TEST OF NEW MELTING CRITERION. ANGULAR STIFFNESS AND ORDER OF 2D MELTING IN LENNARD-JONES AND WIGNER LATTICES ☆

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On the basis of the parameter l^2 of angular stiffness, I explain why a Lennard-Jones lattice in two dimensions melts in a first order transition, with decreasing transition entropy at increasing density, while a Wigner lattice undergoes a single sharp, nearly continuous transition with a specific heat curve of the "λ"-type and the shear elastic constant collapsing near the universal Kosterlitz–Thouless value.

Recently [1], the old controversy of 2D melting has apparently been resolved. It has been shown that the parameter l^2, which characterizes the angular stiffness of a crystal, is decisive in determining whether dislocations and disclinations in a crystal undergo a single first order or two successive continuous melting transitions. The separation point lies around [2] $l_s^2 \sim 0.1$–0.2. Thus, we now possess a new criterion of 2D melting: For $l^2 < l_s^2$ there is a single first order transition, for $l^2 \approx l_s^2$ the transition is sharp but continuous, and for $l^2 \gg l_s^2$ there are two well separated very smooth Kosterlitz–Thouless transitions. In the continuum, the parameter l^2 is defined by the higher elastic energy

$$E = \int \mathrm{d}^3x \, [\mu u_{ij}^2 + \tfrac{1}{2}\lambda u_{kk}^2 + \tfrac{1}{2}(2\mu+\lambda) l'^2 (\partial_i u_{kk})^2 + 2\mu l^2 (\partial_i \omega)^2 + \ldots] , \quad (1)$$

where $u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i)$ is the usual strain tensor and $\omega = \frac{1}{2}(\partial_1 u_2 - \partial_2 u_1)$ the local rotation field. By rotation symmetry, there are only two independent second gradient terms $\partial_i \partial_l u_l \partial_j \partial_l u_l$ and $\partial_i^2 u_l \partial_j^2 u_l$ which, by a partial integration, can be brought to the new terms in (1). The new parameters l^2, l'^2 are observable in the dispersion curves of the sound waves when expanded in powers of the momentum $\boldsymbol{k}$,

$$\omega_T^2(\boldsymbol{k}) = \mu k^2 (1 + l^2 k^2 + \ldots) ,$$
$$\omega_L^2(\boldsymbol{k}) = (2\mu+\lambda) k^2 (1 + l'^2 k^2 + \ldots) . \quad (2)$$

In the discussion to follow, the parameter l'^2 is irrelevant and will be dropped. The Monte Carlo evaluation of the separation point was done on a square lattice with an energy like (1) but written down in terms of lattice gradients. There, the spectrum for small $\boldsymbol{k}$ is

$$\omega_T^2(\boldsymbol{k}) = 4\mu \sin^2(\tfrac{1}{2}k)(1 + l^2 k^2) + \ldots .$$

It has the continuum limit

$$\omega_T^2(k) \approx \mu k^2 [1 + (l^2 - \tfrac{1}{12}) k^2 + \ldots] .$$

Hence, in the continuum form of the energy, the separation point is expected to lie in the range

$$l_s^2 \approx 0.05 \pm 0.05 . \quad (3)$$

Let us test the new criterion. First we consider a Lennard-Jones system with a potential ($m > n$)

$$V = 4\epsilon [(\sigma/r)^m - (\sigma/r)^n] , \quad (4)$$

which has its minimum at $r_0 = (m/n)^{1/(m-n)}\sigma$. The triangular lattice vectors are

$$\boldsymbol{x}(l) = a_0 (l_1 + \tfrac{1}{2} l_2, \tfrac{1}{2}\sqrt{3}\, l_2) . \quad (5)$$

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The dispersion matrix $C_{ij}(k)$, whose eigenvalues are $\omega^2(\boldsymbol{k})$, is given by ($r \equiv |\boldsymbol{x}(l)|$, a prime denotes d/d$r$)

$$C_{ij}(\boldsymbol{k}) = -\sum_{l\neq 0}\left[\frac{V'}{r}\delta_{ij} + \left(\frac{V''}{r^2} - \frac{V'}{r^3}\right)x_i x_j\right] \times [\cos(\boldsymbol{k}\cdot\boldsymbol{x}) - 1] . \quad (6)$$

Expanding the cosine in powers of $\boldsymbol{k}$ we find the quadratic and quartic terms

$$C_{ij}^{(2)}k^2 + C_{ij}^{(4)}k^4 = \sum_{l\neq 0}\left[\frac{V'}{r}\delta_{ij} + \left(\frac{V''}{r^2} - \frac{V'}{r^3}\right)x_i x_j\right] \times [\tfrac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{x})^2 - \tfrac{1}{24}(\boldsymbol{k}\cdot\boldsymbol{x})^4] . \quad (7)$$

In the quadratic term, the sixfold symmetry of the $\boldsymbol{x}(l)$ vectors is sufficient to guarantee isotropy, so that (with $\hat{\boldsymbol{k}} = \boldsymbol{k}/|k|$)

$$\langle(\boldsymbol{k}\cdot\boldsymbol{x})^2\rangle = \tfrac{1}{2}k^2r^2 ,$$

$$\langle x_i x_j(\boldsymbol{k}\cdot\boldsymbol{x})^2\rangle = \tfrac{1}{8}k^2r^4(\delta_{ij} + 2\hat{k}_i\hat{k}_j)$$

and

$$C_{ij}^{(2)} \approx \sum_{l\neq 0}[(\tfrac{3}{16}V'r + \tfrac{1}{16}V''r^2)\delta_{ij} + \tfrac{1}{8}(V''r^2 - V'r)\hat{k}_i\hat{k}_j] . \quad (8)$$

In $C_{ij}^{(4)}$, the sixfold symmetry guarantees isotropy only up to the tensor $x_i x_j x_k x_l$, with the angular average being

$$\langle(\boldsymbol{k}\cdot\boldsymbol{x})^4\rangle = \tfrac{3}{8}k^4r^4 .$$

The average of the tensor $t_{ijklmn} \equiv \langle x_i x_j x_k x_l x_m x_n\rangle / r^6$ differs from the isotropic form

$$t^{\mathrm{iso}}_{ijklmn} = \tfrac{1}{48}(\delta_{ij}\delta_{kl}\delta_{mn} + 14 \text{ pair contractions}) , \quad (9)$$

but the anisotropy is very small: when ordered according to increasing number of indices the matrix elements are (after an average over the vector $\boldsymbol{x} = (\cos\varphi, \sin\varphi)$ and its six rotated versions)

$$\tfrac{1}{32}[10 + \cos(6\varphi)], \quad \tfrac{1}{32}\sin(6\varphi), \quad \tfrac{1}{32}[2 - \cos(6\varphi)] ,$$

$$-\tfrac{1}{32}\sin(6\varphi), \quad \tfrac{1}{32}[2 + \cos(6\varphi)], \quad \tfrac{1}{32}\sin(6\varphi) ,$$

$$\tfrac{1}{32}[10 - \cos(6\varphi)] .$$

The average $\langle(\boldsymbol{k}\cdot\boldsymbol{x})^6\rangle$ varies at most by $\pm\frac{1}{32}$ as compared with the isotropic $\frac{10}{32}$, so the deviation from isotropy is at most 10% We shall therefore be content with the isotropic approximation with

$$\langle x_i x_j(\boldsymbol{k}\cdot\boldsymbol{x})^4\rangle = \tfrac{1}{16}(\delta_{ij} + 4\hat{k}_i\hat{k}_j) ,$$

so that

$$C_{ij}^{(4)} \approx -\sum_{l\neq 0}\left[\left(\frac{5}{16\times 24}V'r^3 + \frac{1}{16\times 24}V''r^4\right)\delta_{ij} + \tfrac{1}{96}(V''r^4 - V'r^3)\hat{k}_i\hat{k}_j\right] . \quad (10)$$

After a transverse projection by $P^{\mathrm{T}}_{ij} = \delta_{ij} - \hat{k}_i\hat{k}_j$, i.e. $C_{\mathrm{T}} \equiv C_{ij}P^{\mathrm{T}}_{ij}$, the ratio $C_{\mathrm{T}}^{(4)}/C_{\mathrm{T}}^{(2)}$ is the desired parameter l^2. Taking only the nearest neighbours into account we find the simple approximation (in units $\sigma = 1$)

$$l^2 = -\frac{a_0^2}{24}\frac{m(m-4) - a_0^{m-n}\,n(n-4)}{m(m-2) - a_0^{m-n}\,n(n-2)} , \quad (11a)$$

i.e., for the common values $m = 12$, $n = 6$,

$$l^2 = -\frac{a_0}{30}\frac{1 - \frac{1}{8}a_0^6}{1 - \frac{1}{5}a_0^6} . \quad (11b)$$

For high density (i.e. high coverage of the substrate), the lattice spacing a_0 is smaller than the size r_0 where the potential is minimal and eq. (11) shows that then l^2 is very small in absolute size and negative in sign. If for decreasing density a_0 approaches

$$r_{\max} = [m(m-2)/n(n-2)]^{1/(m-n)}$$

(i.e. $5^{1/6} \approx 1.30760$), then l^2 becomes more and more negative (see fig. 1). Thus, according to the present theory [1], the transition entropy must increase with lower density. This is indeed what happens in adsorbed monolayers of rare gases [#1]. The same feature is observed in Monte Carlo simulations of these systems [4], which for $a_0 \approx r_0$ always show a single first order melting transition.

It is curious to see that l^2 diverges at $a_0 \approx r_{\max} \approx 1.30760$. Looking at experimental phase diagrams, we see that the liquid–gas transition lies near that value.

If the approximate solution is extended to include the full lattice sum, the result is changed only very little, except very near $r_{\max}$.

Consider now a 2D Wigner lattice of electrons which can be prepared on a surface of liquid helium [5]. The lattice dynamics has been studied by Bon-

[#1] See, for instance, the phase diagram of Xe on graphite [3].

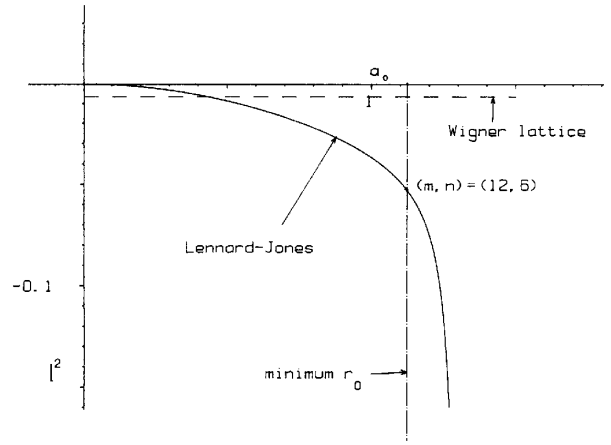

Fig. 1. The parameter l^2 as a function of the nearest neighbour distance for the Lenard-Jones system with n, $m=12$, 6, and for the Wigner lattice (- - -). The vertical line indicates the position of the potential minimum with the equilibrium position being ~ 1% smaller than that.

sall and Maradudin [6]. From their paper, eq. (5.2), we extract the transverse part of the matrix C_{ij} divided by ω_p^2 where $\omega_p^2 \equiv 2\pi e^2/ma_0 v_c$, $v_c \equiv \frac{1}{2}\sqrt{3}\,a_0^2$ = cell area,

$$C_T = \frac{1}{2\pi}\frac{\sqrt{v_c}}{a_0}\Bigg(\sum_{G\neq 0}\{[G^2-(\boldsymbol{G}\cdot\boldsymbol{k})^2/k^2] \times[\varphi_{-1/2}((G+k)^2/4\epsilon)-\varphi_{-1/2}(G^2/4\epsilon)]\} + \sum_{l\neq 0}\{[1-\cos(\boldsymbol{k}\cdot\boldsymbol{x})][4\epsilon^2(r^2-(\boldsymbol{x}\cdot\boldsymbol{k})^2/k^2)] \times\varphi_{3/2}(\epsilon r^2)-2\epsilon\varphi_{1/2}(\epsilon r^2)\}\Bigg), \tag{12}$$

where $\epsilon=\pi/v_c$ and $\sqrt{\epsilon}\,\boldsymbol{x}$, $\boldsymbol{G}/2\sqrt{\epsilon}$ run through the direct and reciprocal lattice via the rescaled vectors (l_i, g_i = integers)

$$\hat{\boldsymbol{x}}(\boldsymbol{l}) = \sqrt{\pi}\sqrt{2/\sqrt{3}}\,(l_1+\tfrac{1}{2}l_2,\ \tfrac{1}{2}\sqrt{3}\,l_2)\,,$$
$$\hat{\boldsymbol{G}}(\boldsymbol{g}) = \sqrt{\pi}\sqrt{\sqrt{3}/2}\,(g_1,\ -\tfrac{1}{3}\sqrt{3}\,g_1+\tfrac{2}{3}\sqrt{3}\,g_2)\,, \tag{13}$$

respectively, both with the same lengths

$$\pi\sqrt{2/\sqrt{3}}\,(l_1^2+l_1l_2+l_2^2)^{1/2}\,,$$
$$\pi\sqrt{2/\sqrt{3}}\,(g_1^2-g_1g_2+g_2^2)\,.$$

The function $\varphi_n(z)$ is defined by

$$\varphi_n(z) \equiv \int_1^\infty \mathrm{d}t\, t^n e^{-zt}\,.$$

Being interested only in the lowest two powers k^2 and k^4 we shall ignore, as before, the small anisotropy of the k^4 term so that C_T can be expanded to give directly the desired $\omega_T^2(\boldsymbol{k})$ (in units of ω_p^2).

The two sums in (12) converge exponentially fast and it is sufficiently accurate for our purpose to include only the nearest neighbours. For them $s\approx 3.376$. For the next-nearest neighbours s is already as large as 10.1276 and $\varphi_n(s)$ is very small. Using the above angular averages, we calculate (with $s\equiv\hat{\boldsymbol{x}}^2=\hat{\boldsymbol{G}}=2\pi/\sqrt{3}$)

$$C_T^{(2)} = \frac{\sqrt{v_c}}{2\pi a_0}\,6\times 2\times[-\tfrac{1}{2}s\varphi_{1/2}(s)+\tfrac{1}{4}s^2\varphi_{3/2}(s)] \approx 0.0362\,, \tag{14a}$$

with $\boldsymbol{x}(\boldsymbol{l})$ and $\boldsymbol{G}(\boldsymbol{g})$ contributing the same amount. Our approximate number is in excellent agreement with the value 0.0362967 obtained from the full sum (see eq. (5.24b), in ref. [6]). For the quartic coefficient we find

$$C_T^{(4)} = \frac{\sqrt{v_c}}{2\pi a_0}\frac{6}{4\epsilon}\{[\tfrac{3}{24}s^2\varphi_{1/2}(s)-\tfrac{1}{24}s^3\varphi_{3/2}(s)] + [\tfrac{1}{4}s\varphi_{3/2}(s)-\tfrac{1}{4}s^2\varphi_{5/2}(s)+\tfrac{1}{24}s^3\varphi_{7/2}(s)]\} \approx -0.000225\,. \tag{14b}$$

Thus, in contrast to the Lennard-Jones system, the Wigner lattice has an a_0 independent almost vanishing ratio $C_T^{(4)}/C_T^{(2)}$,

$$l^2 \approx -0.00622\,. \tag{15}$$

This value puts the Wigner lattice very close to the regime (3) where the single first order melting transition begins to split into two Kosterlitz–Thouless transitions. The specific heat is expected to have a sharp peak just as in our model simulation, fig. 2 of ref. [2], i.e. it should look like a λ transition. The latter feature was first observed in Monte Carlo simulations of the Wigner lattice [7]. The fact that the transition lies near the merging regime of the two transition lines explains also why the elastic constant collapses at the melting transition near the universal value of the Kosterlitz–Thouless theory [8].

Fig. 1 of ref. [2] shows the line in the l^2, T plane at which the elastic constants at the universal ratio $2v_c\mu(\mu+\lambda)/k_BT(\mu+\frac{1}{2}\lambda)=1$, with $\lambda=\infty$ for the Wigner lattice and the transition at (15) lies very close to the end of this line.

In conclusion, it appears that the angular stiffness parameter l^2, which can easily be extracted from the transverse branch of the dispersion curve, can indeed serve as a guide for predicting the discontinuity of the melting transition. Certainly, the new criterion can only be very crude, no better than the good old Lindeman criterion for the melting transition in three dimensions for two reasons: First, the model Monte Carlo determination of l^2 was done on an unphysical square lattice and a simulation on a triangular lattice will be necessary to make the value more precise. Second, at no place in the defect model is the effect of atomic hard cores taken into account. All such questions remain to be investigated, just as it will be interesting to study systems with large positive l^2 and two continuous transitions. Two particularly interesting systems, which have recently been investigated experimentally and whose differences should be explained by the present theory, are layers of methane and ethylene adsorbed on graphite [9]. A measurement of l^2 would be feasible and a theoretical value can be extracted from the dispersion calculations in ref. [10]. This should yield an important test of the theory.

A more detailed discussion of the present theory will be found in ref. [11].

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