Vol. 35 (2004) *ACTA PHYSICA POLONICA B* No 4

METRICAL VS. TOPOLOGICAL NEIGHBORHOOD RELATIONS AND LINDEMANN MELTING CRITERION IN TWO DIMENSIONS*

A.C. Mituś, R. Orlik

Institute of Physics, Wrocław University of Technology
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

and A.Z. Patashinski

Department of Physics and Astronomy, Northwestern University
Evanston, IL 60208, USA

(Received December 29, 2003)

A concept of "topological" atom–atom neighborhood relation in a strongly fluctuating solid is introduced. The divergence of metrical and topological definitions of a cluster of atoms for a sufficiently high level of atom's displacement $\xi > \xi_{\mathrm{tr}}$, and its consequences for an analysis of local structure in locally solid-like ordered liquids are discussed. The threshold amplitude ξ_{tr} is calculated for a two-dimensional (2D) close-packed lattice. The Monte Carlo simulations of a 2D system of Lennard–Jones atoms lead to a hypothesis, closely related to Lindemann's melting criterion: melting occurs for $\xi = \xi_{\mathrm{m}} \simeq \xi_{\mathrm{tr}}$, *i.e.* when metrical and topological approaches diverge.

PACS numbers: 64.70.Dv, 61.20.Ja

1. Outline of the problem

Melting of crystals has been, since long, an object of numerous experiments and theoretical studies. The phase diagrams of simple systems can be calculated, but the general questions related to the liquid structure and the nature of changes in the local and global structure at melting-crystallization remains a challenge [1, 2]. According to a large experimental evidence (see, *e.g.*, in Ref. [3]) a three dimensional (3D) crystal melts when the root-mean-square (r.m.s.) displacement ξ of an atom from its vibration-averaged position exceeds a small fraction ξ_{m} of an equilibrium atom–atom distance a_0:

---

[*] Presented at the XVI Marian Smoluchowski Symposium on Statistical Physics, Zakopane, Poland, September 6–11, 2003.

$\xi_{\mathrm{m}}/a_0 = 0.07$–$0.20$. This phenomenological rule is known as Lindemann's melting criterion [4]. Numerous attempts to explain the value of Lindemann's parameter ξ_{m}/a_0 (see Refs. [5–9] for recent results) have not yielded a simple and intuitive physical picture of this effect.

Local-structure analysis of computer simulated liquids has revealed important correlations between the structure in small clusters and freezing/melting phenomena [1, 2]. Recently, a scenario of freezing (or of an onset of hexatic phase, see below) in two-dimensional simple liquids, and a melting criterion were presented based on the statistics of shapes of small clusters [1,10] consisting of a central particle and its nearest neighbors. The clusters were defined using snapshots of particle positions. As will be described below (see Section 2), close to the melting point the relatively high level ξ of fluctuations in the liquid and especially in the two-phase region may result in ambiguities when applying this metrical approach. Then, the concept of a cluster requires a careful re-examination and generalization. In particular, clusters defined using non-metrical (*e.g.* topological) criteria may contain important new information about the local structure not accounted for by metrically-defined clusters.

The aim of the current paper is to study the divergence between metrical and a simple topological definitions of a cluster of atoms in a model 2D solid and to interpret the Lindemann's melting parameter for 2D systems in terms of this divergence.

It is important to bear in mind that 2D systems exhibit some peculiarities due to large (as compared to 3D) long-wavelength fluctuations [3]. For historical reasons we describe the system in terms of melting and liquid–solid coexistence between liquidus and solidus lines, although the solid phase may be actually a hexatic phase [11,12] separating the liquid and crystalline phases. In finite and not too large systems used for computer simulations, differences between the hexatic and the true crystalline phases are negligibly small. As observed in computer simulations, the characteristic length scale of the mosaic of hexagonal and non-hexagonal structures near melting is of the order of only few inter-particle distances, so that the difference in the long-range order between the hexatic and the crystalline state may be assumed irrelevant for the problem under discussion. More information can be found in [1].

The paper is organized as follows. In the next section we discuss and compare metrical and topological definitions of a cluster of atoms at various amplitudes of fluctuations in a strongly fluctuating solid. In Section 3 we calculate, using Monte Carlo simulations, the amplitude ξ_{m} of fluctuations at the onset of melting for a 2D Lennard–Jones (LJ) solid. In Section 4 we formulate a hypothesis about the onset of melting in terms of a divergence between metrical and topological definitions.

2. Metrical and topological neighborhood relations

2.1. General concepts

A cluster of atoms in a fluctuating system can be defined as a "metrical" or a "topological" unit; these definitions contain, in general, different kinds of information about the local structure. A metrical cluster is a local object defined irrespective of any pattern of structure and history. Inspired by peaks in the radial distribution function (RDF), one takes the first N nearest atoms to be the N "neighbors" of the central atom. This approach is commonly used in computer simulations. With increasing temperature, the displacement amplitude ξ increases, resulting in a broadening of the peaks of RDF. Computer simulations and experiments indicate [16] that close to the melting temperature, the first and second peaks of the RDF in 3D fcc crystal start to overlap, implying that atoms from the second coordination shell may occupy positions in the first coordination shell and vice versa. This exchange leads to difficulties with defining a cluster based on metric concepts. At the threshold $\xi_{\rm tr}$ (and above it), some of the metrical clusters are no longer generated from the ideal, symmetrical structure by thermal fluctuations. The information about the local topology of the crystal lattice (defined by average positions of atoms) contained in "metrical" clusters, decays rapidly as ξ increases above $\xi_{\rm tr}$. In this sense, a metrical local order does not exist above this threshold. In particular, if the local crystal order hypothesis holds [2], the metrically defined clusters may be inadequate for a demonstration of the existence of "good" matter in liquids.

The generalization, beyond the threshold, of the concept of a metrical cluster preserving the information discussed above, becomes an important and non-trivial task. The solution is straightforward in the case of a model hot solid where the atoms always remember their parental lattice sites, irrespective on the magnitude of their displacement. The prescription "atom-lattice site" has then a topological and not metrical character. The topological clusters result, by the definition, from the fluctuations of an initial cluster in the symmetric structure (crystal lattice). Thus, contrary to the concept of metrical clusters based on the ensemble of snapshots regardless to time and causality, a topological cluster consists of the same atoms and is conserved by the evolution of the system. In other words, a topological definitions requires tracing the history of atoms positions. Topological clusters contain only gradually decaying (with increasing ξ) information about the symmetric structure. The topological local order persists at least in a "hot" 3D fcc solid at fluctuation levels exceeding $\xi_{\rm tr}$ [15, 16].

The aim of the current paper is to analyze both definitions in a hot 2D solid. This represents the first step towards quantification of the topological definition in locally ordered systems, in the first place liquids. The task of defining clusters topologically requires tracking the history of atoms positions and mapping of atoms onto regular patterns of structure. Those further topics are beyond the scopes of the present paper, and will be discussed in a separate communication.

2.2. Two-dimensional case

The threshold $\xi_{\rm tr}$ for a 2D close-packed triangular lattice ($a_0 = 1$) was calculated in Ref. [16] in the assumption that atoms undergo independent 2D Gaussian fluctuations:

$$\xi_{\rm tr}^{(2{\rm D})} = 0.14\text{--}0.16\,. \tag{1}$$

A close but larger value can be obtained from simple geometrical arguments. When particles fluctuate, particle position distributions representing the first and the second coordination shell overlap. At some distance from the center probabilities to find a particle from each shell coincide. This distance is about $(\sqrt{3}-1)/2 \approx 0.37$ of the interatomic spacing, it divides the space into first and second coordination shells for lattice of fluctuating atoms. Particles of the first coordination shell that penetrate the region assigned to the second shell, and particles of the second shell in the region assigned to the first one, may be erroneously recognized as belonging to a wrong shell. These are the atoms that can be differently treated in the metrical or topological definitions. The threshold r.m.s. displacement $\xi_{\rm tr}^{(2{\rm D})}$ is determined by the condition that in average one particle may be erroneously assigned to the wrong coordination sphere. As a rough estimate, one assumes uniform distribution for atoms displacements in a circle, and statistical independence of different atoms motions, to find

$$\xi_{\rm tr}^{(2{\rm D})} = 0.20 \tag{2}$$

close to result (1). This rough estimation does not take into account correlations in atomic motions, and neglects effects of possible defects of the structure of vacancy or dislocation types.

3. Melting of 2D Lennard–Jones liquid: Monte Carlo study

To find the amplitude of atom's displacement $\xi_{\rm m}^{(2{\rm D})}$ for a 2D crystal, we have simulated, using a standard constant-volume NVT Monte Carlo method [13,18], a 2D system of $N = 1024$ atoms interacting via the Lennard–Jones potential

$$V_{\rm LJ}(r) = 4\epsilon_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{3}$$

where σ is a diameter of an atom, ϵ_0 — the depth of Lennard–Jones potential; cut-off radius for potential was chosen to be $2.5\,\sigma$. Minimal image convention and periodic boundary conditions were used and a list of neighbors (inside a sphere with radius 2.5σ) was updated every 50 Monte Carlo Steps (MCS). Total length of the simulation was 4×10^6 MCS. We point out that in 2D no special methods to avoid overheating effects (see Refs. [1,19]) have to be used.

All simulations, for different reduced densities $\rho^* \equiv \rho \cdot \sigma^2$, were done at reduced temperature $T^* \equiv \frac{k_{\mathrm{B}}T}{\epsilon_0} = 0.7$, where k_{B} is Boltzmann constant.

To localize the solidus line (*i.e.* line which discriminates between crystal and two phase region) in the simulations we monitored chosen thermodynamical quantities (like energy and heat capacity) and structural parameters: average distance $\langle l \rangle$ between two chosen neighboring particles and the m.r.s. displacements ξ_1, ξ_2 of an atom. The fluctuation ξ_1 was calculated with respect to a fixed (initial) position of an atom. In an infinite 2D system this parameter diverges [20]; it can be generalized by considering relative displacement vectors and their r.m.s fluctuation ξ_2 between neighboring atoms only [9]. Finally, the fluctuations were averaged over all the atoms.

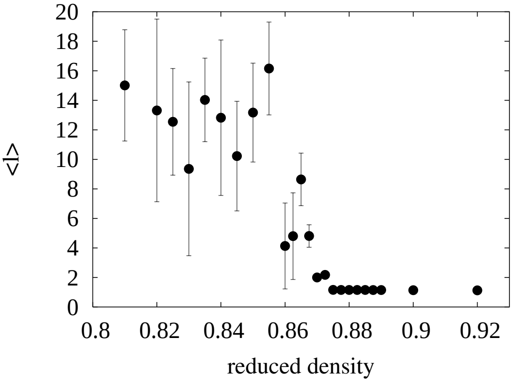

Fig. 1. Plot of an average distance $\langle l \rangle$ between two atoms (initially nearest neighbors) against reduced density.

In Fig. 1 we present the plot of the distance $\langle l \rangle$ against reduced density. At high densities ($\rho^* > 0.875$) this parameter does not depends (up to the fluctuations) on ρ^*. Below this density $\langle l \rangle$ takes much larger values. Close to this density we observe also both qualitative and quantitative change in the relation $\xi_1(\rho^*)$ and $\xi_2(\rho^*)$, see Figs. 2 and 3. The unit on vertical axis is σ; the atom–atom distance at zero temperature is then $2^{1/6}$. We conclude that in our studies the solidus density is $\rho^*_{\mathrm{S}} = 0.875$, in a good agreement with the results of local structure analysis. [1] The values of the fluctuation level on the solidus line constitute $\xi_{1\mathrm{S}} \equiv \xi_1(\rho^*_{\mathrm{S}}) = 0.82 \pm 0.09$,

$\xi_{2\mathrm{S}} \equiv \xi_2(\rho_{\mathrm{S}}^*) = 0.25 \pm 0.12$, in units $a_0 = 1$. Large values of $\xi_1(\rho_{\mathrm{S}}^*)$ and, in particular of the uncertainty of $\xi_{2\mathrm{S}}$, are typical manifestations of large long-wavelength fluctuations in 2D. To estimate, in a rather crude way, the amplitude of the fluctuation of a *single* atom we divide those results by $\sqrt{2}$, in an analogy with the addition of two Gaussian random variables. Finally,

$$\xi_{\mathrm{m}}^{(2\mathrm{D})} \equiv \frac{\xi_{2\mathrm{S}}}{\sqrt{2}} = 0.18 \pm 0.09. \tag{4}$$

The physical consequences of results (1) and (4) are discussed in the next section.

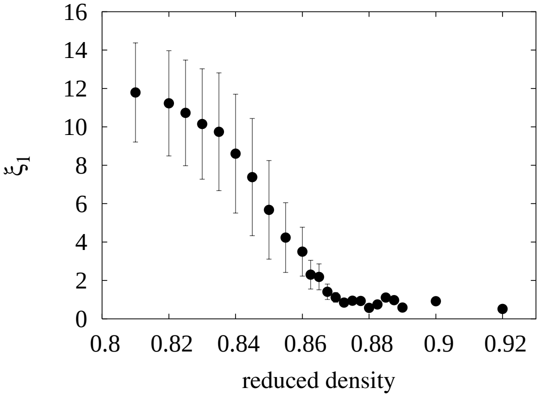

Fig. 2. Plot of the r.m.s. displacement ξ_1 of an atom (see text) against reduced density.

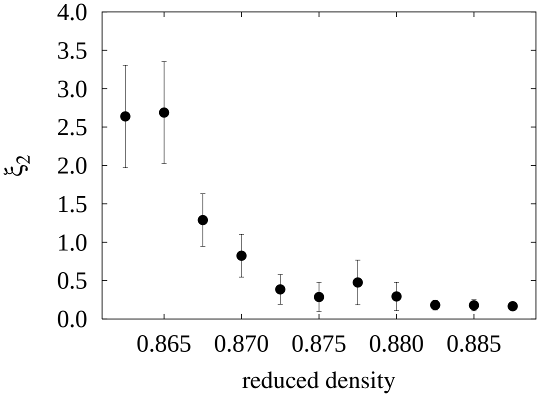

Fig. 3. Plot of the r.m.s. displacement ξ_2 of an atom (see text) against reduced density.

4. Discussion and conclusions

The necessity to distinguish between metrical and topological concepts of atom–atom neighborhood relations becomes actual in strongly fluctuating solids. For a low level ξ of fluctuation displacements, the two approaches coincide. When ξ exceeds a threshold value $\xi_{\rm tr}$ the two definitions yield different results. Using Monte Carlo simulations for a 2D Lennard–Jones liquid, we have localized the melting point (*i.e.* solidus density, or the high-density boundary of hexatic phase) and calculated the fluctuation level $\xi_{\rm m}^{\rm (2D)} = 0.18 \pm 0.09$, *cf.* (4), representing the short-wavelength part of the r.m.s. displacement of an atom from its equilibrium position at the melting point. This result is in agreement with the threshold fluctuation level on a 2D triangular lattice, calculated from independent Gaussian fluctuations in a hot solid: $\xi_{\rm tr}^{\rm (2D)} = 0.14$–$0.16$, *cf.* (1).

Those observations suggest a criterion for the onset of the melting in 2D (or: about the high-density boundary of hexatic phase). We assume that melting takes place when the r.m.s. displacement $\xi_{\rm m}^{\rm (2D)}$ becomes comparable with the threshold value $\xi_{\rm tr}$, determined by the divergence between metrical and topological definitions of neighborhood relations:

$$\xi_{\rm m}^{\rm (2D)} \simeq \xi_{\rm tr}^{\rm (2D)} \,. \tag{5}$$

This criterion offers a new physical interpretation of the Lindemann's parameter $\xi_{\rm m}^{\rm (2D)}$. The basic concept behind the original formulation of Lindemann's criterion was that of a loss of information about the parental lattice site of an atom. In this scenario, melting is triggered by an exchange of *neighboring* atoms. In the current formulation, *cf.* (5), melting is related to the loss of information about the *parental topological cluster* lattice site of an atom belonging to a metrically defined cluster; it is triggered by exchange of nearest and next-nearest *neighbors* of an atom.

Preliminary results indicate that the formulation of Lindemann's criterion in form (5) is also valid in higher spatial dimensions $\mathrm{D} = 3, 4, 5$. This might suggest an existence of a general topology-based mechanism of melting. Those studies are still in progress.

Part of this paper was completed during the stay of one of us (ACM) in 2001 at TU Braunschweig, Germany, as Alexander von Humboldt Fellow; the financial support of AvH Stiftung is gratefully acknowledged. ACM and AZP thank Prof. Harro Hahn and Dr. Frank Smolej for stimulating discussions on local structure of liquids. ACM thanks Prof. H. Hahn for a warm hospitality extended to him during his stay in Prof. Hahn's research group at TU Braunschweig.

REFERENCES

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

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

[3] K.J. Strandburg, *Rev. Mod. Phys.* **60**, 161 (1988).

[4] F.A. Lindemann, *Z. Phys.* **11**, 609 (1910).

[5] G.P. Hoffmann, H. Loewen, *J. Phys.: Condens. Matter* **13**, 9197 (2001).

[6] R. Finken, M. Schmidt, H. Loewen, *Phys. Rev.* **E65**, 016108 (20010).

[7] Zh. Jin, P. Gumbsch, K. Lu, E. Ma, *Phys. Rev. Lett.* **87**, 055703 (2001).

[8] A.C. Lawson, *Philos. Mag.* **B81**, 255 (2001).

[9] K. Zahn, G. Maret, *Phys. Rev. Lett.* **85**, 3656 (2000).

[10] R. Orlik, A.C. Mitus, A. Patrykiejew, S. Sokolowski, A.Z. Patashinski, O. Riefert, *Acta Phys. Pol. B* **34**, 3751 (2003).

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

[12] M. Kosterlitz, P.J. Thouless, *J. Phys. C* **6**, 1181 (1973); V. L. Berezinskii, *Sov. Phys. JETP* **32**, 493 (1971); *Sov. Phys. JETP* **34**, 610 (1972); B.I. Halperin, D.R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D.R. Nelson, B.I. Halperin, *Phys. Rev.* **19**, 2457 (1979); A.P. Young, *J. Phys. C* **11**, L453 (1978); *Phys. Rev.* **B19**, 1855 (1979).

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

[14] A.Z. Patashinskii, B.I. Shumilo, *Sov. Phys. JETP* **62**, 177 (1985).

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

[16] F. Smolej, *Ein effizientes Verfahren zur Erkennung symmetrischer Nahordnungsmuster in computersimulierten einfachen Fluessigkeiten und Glaesern, PhD Thesis*, Cuvilier Verlag, Goettingen 1995.

[17] A.C. Mitus, A.Z. Patashinskii, *Physica A* **150**, 383 (1988).

[18] D.P. Landau, K. Binder, *A guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press, 2000.

[19] J.R. Morris, C.Z. Wang, K.M. Ho, C.T. Chan, *Phys. Rev.* **B49**, 3109 (1994); A.B. Belonoshko, *Phys. Rev.* **B63**, 096101 (2001); A.B. Belonoshko, R. Ahuja, O. Eriksson, B. Johansson, *Phys. Rev.* **B61**, 3838 (2000); A. Strachan, T. Cagin, W. Goddard III, *Phys. Rev.* **B63**, 096102 (2001).

[20] J. Froehlich, C. Pfister, *Commun. Math. Phys.* **81**, 277 (1981).