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Published in:

Physical Review. B, Condensed Matter

DOI:

[10.1103/PhysRevB.35.279](https://doi.org/10.1103/PhysRevB.35.279)

[Link to publication](#)

Citation for published version (APA):

Udink, C., & van der Elsken, J. (1987). Determination of the algebraic exponents near the melting transition of a two-dimensional Lennard-Jones system. *Physical Review. B, Condensed Matter*, 35(1), 279-283. DOI: 10.1103/PhysRevB.35.279

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Determination of the algebraic exponents near the melting transition of a two-dimensional Lennard-Jones system

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(Received 24 June 1986)

We report a calculation of algebraic exponents for translational order as well as for orientational order in a two-dimensional molecular-dynamics system containing 12 480 Lennard-Jones particles, near the melting transition. Results of the calculation, which proceeds via finite-size scaling, show that values of algebraic exponents are in better agreement with the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory than was hitherto assumed. Higher moments of the orientational order parameter, however, produce exponents deviating from those obtained with the zeroth moment. This observation of imperfect scaling is an illustration of the discriminative ability of the finite-size scaling approach, in the identification of algebraically ordered phases in molecular-dynamics simulations of large systems.

Since the extension of Nelson and Halperin¹ and Young² of the Kosterlitz-Thouless theory³ of two-dimensional melting, a great many papers have appeared, dedicated to computer simulations of this transition in several two-dimensional systems.⁴ Focusing here on simulations of Lennard-Jones systems, all authors agree as to the existence of an intermediate region, which is observed between the solid and the liquid phase.⁵⁻¹¹

There is however no consensus about the nature of that intermediate region. Visual inspection shows that the theory of dislocation and disclination unbinding does not seem to apply, which leaves open the possibility of a different physical mechanism. Calculation of the thermodynamic properties shows compatibility with a first-order melting transition,¹¹ and an intermediate two-phase coexistence, and so does a calculation of the bond angle susceptibility on various length scales.¹²

The only truly quantitative test, however, is given by a calculation of the exponents in the correlation functions of translational and orientational order. Early attempts were made on too small systems, whereas a more recent molecular-dynamics simulation of over 10 000 particles⁸ paid no special attention to the calculation of the exponents. This led us to the investigation of the decay of the orientational correlation in a molecular dynamics simulation of a system of 12 480 Lennard-Jones particles with a finite-size scaling method. The first aim of this paper is to point out that this method can produce reliable results in investigations of phases with algebraic decay of the order parameter correlation function. It is important to stress at this point that in order to obtain useful results, one has to simulate large systems. The results will show that at least the values of the algebraic exponents determined in this way are in agreement with the predictions of the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory. We also present the results of calculations of the thermodynamical properties and orientational order correlation functions, to allow comparison with earlier work, especially.⁸ We start with a calculation of the

decay of translational order in the traditional way from the decay of $S(k)$, Eq. (4). These last calculations are used as a test on the validity of the results obtained by scaling methods.

We performed molecular dynamics simulations at constant density for several temperatures near the melting transition. Most of the calculations were performed on the Cyber 205 of SARA (Stichting Academisch Rekencentrum Amsterdam). Initial runs were made on the Cray-1 of the University of London Computer Center. The system consisted of 12 480 particles, interacting through the commonly used Lennard-Jones potential.

In the following we use reduced units: $r^* = r/2^{1/6}\sigma$ for the length scale and the usual scaling for the temperature $T^* = k_B T/\epsilon$. In these units our cutoff radius amounts to $r_C^* = 3.0$, the time step to $\Delta t^* = 0.005$ and the density is $\rho^* = 1.10$. The simulation time per temperature point varies from 10 000 time steps for points in the solid phase to 30 000 time steps for temperatures in the intermediate region.

Translational order is reflected in the structure factor $S(\mathbf{k})$ defined as a function of the wave vector \mathbf{k}

$$S(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \langle e^{i\mathbf{k}\cdot\mathbf{u}(\mathbf{R})} e^{-i\mathbf{k}\cdot\mathbf{u}(0)} \rangle \quad (1)$$

in which $\mathbf{u}(\mathbf{R})$ is the displacement vector of the particle with equilibrium position \mathbf{R} and the sum is over all equilibrium positions \mathbf{R} (the lattice vectors in the direct lattice).

This structure factor can be rewritten as

$$S(\mathbf{k}) = 1 + \frac{2}{N} \sum_{r_{ij}} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \quad (2)$$

with N the number of particles in the system, and \mathbf{r}_{ij} is the vector difference between the instantaneous positions of particle i and particle j . The summation is over all particle pairs.

After integrating over the angle this expression goes into

$$S(k) = 1 + \frac{2}{N} \sum_{r_{ij}} J_0(kr_{ij}) \quad (3)$$

in which J_0 is the zeroth-order Bessel function of the first kind. This expression is especially useful in reaching statistically reliable results from one configuration. The disadvantage of using (3) is the loss of information on angle-dependent properties. The behavior of $S(k)$ in the vicinity of the first reciprocal-lattice vector G , is predicted as^{1,13}

$$S(k) \sim |k - G|^{-2 + \eta_G(T)} \quad (4)$$

with

$$\eta_G(T) = \frac{k_B T |\mathbf{G}|^2 (3\mu + \lambda)}{4\pi\mu(2\mu + \lambda)}, \quad (5)$$

where μ and λ are the usual elastic constants. In the solid phase $\eta_G(T)$ should reach the limiting value $\frac{1}{3}$ at the melting transition, the point at which algebraic translational order is replaced by exponentially decaying translational order.

To calculate orientational order of bonds between neighboring particles, we must have a criterion to determine whether two particles are neighbors. There are several ways to do this. A straightforward way is to take the six nearest particles as neighbors. The exact definition of neighbors however, is provided by the Voronoi construction. To perform a Voronoi construction in a system with over 10 000 particles is not trivial. We used an algorithm by Watson¹⁴ originally devised for the contouring of raw data, which is mathematically speaking the same problem.

The order parameter of the sixfold order is calculated as

$$\psi_6(r_i) = \frac{1}{N_{nb}} \sum_{j=1}^{N_{nb}} \exp(6i\theta_{ij}), \quad (6)$$

in which the sum is over all neighbors j of the particle i , as determined in the Voronoi construction. The orientational correlation function

$$g_6(r) = \langle \psi_6(r) \psi_6^*(0) \rangle \quad (7)$$

is then obtained by taking the product of the Fourier transformed order parameters, and transforming back to real space.¹⁵ The Fourier transforms were performed on a square grid. According to the KTHNY theory the orientational correlation function should decay algebraically,

$$g_6(r) \sim r^{-\eta_6}, \quad (8)$$

in the intermediate phase, with a limiting value $\eta_6 = \frac{1}{4}$ at the second transition.

Finite-size scaling was originally devised by Binder in the Monte Carlo calculation of spin systems.¹⁶ The method can be used to study properties near critical points and consequently is well suited to calculate algebraic exponents in quasi-long-range-ordered phases. Frenkel *et al.*¹⁷ used this method to identify algebraic order in a two-dimensional hard-core nematic in a Monte Carlo simulation. The application to a molecular dynamics

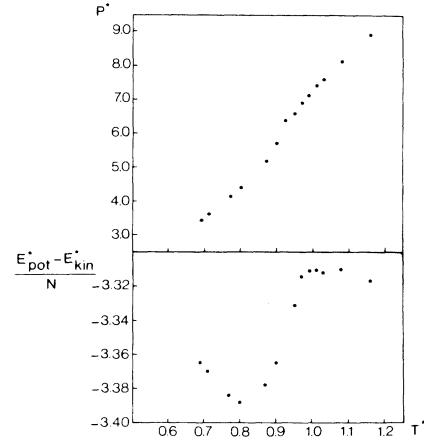


FIG. 1. Pressure and potential energy minus kinetic energy per particle versus temperature.

simulation is straightforward. An algebraically ordered phase means that the appropriate correlation function behaves like

$$\langle O_i O_j^* \rangle \sim |r_i - r_j|^{-\eta} \quad (9)$$

in which O_i is the molecular order parameter. Consequently, we can derive an expression for the system size dependence of the block-averaged order parameter $O = (1/N_s) \sum_i O_i$ as

$$|O| \sim L^{-\eta/2}, \quad (10)$$

where N_s is the number of particles in the subsystem considered; $L = (N_s)^{1/2}$ is the length of the subsystem. For translational order the relevant molecular order parameter is $O_i = \exp(i\mathbf{G} \cdot \mathbf{u})$ and for orientational order $O_i = \psi_6(r_i)$.

We now turn to our results. A rough way to locate the intermediate region is to plot pressure and potential energy minus kinetic energy versus temperature (see Fig. 1).

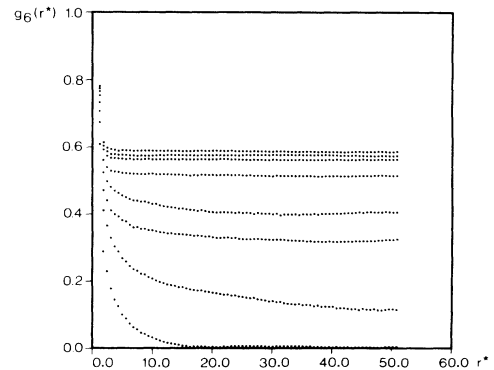


FIG. 2. The orientational correlation function $g_6(r)$ as a function of reduced distance r , for the temperatures $T = 0.69, 0.71, 0.77, 0.80, 0.90, 0.95,$ and 1.16 from top to bottom.

There was no hysteresis observed in traversing the transition. These results are consistent with those of Ref. 8 (a simulation at a slightly higher density). The sharp minimum at $T=0.83$ may be seen as the beginning of the melting process. Figure 2 shows the orientational correlation functions for various temperatures. These functions are smooth because the orientational order parameter was averaged in a small square neighborhood of the particle before the Fourier transform was taken. The functions show an asymptotic behavior which may be in qualitative agreement with Ref. 8, but is no more suited to extract quantitative data. To find the values of the algebraic exponents we have to study the system size dependence of the order parameter. Out of the system of 12 480 particles we constructed subsystems of four different sizes, respectively, $\frac{1}{4}$, $\frac{1}{16}$, $\frac{1}{64}$, and $\frac{1}{256}$ of original system size. The order parameters in the systems of different sizes were evaluated and plotted in a log-log plot versus linear box size. The slope of a weighted fit then provides us with the algebraic exponents according to Eq. (10). The result for the translational order parameter is displayed in Fig. 3. The dotted line corresponds with the predicted stability boundary, i.e., no stable translationally ordered phase can exist with a value η above the critical value $\frac{1}{3}$. The plot of η as a function of temperature shows a sharp increase at the temperature $T=0.83$. Moreover the KTHNY value $\eta=\frac{1}{3}$ is passed at that temperature. The coincidence with the transition temperature obtained from the potential-energy plot shows that in this simulation there is no overestimation of stability of the low-temperature phase, as is often the case in simulations of finite systems.

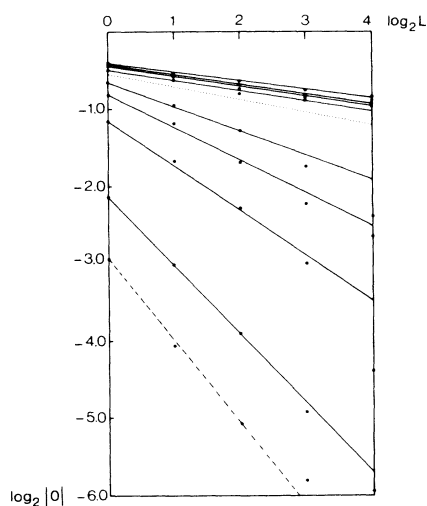


FIG. 3. The logarithm of the translational order parameter plotted versus the logarithm of the box length of the system, for five different system sizes, and for the temperatures $T=0.69$, 0.71 , 0.77 , 0.80 , 0.87 , 0.90 , 0.95 , and 1.16 from top to bottom. The slope of the line in this plot is the algebraic exponent $\eta/2$. The dotted line designates a line with a slope which equals the critical value $\eta/2 = \frac{1}{6}$. The dashed line is a calculation of a random configuration.

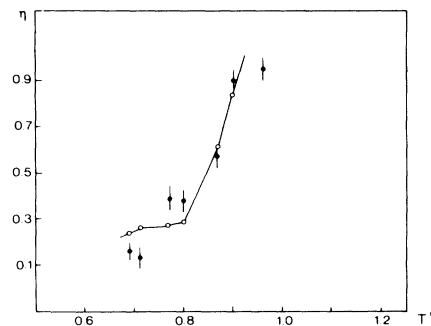


FIG. 4. Values of the algebraic exponent for translational order as a function of temperature, calculated from the behavior of the structure factor near the first reciprocal-lattice vector (solid circles) and from the scaling procedure (open circles).

The dashed line in Fig. 3 is the result of a randomly generated configuration, which shows the typical $1/\sqrt{N}$ dependence, a reflectance of lack of correlation. The configuration in the fluid phase $T=1.16$ is seen to approach this line. A comparison of η values obtained from this method and η values obtained from the structure factor is made in Fig. 4. The traditional way of determining η is seen to produce more scatter in the datapoints and does not show a sharp transition. This is partly due to the fact that the structure factor is obtained from a single-particle configuration, according to the analytical averaging procedure (3), and the scaling procedure incorporates 100 configurations, but the scatter is also a product of the inherent difficulty in fitting power-law behavior.

The algebraic exponent for orientational order η_6 in the intermediate phase was calculated with the same scaling procedure. The results are displayed in Fig. 5. The most

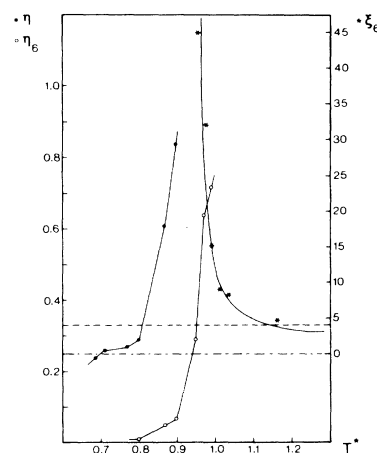


FIG. 5. Scaling results for the algebraic exponent for translational order η (solid circles); the dotted line is the critical value $\eta = \frac{1}{3}$, and for orientational order η_6 (open circles); the dash-dotted line is the critical value $\eta_6 = \frac{1}{4}$. The solid curve is the fit through the experimental points of the orientational correlation length ξ_6 in the fluid phase, as in Eq. (13).

relevant temperature points in this plot are averaged over five configurations. The sudden increase of η_6 as a function of temperature is almost as sharp as in the translational case, the value of $\frac{1}{4}$, associated with the second transition is reached at the temperature $T=0.94$. The orientational correlation length ξ_6 in the fluid is calculated in a straightforward way from a fit of the orientational correlation function

$$g_6(r) \sim \exp\left\{\frac{-r}{\xi_6(T)}\right\}. \quad (11)$$

From the predicted behavior

$$\xi_6 = \exp\left\{\frac{b}{|T - T_i|^{1/2}}\right\} \quad (12)$$

we can also calculate the temperature of the second transition point, the result is $T=0.93$. The fit

$$\xi_6 = \exp\left\{\frac{0.65}{|T - 0.93|^{1/2}}\right\} \quad (13)$$

is shown in the figure as a solid line. The combined results shown in Fig. 5 of the temperature dependence of the algebraic exponents and of the orientational correlation length are in complete and quantitative agreement with the KTHNY theory and give the two transition temperatures $T_1=0.83$ and $T_2=0.93$.

With the same scaling procedure we can also obtain the higher moments of the orientational order parameters as a function of system size. From these moments we can calculate the same algebraic exponent η_6 . If the scaling law is perfectly obeyed the values obtained from the higher moments should be the same as those obtained from the zeroth-order moment. Comparison of these values is made in Fig. 6. There is a small but significant difference

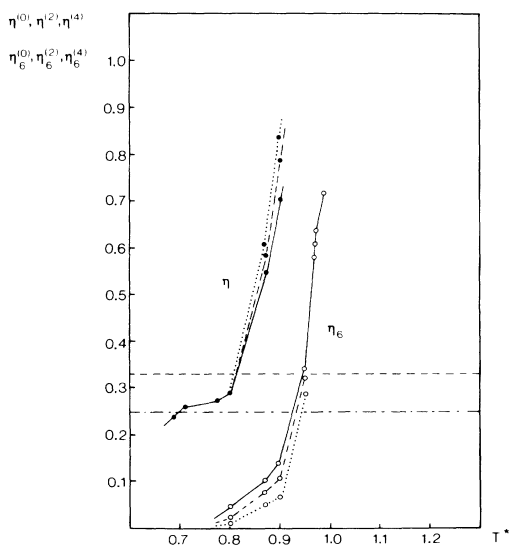


FIG. 6. $\eta^{(i)}$ values and $\eta_6^{(i)}$ values obtained from the zeroth moment ($i=0$: dotted line); second moment ($i=2$: dashed line); fourth moment ($i=4$: solid line).

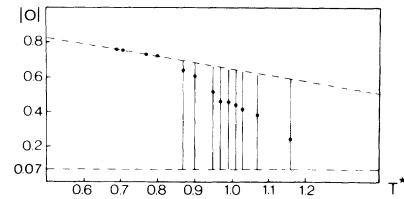


FIG. 7. Illustration of the procedure used to obtain solid fractions in the intermediate region, here shown in the case of $\frac{1}{256}$ of the system. The solid order parameter is linearly extrapolated from the solid phase, the fluid order parameter is taken as a constant with the value of the random configuration.

between the results obtained from the different moments. Such a flaw in the scaling behavior means that the simulated systems in the transition region are not homogeneous. Strandberg, Zollweg, and Chester¹² have come to a similar conclusion by comparing the distribution values of the angular susceptibility, which corresponds to the second moment of the orientational order parameter. It is however an altogether different matter to conclude from the inhomogeneity of the system on the scales considered here, that we have to deal with a solid-liquid coexistence region and a first-order transition.

To illustrate this point we can calculate the apparent solid fraction in the presumed coexistence region. In an actual mixture the order parameter $|O|$ should be linearly composed of the order parameter in the solid phase and the order parameter in the fluid phase and so should all the moments. The solid fraction can thus simply be determined from the calculated values of the order parameter or its moments and a knowledge of the values in the solid and in the fluid phase. The solid phase values are slightly temperature dependent and were therefore extrapolated from the true solid phase points. The order parameter of the fluid phase is taken as the temperature-independent one from the randomly generated configuration. The procedure is illustrated in Fig. 7 which is a calculation of a system with size $\frac{1}{256}$ of the entire simulated system. Solid fractions are calculated in this way as a function of temperature for different system sizes and from zeroth, second, and fourth moments. The results show an approximately linear behavior with temperature irrespective of system size or the order of the moment, as to be expected in a two-phase region with a temperature-independent heat of fusion. However, the values of the fractions obtained from the different moments differ widely thus refuting the presumption of the presence of two phases. In Fig. 8 it is shown for a temperature in the intermediate region that although the discrepancy diminishes with decreasing system size, even for the smallest system there is no coincidence. This means that the established inhomogeneities of the system persist up to dimensions of a few interparticle distances only. Therefore there is no two-phase coexistence in the sense that there are distinguishable solid and liquid regions. The intermediate phase may not be perfectly homogeneous but considering the tem-

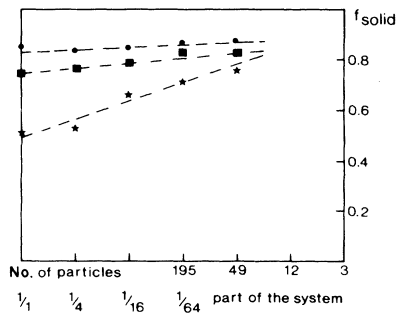


FIG. 8. Solid fraction at $T^* = 0.90$ under the assumption of coexisting phases according to zeroth moment (solid circles), second moment (solid squares), and fourth moment (asterisks), of the order parameter.

perature behavior of the algebraic exponent for orientational order and of the orientational correlation length we cannot but conclude that the intermediate region has the characteristics of an orientationally ordered phase.

Finally we remark that in the determination of the algebraic exponent for orientational order, we noticed very long relaxation times for the larger systems. This is what makes the observation of the algebraic decay in the correlation functions such a problem. Efforts to capture the mechanism of the melting transition by simulating still larger systems will be limited by the long simulation times needed to assure orientational equilibration.

ACKNOWLEDGMENTS

The authors wish to thank Dr. D. Frenkel, Rijks Universiteit Utrecht, for his continuous interest in the subject. The work is part of the research program of the Foundation for Fundamental Research of Matter (FOM), supported by the Netherlands Foundation for Chemical Research (SON) and was made possible by financial support from the Netherlands Organization for Pure Research (ZWO).

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