Q_{6m}(\vec{r})|^2. \tag{2}$$

In the spirit of the method of analysis of local 2D structures [1, 9–11], we use two patterns as the candidates for the local structure in the system. Pattern $\Gamma_6$ is a 2D hexagon, *i.e.* a $N_0+1 = 7$-atom cluster from 2D triangular lattice. The nearest-neighbor distance is taken as the unit of length. Pattern $\Gamma_5$ is a 7-atom cluster centered around a 5-coordinated atom (disclination in 2D triangular lattice). Fluctuating patterns $\Gamma_6$ and $\Gamma_5$ are described in terms of the probability density functions (PDF) $\rho_6(Q)$ and $\rho_5(Q)$, which depend on the choice of an ensemble of the atoms' fluctuations.

The statistics of invariant $Q$ in the trial configuration is described by PDF $\rho(Q)$ which is approximated by the histogram of random variable $Q$, calculated from the set of data $\{Q(\vec{r}_i)\}$, $i = 1, \ldots, N$, where $N$ denotes the total number of the atoms in the configuration.

The analysis of local structures is done using the methods of mathematical statistics [9]. We assume that $\rho(Q)$ depends linearly on PDFs $\rho_k(Q)$ $(k = 5, 6)$:

$$\rho(Q) = \sum_{k=5,6} c_k \, \rho_k(Q) \, . \tag{3}$$

The "best" decomposition (3) is obtained by maximizing the significance level

$$\alpha(c_5, c_6), \; (c_5 + c_6 = 1, c_5, c_6 \geq 0) \, ,$$

calculated from $\chi^2$-test (see, *e.g.*, in Ref. [15]) verification of the hypothesis which states that the data corresponding to the left-hand side and the right-hand side of (3) are drawn from the same distribution. Very small values of $\alpha$ (of order of $10^{-6}$ and smaller) indicate that the decomposition (3) is statistically not reliable. Significance level $\alpha$ plays a central role in our analysis of ensembles of fluctuations. More details the interested reader can find, *e.g.*, in [1, 12, 16].

### *2.2. Model ensembles of fluctuations*

In this paper two ensembles of atoms' fluctuations are studied. The first one [1, 9–11] uses independent gaussian fluctuations for the modeling of the fluctuations of the atoms. Each of the six neighbors of the central

particle fluctuates independently of the other atoms, according to a gaussian distribution

$$P(\delta \boldsymbol{r}; \xi) = \frac{1}{\xi\sqrt{\pi}} \exp\left[-\frac{(\delta \boldsymbol{r})^2}{\xi^2}\right], \tag{4}$$

with random displacement vectors $\delta\mathbf{r}$ and root-mean-square (r.m.s.) displacement $\xi$. The resulting PDFs $\rho_6(Q,\xi)$ and $\rho_5(Q,\xi)$ for $\Gamma_6$ and $\Gamma_5$, respectively, are dependent on the amplitude $\xi$ of the fluctuations.

The second ensemble accounts for solid-like fluctuations (SF) present in a 2D solid with triangular lattice. Their characteristic feature are strongly developed long-wavelength fluctuations, leading to collective movements of small parts of a system as a whole (the role of long-range fluctuations in restoring, in the thermodynamic limit, of translational symmetry in 2D solids was established long ago by Peierls [17] and Landau [18]; see also in [19]). In the present study we calculate the corresponding PDFs $\rho_6(Q)$ from the simulations in the solid phase, see next Section. Those functions depend on the temperature and density: $\rho_6(Q) = \rho_6(Q; T, \rho)$.

## 3. Two-dimensional Lennard–Jones liquid

### *3.1. Simulations*

We have simulated a 2D system of $N = 2500$ atoms interacting via Lennard–Jones potential $v_{\mathrm{LJ}}(r)$

$$v_{\mathrm{LJ}}(r) = 4\,\epsilon\,\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{5}$$

at $T^* \equiv k_{\mathrm{B}}T/\epsilon = 0.7$. Here $k_{\mathrm{B}}$ stands for Boltzmann constant and $T$ for temperature. A standard NVT molecular dynamics (MD) method [20] with velocity Verlet algorithm was used; the time step was $t_0 = 0.064\tau$, where the time unit $\tau = 0.3113$ ps. Long-range corrections for potential energy and pressure were calculated; potential cutoff was chosen to be 2.5 $\sigma$. The equilibrium characteristics were sampled after 5000 equilibration steps. The local structure parameters were averaged over 20 configurations.

Melting at $T^* = 0.7$ was also studied via a standard NVT Monte Carlo method [20,21] for a system of 1024 atoms. For thermalization $2\times10^6$ Monte Carlo steps (MCS) (1 MCS corresponds to one sweep over all particles) were used and the equilibrium parameters were calculated using $2 \times 10^6$ MCS. In Fig. 1 we present the plot $d(\rho^*)$ of the dependence of the distance $d$ between two chosen particles, being initially nearest neighbours, on the reduced density $\rho^* = \sigma^2\,\rho$. The data were averaged over 2000 configurations after equilibration. We find that a dramatic increase of $d$ occurs close to the density $\rho^* = 0.87$, in agreement with MD results [1]. Thus, we assume

that the density $\rho^* = 0.87$ corresponds to the solidus line at $T^* = 0.7$. A short discussion of this topic is given in Section 4. The PDFs $\rho_6(Q, T^*, \rho^*)$ for $T^* = 0.7$ and $\rho^* \geq 0.87$ (*i.e.*, for a solid) were calculated from MC simulations.

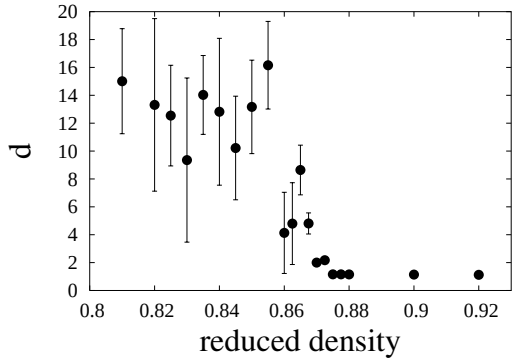


Fig. 1. Plot of an average distance between two atoms (see text) against reduced density for a 2D LJ system at $T^* = 0.7$ close to the two-phase region.

### *3.2. Local structure analysis*

A typical PDF $\rho(Q)$ calculated from MD simulations at $T^* = 0.7$, $\rho^* = 0.82$ is shown in Fig. 2. The results of the decomposition (*cf.* (3)) of $\rho(Q)$ into patterns fluctuating according to IGF [1] and SF ensembles are shown in Fig. 3. In the latter case, we have used the function $\rho_6(Q; T^*, \rho^*)$ calculated at $\rho^* = 0.87$, *i.e.*, at the lowest density corresponding to the solid phase. In both cases the non-solid-like component of local structure was described by $\rho_5(Q, \xi)$. The vertical lines denote the boundaries (liquidus and solidus) of the coexistence region found via LSA in [1].

The results are as follows. Similarly as in the case of IGF ensemble [1], the reliability of the decomposition using SF ensemble undergoes a dramatic change. This time, however, the decomposition is not reliable on the liquidus line ($\rho^* = 0.825$), where the significance level is low: $\alpha < 10^{-6}$. This means that the fluctuations of the atoms forming local solid-like structures (*i.e.*, solid-like atoms) cannot be described in a satisfactory way via solid-like SF ensemble; IGF ensemble, on the contrary, can be safely used. On the other hand, close to the solidus line ($\rho^* = 0.87$) the significance level $\alpha$ takes values larger than 0.1, which implies that SF ensemble is a good candidate for the description of the fluctuations of solid-like atoms. This time, IGF ensemble is not reliable since the corresponding significance level drops below $10^{-6}$. We conclude that in the coexistence region a crossover between IGF and SF ensembles takes place. Some comments on the size-dependence of significance analysis are given in the next section.

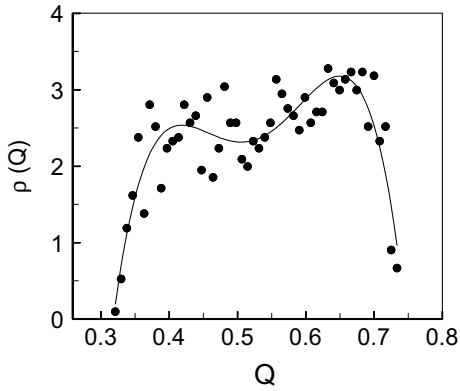


Fig. 2. A typical PDF $\rho(Q)$ calculated from one configuration of a 2D LJ system of 2500 atoms at $T^* = 0.7$, $\rho^* = 0.82$. Solid line (fourth-order polynomial fit) serves as a guide for an eye.

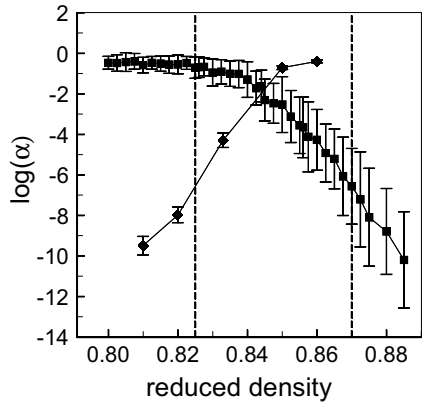


Fig. 3. Plot of the significance level $\log \alpha$ against reduced density $\rho^*$ for a 2D LJ system of 2500 atoms at $T^* = 0.7$ close to the two-phase region. Squares and diamonds denote, respectively, the results obtained from decomposition (3) using IGF [1] and SF ensembles for PDF $\rho_6(Q)$. Vertical lines mark the coexistence region found in [1].

## 4. Discussion

In this paper we have presented some preliminary results concerning the quantification of the concept of fluctuations in a two-phase region of 2D liquids.

First of all let us comment on a simulation of 2D systems in this region. It has been pointed out [22, 23] that standard simulations may lead to discrepancies of results due to possible overheating of simulated systems,

originated by a slow nucleation in computer experiments. This is probably not true in the 2D case. Melting/freezing of hard disks takes place either via two continuous phase transitions (KTHNY) or is a very weak I-order transition [8]. In the first case there are no hysteresis effects (overheating, supercooling) at all, in the second — they are very small. We believe that this is also true for 2D LJ system.

In this context, we report the following unexpected observation. The 2D LJ system at the temperature $T^* = 0.7$ and at the density $\rho^* = 0.86$, *i.e.* in the two-phase region very close to the solidus line, displays nearly perfect instantaneous local solid-like structure; nevertheless the atoms are not bound to fixed positions in space, as seen from Fig. 1. Whether this effect has any relation to the hypothetical hexatic phase of KTHNY theory, where the orientational correlations are much stronger (power law) than the spatial correlations (exponential law), is an interesting question.

The main methodological result of the paper is an introduction of a reliable (in a probabilistic sense) ensemble of fluctuations of solid-like atoms in a two-phase region of a 2D LJ liquid. This SF ensemble is truly solid-like in nature; actually, we have used simulations of a 2D triangular solid to calculate the fluctuations of patterns of local solid-like structure. We point out that a priori it is by no way a trivial result in spite of its apparent simplicity. Together with earlier introduced ensemble of independent gaussian fluctuations IGF [1, 9–11] those two ensembles yield a statistically reliable description of local solid-like structures in the two-phase region of a 2D LJ liquid. Both ensembles undergo a spectacular breakdown in this regime; on the liquidus line IGF ensemble yields reliable results while SF ensemble does not. Close to the solidus line the situation changes: SF are acceptable while IGF are not. Let us point out, in this context, that the results of the statistical analysis are strongly dependent on the size of the system [1]. In the light of this observation we expect that for larger systems the breakdown of the ensembles will be more spectacular, *i.e.*, the intervals of the densities where IGF and SF ensembles become non-reliable will be narrower.

The next remark concerns the fact that we have used the PDF $\rho_6(Q, T^* = 0.7, \rho^* = 0.87)$ for a solid-like pattern under SF fluctuations. We have repeated an analysis using patterns fluctuating at higher densities, *e.g.* $\rho_6(Q, T^* = 0.7, \rho^* = 0.88)$. The results were also reliable, but the significance level, see Fig. 3, was smaller. Still higher densities gave no statistically acceptable results. We point out in this context that two PDFs, $\rho_6(Q, T^* = 0.7, \rho^*)$ and $\rho_6(Q, T^* = 0.7, \rho^* + \Delta\rho^*)$, with $\Delta\rho^* = 0.01$ were identical in the sense of Kolmogorow–Smirnow test [15], while it was not the case for $\Delta\rho^* \geq 0.02$.

The results presented in the paper provide further quantification of the physical picture of 2D liquids close to the two-phase region, formulated re-

cently in Ref. [1]. Namely, those liquids have both solid-like features (large concentration of local solid-like structures) and gas-like features (IGF ensemble). The onset of freezing is accompanied by a disappearance of gas-like features in local solid-like component of a liquid; the fluctuations become solid-like in nature (ensemble crossover). Those statements quantify qualitative concepts formulated earlier [24–26].

Finally, let us note that the quantification of the concept of ensembles of fluctuations might be important in view of the behaviour of heat capacity at constant volume $c_V$ in 2D systems. Namely, the maximum of the heat capacity at $\rho^* = 0.833$ appeared at $T^* \simeq 0.65$, well below the temperature interval $T^* = 0.72 - 0.75$ where the two-phase region starts [1]. Similar observations were made for $T^* = 0.7$. In Fig. 4 we present the plot of $c_V(\rho^*)$ for a 2D LJ system of 1024 atoms, calculated from MC simulations described in Section 3. Its maximum is located at $\rho^* \simeq 0.85$, close to the density where the two significance plots in Fig. 3 intersect. The energy relations in the system are determined by fluctuations both of local solid-like and of non solid-like components of local structure. Ensemble crossover from IGF to SF may be of a noticeable interest in this context.

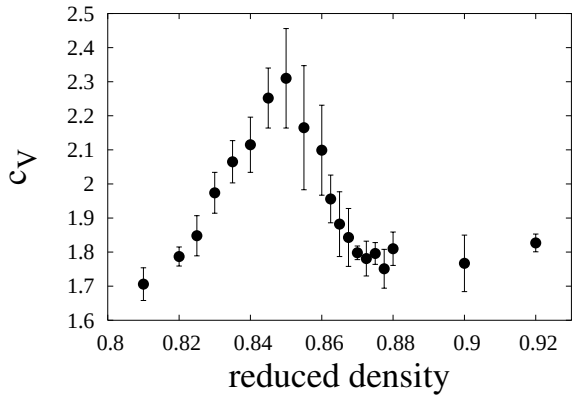


Fig. 4. Plot of the heat capacity $c_V$ against reduced density for a 2D LJ system of 1024 atoms at $T^* = 0.7$ close to the two-phase region.

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## REFERENCES


[1] A.C. Mitus, A.Z. Patashinski, A. Patrykiejew, S. Sokolowski, *Phys. Rev.* **B66**, 184202 (2002).

[2] S.T. Chui, *Phys. Rev. Lett.* **48**, 933 (1982); *Phys. Rev.* **B28**, 178 (1983).

[3] M. Kosterlitz, P.J. Thouless, *J. Phys. C* **6**, 1181 (1973).

[4] V.L. Berezinskii, *Sov. Phys. JETP* **32**, 493 (1971); *Sov. Phys. JETP* **34**, 610 (1972).

[5] B.I. Halperin, D.R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978).

[6] D.R. Nelson, B.I. Halperin, *Phys. Rev.* **19**, 2457 (1979).

[7] A.P. Young, *J. Phys. C* **11**, L453 (1978); *Phys. Rev.* **B19**, 1855 (1979).

[8] K. Binder, S. Sengupta, P. Nielaba, *J. Phys.: Condens. Matter* **14**, 2323 (2002).

[9] A.C. Mitus, A.Z. Patashinskii, S. Sokolowski, *Physica A* **174**, 244 (1991).

[10] A.C. Mitus, H. Weber, D. Marx, *Phys. Rev.* **E55**, 6855 (1997).

[11] A.C. Mitus, D. Marx, S. Sengupta, P. Nielaba, A.Z. Patashinskii, H. Hahn, *J. Phys.: Condens. Matter* **5**, 8509 (1993).

[12] A.Z. Patashinski, A.C. Mitus, M. Ratner, *Phys. Rep.* **288**, 409 (1997).

[13] D.R. Nelson, J. Toner, *Phys. Rev.* **B24**, 363 (1981).

[14] J.P. Steinhardt, D.R. Nelson, M. Ronchetti, *Phys. Rev.* **B28**, 784 (1983); *Phys. Rev. Lett.* **47**, 1297 (1981).

[15] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes*, Cambridge University Press, Cambridge 1986.

[16] H. Gades, A.C. Mitus, *Physica A* **176**, 297 (1991).

[17] R. Peierls, *Helv. Phys. Acta* **7**, (Suppl. II), 81 (1934); *Ann. Inst. Henri Poincare* **5**, 177 (1935).

[18] L.D. Landau, *Physikalische Zeitschrift der Sowjet Union* **11**, 545 (1937).

[19] N.D. Mermin, H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966).

[20] M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford, 1987.

[21] *Monte Carlo Methods in Statistical Physics, Topics in Current Physics*, ed. K. Binder, Vol. 7, Springer-Verlag, Berlin 1979.

[22] J.R. Morris, C.Z. Wang, K.M. Ho, C.T. Chan, *Phys. Rev.* **B49**, 3109 (1994).

[23] A.B. Belonoshko, *Phys. Rev.* **B63**, 096101 (2001); *Phys. Chem. Miner.* **25**, 138 (1998).

[24] J. Frenkel, *Kinetic Theory of Liquids*, Oxford, Clarendon Press, 1946.

[25] A.R. Ubbellohde, *The Molten State of Matter*, J.Wiley & Sons Ltd., 1978.

[26] J.M. Ziman, *Models of Disorder*, Cambridge Univ. Press, Cambridge 1979.