Static Structure Factor for a Finite Incommensurate Monolayer

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The static structure factor for a finite two-dimensional classical harmonic lattice is evaluated, including finite-size effects from both lattice sums and the lower k cutoff on the phonon spectrum. The numerical results show that the power-law behavior of $S(\vec{q})$ expected in an infinite two-dimensional crystal should be already quite apparent in crystallites of size $L \sim 1000-5000$ Å.

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Because of the absence of long-range order, the static structure factor $S(\vec{q})$ of a two-dimensional (2D) harmonic crystal exhibits[1] power-law singularities at the 2D reciprocal-lattice vectors $\{\vec{K}\}$ instead of the usual δ-function Bragg peaks found in 3D lattices. In the present Letter, we present a detailed study of $S(\vec{q})$ for a *finite* 2D lattice of area L^2. We show that, typically, the power-law behavior[2,3] characteristic of the infinite lattice is already quite apparent when L is in the range 1000–5000 Å. Secondly, our numerical results indicate the inadequacy of the usual Warren line-shape approximation even for monolayers of size $L \sim 200-500$ Å. Our results are directly applicable to the analysis of diffraction studies on physisorbed, incommensurate monolayers on graphite substrates, a subject of great current interest (see, for example, Refs. 4–6).

The static structure factor of a 2D harmonic crystal is given by the standard expression[7]

$$S(\vec{q}) = N^{-1} \sum_{\vec{R},\vec{R}'} \exp[-i\vec{q}\cdot(\vec{R}-\vec{R}')]\exp[-\tfrac{1}{2}\sigma^2(\vec{q};\vec{R},\vec{R}')], \quad (1)$$

where

$$\sigma^2(\vec{q};\vec{R},\vec{R}') \equiv \langle\{\vec{q}\cdot[\vec{u}(\vec{R})-\vec{u}(\vec{R}')]\}^2\rangle. \quad (2)$$

Here $\vec{R}$ is a Bravais lattice vector of our 2D crystal. In principal at least, it is straightforward to evaluate $S(\vec{q})$ for a 2D harmonic lattice of finite size (say a square for side L). Imposing fixed boundary conditions, for example, one can work out $\sigma^2(\vec{q};\vec{R},\vec{R}')$ by expanding the lattice displacements $\vec{u}(\vec{R})$ in terms of the appropriate normal modes of the finite 2D harmonic crystal. However, this kind of calculation is fairly involved and is not really appropriate in our study, which is to find the qualitative effect of finite size on the characteristic Landau-Peierls singularities exhibited by $S(\vec{q})$ in an infinite crystal for $\vec{q}$ close to a 2D reciprocal lattice vector $\vec{K}$. We are *not* interested in the effect of the boundaries insofar as they modify the bulk phonon dispersion relations or give rise to surface modes. In a word, we are interested in finite-size effects but not surface effects. Thus, in evaluating σ^2 in (2), we shall use the usual infinite-crystal result[2] but shall exclude phonons with a wavelength exceeding the size of the system,[8] i.e.,

$$\sigma_L^2(\vec{q};\vec{R},\vec{R}') = \frac{4T}{T_q}\int_{\pi/L}^{k_0} dk \frac{[1-J_0(k|\vec{R}-\vec{R}'|)]}{k}, \quad (3)$$

where $J_0(x)$ is the zero-order Bessel function. This only includes the interesting contribution from phonons $\hbar\omega \lesssim k_B T$ and hence the cutoff is $k_0 \sim (\pi/a)(T/T_D)$, where T_D is the 2D Debye temperature. We have defined a characteristic temperature[1]:

$$\frac{1}{k_B T_q} \equiv \frac{q^2}{4\pi}\frac{1}{2\rho}\left(\frac{1}{v_l^2}+\frac{1}{v_t^2}\right), \quad (4)$$

where v_l (v_t) is the longitudinal (transverse) sound velocity and ρ is the areal density of our 2D crystal. This result follows from continuum elasticity theory of a 2D isotropic crystal[9] and hence is appropriate for the triangular lattices one generally finds on graphite substrates. One may evaluate (3) by using an asymptotic expansion of the k integral to give

$$\sigma_L^2(\vec{q};R) \simeq (4T/T_q)\ln[k_0\mu R(\pi R/L)^{J_0(\pi R/L)-1}], \quad (5)$$

where $\mu = 0.5\exp(0.577) = 0.89$. This is not valid for R smaller than a few lattice constants.

The lower k cutoff in (3) will clearly damp out the effect of the long-range fluctuations[10] which gives rise to the anomalous behavior of 2D crystals.[3,11] We recall that the mean-square displacement in the same approximation is[8]

$$2W(q) \equiv \langle [\vec{q}\cdot\vec{u}(\vec{R})]^2\rangle = (2T/T_q)\ln(k_0 L/\pi), \qquad (6)$$

which can be quite small even if L is large. While Imry and Gunther[2] included the lower k cutoff in computing the Debye-Waller factor $\exp(-2W)$, they used the infinite-L approximation

$$\sigma_\infty^2(\vec{q};R) = (4T/T_q)\ln(k_0\mu R). \qquad (7)$$

For a finite crystal, the *two* lattice sums in (1) must be treated carefully. A change of variable to $\vec{R}-\vec{R}'$ must take into account that the limits are also altered. If $\vec{q}$ is close to some *given* reciprocal lattice vector $\vec{K}$ of the 2D lattice, one can use the continuum approximation for the two lattice sums. We have been able to reduce the resulting fourfold integral to a much simpler twofold integral. For the specific case when $\vec{q}-\vec{K}$ is along the x axis, we obtain

$$S(\vec{q}) = (4/L^2)\int_0^L dR_x \int_0^L dR_y (L-R_x)(L-R_y)\cos(q_x-K_x)R_x \min\{1, \exp[-\tfrac{1}{2}\sigma_L^2(\vec{q};R)]\}, \qquad (8)$$

where $R=(R_x^2+R_y^2)^{1/2}$. Since we are assuming that $\vec{q}$ is very close to $\vec{K}$, it is an excellent approximation to use $\sigma_L^2(\vec{K},R)$ in the integrand of (8). Further details will be given elsewhere[12] but we note that use has been made of the identity

$$\int_0^L dx \int_0^x dy F(y) = \int_0^L dy (L-y)F(y). \qquad (9)$$

It is to be emphasized that (8) does not involve any one-phonon expansion and that it includes finite-size effects in *both* real space (R) and momentum space (k). The former turns out to be most important and is not adequately treated in the previous literature[2] on this topic.

It is straightforward to numerically evaluate $S(\vec{q})$ in (8) and see how the static structure factor depends on the lattice size L, for a given value of T/T_q. Before turning to a discussion of some examples, it is convenient to relate the Jancovici characteristic temperature[1] defined in (4) to the Kosterlitz-Thouless expression for the melting temperature T_M due to the unbinding of dislocation pairs in a 2D lattice (see Ref. 9). For a 2D triangular lattice, the melting temperature is related to the sound velocities according to

$$\frac{1}{k_B T_M} = \frac{4\pi}{a^2}\frac{1}{\rho}\left(\frac{1}{v_l^2 - v_t^2} + \frac{1}{v_t^2}\right), \qquad (10)$$

where a is the lattice spacing. Evaluating the Jancovici temperature at the minimum reciprocal lattice vector of a triangular lattice ($K_0 = 4\pi/\sqrt{3}a$), one finds with a little algebra that

$$T_{K_0}/T_M = 6/[1-(v_t/v_l)^4]. \qquad (11)$$

This indicates that T_{K_0} is always somewhat greater than 6 times the Kosterlitz-Thouless melting temperature T_M. Most diffraction studies of physisorbed monolayers on graphite[4] concentrate on the first Bragg peak arising from $\vec{K}_0$ and for temperatures fairly close to melting,[11] we conclude that a realistic value of T/T_q to take in the evaluation of (8) is $\lesssim 0.1$.

In Figs. 1–3, we plot $S(\vec{q})$ for $\vec{q}$ very close to $\vec{K}$, i.e., $q-K \ll a^{-1}$. We have somewhat arbitrarily taken $a = 3$ Å. Figure 1 might be viewed as appropriate to ZYX exfoliated graphite, where crystal planes of size $L \sim 500$ Å are expected under optimum conditions.[13] The curve marked "without k cutoff" means that we have evaluated

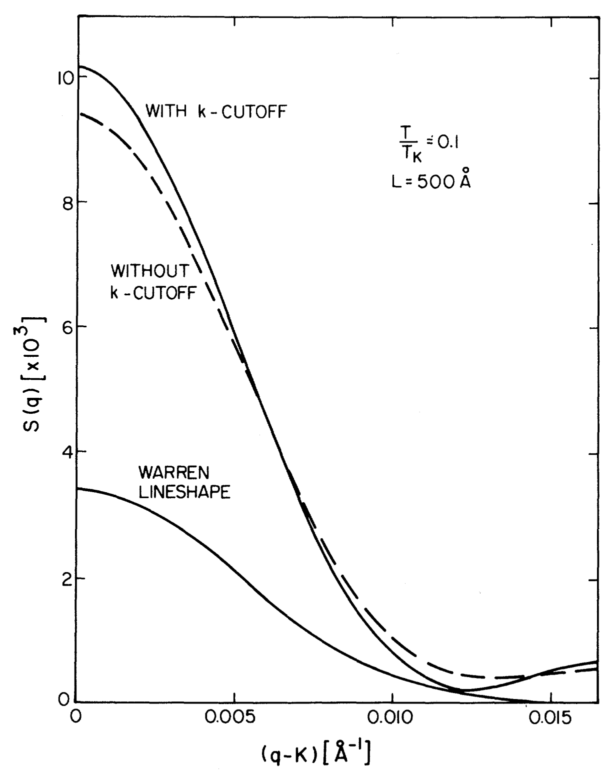

FIG. 1. The static structure factor $S(\vec{q}) = S(q_x, q_y = K_y)$ as a function of the wave vector $k \equiv |\vec{q}-\vec{K}| = q_x - K_x$, for $\vec{q}$ close to $\vec{K}$, the reciprocal lattice vector of the 2D lattice. In all the figures, the 2D lattice is taken to be a square of side L and the lattice spacing is a = 3 Å. All results are based on (8), with the Jancovici temperature T_K defined in (4).

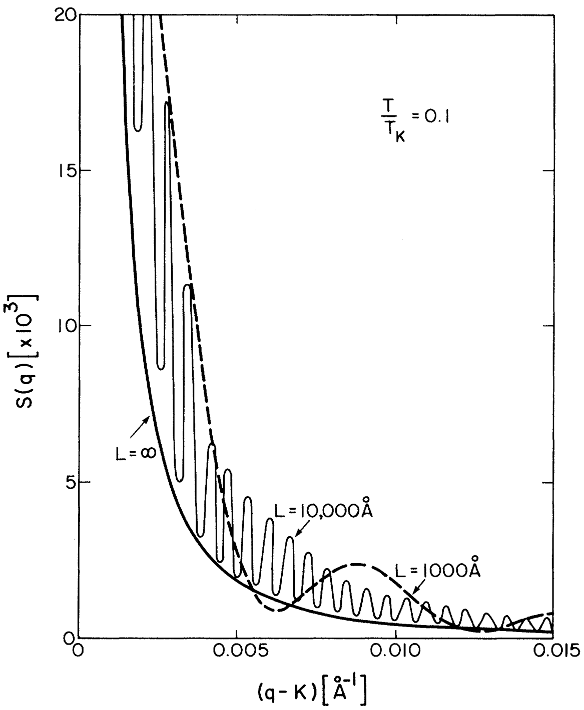

FIG. 2. $S(\vec{q})$ vs wave vector $k = |\vec{q} - \vec{K}|$ for three different monolayer sizes L. See caption of Fig. 1.

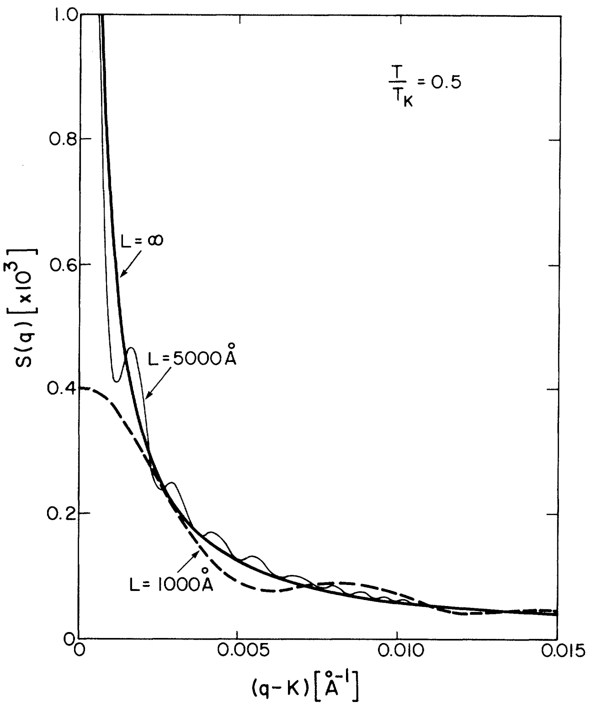

FIG. 3. $S(\vec{q})$ vs wave vector $k \equiv |\vec{q} - \vec{K}|$ for three different monolayer sizes L in the case $T/T_K = 0.5$. A physical realization of this case would involve a higher-order diffraction peak, corresponding to a smaller value of T_K than that given by (11).

(8) using (7) instead of (5). As can be seen, the effect of the finite k cutoff in (3) is already quite small for lattices of this size.[14] In Fig. 1, for comparison, we have also plotted the often-used Warren (or Gaussian) line-shape approximation[15,16]

$$S(\vec{q} \simeq \vec{K}) = N \exp[-2W(K)] \exp[-(q-K)^2 L^2/4\pi], \qquad (12)$$

where $W(K)$ is given by (6). While it is clearly inadequate for $T/T_K \sim 0.1$, we note that (12) is a very good approximation at low temperatures ($T \ll T_M$), where T/T_K can be in the range 10^{-2}–10^{-3}.

In Fig. 2, we give results for $L = 1000$ Å and 10 000 Å as well as for an infinite lattice where $S(\vec{q}) \sim (q-K)^{-2+\eta_K}$, with $\eta_K \equiv 2T/T_K$. These curves show in a dramatic way how $S(\vec{q})$ for a 2D lattice develops the characteristic Landau-Peierls singular behavior as we let the size L increase. As one might have expected, the oscillations have a wave vector $\Delta k \sim 2\pi/L$ and thus become increasingly rapid as $L \to \infty$. From an experimental point of view, the curves in Fig. 2 are especially significant since they clearly indicate that, for $T/T_K \sim 0.1$, 2D crystals of size ~1000–5000 Å already give rise to a static structure factor which is quite close to an infinite crystal. By way of contrast, Fig. 1 shows that such power-law Bragg singularities are not really present in lattices of size $L \lesssim 500$ Å. Unfortunately most experimental data available are for crystallites in the range $L \sim 100$–500 Å. Our present results show that one should not try to analyze such data in terms of the infinite-lattice power-law singularities.[16]

In Fig. 3, we give some results for $T/T_K = 0.5$. Here again, one sees that by the time one reaches $L \sim 5000$ Å, $S(\vec{q})$ is very similar (in an average sense) to the $L = \infty$ case.

In summary, we have given the first satisfactory calculation of the effect of finite size on the power-law singularities exhibited by 2D crystals. The key step in our study lies in our finding a new two-dimensional integral representation for the four-dimensional integral in (1). Our expression[12] in (8) is very easy to evaluate by computer and should be of considerable use in analysis of diffraction data from physisorbed incommensurate monolayers (such as CD_4, Xe, and Kr). Our results for $S(\vec{q})$ in Figs. 2 and 3 show how the power-law behavior grows out of the characteristic diffraction pattern of a finite lattice. The picture which emerges is quite different from that of a single Bragg peak of width $1/L$ combined with a power-law singularity, such as suggested by previous workers.[2,3]

The most important implication of our results is that one can expect to see the Landau-Peierls power-law behavior characteristic of the infinite lattice $S(\vec{q})$ as soon as one is dealing with crystallites of size $L \sim 5000$ Å. This seems especially significant in view of the recent report[17] of crystallites of just such a size in a new form of exfoliated graphite.

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Scales and Scaling in the Kondo Model

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The thermodynamics of the Kondo model are formulated in terms of coupled integral equations and various properties, in particular the scaling property, are deduced. Then, with definition of the various scales parametrizing various asymptotic regions of the *H-T* plane, universal numbers are calculated and, in particular, Wilson's result is obtained analytically.

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Recently it was shown[1] that the Kondo Hamiltonian[2] can be exactly diagonalized with use of Bethe-*Ansatz* techniques. It is our purpose in this note to extend the formulation to nonzero temperatures, showing how the phenomenon of scaling arises in the model. Then, by means of explicit perturbative and nonperturbative calculations, we shall determine the dimensional scales

