Analytic Form for the Static Structure Factor for a Finite Two-Dimensional Harmonic Lattice

P. Dutta and S. K. Sinha
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 12 March 1981)

The static structure factor $S(\vec{K})$ for a two-dimensional harmonic lattice of finite size L is expressed analytically. Although one consequence of finite size is the absence of very-long-wavelength phonons, we find that the explicit introduction of a phonon cutoff has very little effect. The structure factor shows an universal behavior for all L, differing only by scale factors: $S(\vec{K})$ always has the infinite-size form far from a Bragg point, but is always rounded off close to the Bragg point. Implications for the interpretation of experimental results are discussed.

PACS numbers: 63.90.+t, 05.50.+q

It is by now well known that for an infinite two-dimensional (2D) crystal, long-range positional order is destroyed by long-wavelength phonons[1,2] so that the Bragg peaks in $S(\vec{K})$ are replaced by power-law singularities of the form $S(\vec{K}) \sim 1/q^{2-\eta}$ (where $q = |\vec{K} - \vec{G}|$ and $\vec{G}$ is a vector of the 2D reciprocal lattice). On the other hand, the effect of *any* finite size is to remove these phonons, so that the above form is expected to be modified. In general, only qualitative arguments have been given[2] as to the form taken by $S(\vec{K})$ for finite 2D crystals. The matter is of considerable importance, since the real world is necessarily finite sized. Diffraction experiments on incommensurate monolayers on graphite[3] (crystallite sizes 200–2000 Å) and on liquid crystals[4] show line shapes with substantial "tails" that are very plausibly fitted with power-law structure factors. The question which arises is to what extent finite-size effects make such an analysis invalid, and force a different interpretation of these "tails." A lack of understanding of finite-size effects on the observed line shape also precludes a reliable determination of correlation lengths across the melting transition.

In a recent Letter,[5] Weling and Griffin (WG) have shown that $S(\vec{K})$ for a square domain of side L can be reduced to a two-dimensional integral; they then evaluated this integral numerically to find structure factors that are increasingly oscillatory as L increases. They claim that "power-law singularities are not really present in lattices of size $L \lesssim 500$ Å," whereas "one can expect to see power-law behavior characteristic of the infinite lattice as soon as one is dealing with crystallites of size $L \sim 5000$ Å." They also state that "the picture which emerges is quite different from that of a single Bragg peak of width $1/L$ combined with a power-law singularity."

We have determined that the structure factors computed by WG are oscillatory because they postulate the domains to be perfect squares of specified orientation. Using a more physical definition, we find that the integrals can be performed analytically and the 2D finite-size structure factor written in terms of known functions. We reach conclusions regarding the behavior of $S(\vec{K})$, and regarding the importance of finite size in experimental situations, that are different from those obtained by WG.

We start from the definition

$$S(\vec{K}) = N^{-1} \sum_{i,j} \exp[-i\vec{K}\cdot(\vec{R}_i - \vec{R}_j)] f_{\vec{K}}(\vec{R}_i - \vec{R}_j),$$

where

$$f_{\vec{K}}(\vec{R}_i - \vec{R}_j) \equiv \langle \exp[-i\vec{K}\cdot(\vec{u}_i - \vec{u}_j)]\rangle,$$

$u_{\vec{i}}$ being the atomic displacement at site i. For a two-dimensional Debye lattice, it has been shown[2] that $f_{\vec{K}}(R)$ can be written as an integral over phonons:

$$f_{\vec{K}}(R) = \exp\{-\eta_{\vec{K}} \int_{q_L}^{q_D} dx\, x^{-1}[1 - J_0(xR)]\}, \qquad (1)$$

where $\eta_{\vec{K}} \propto K^2$. The Debye cutoff is at $q_D \sim \pi a^{-1}$, where a is the lattice spacing. Finite size manifests itself in two ways: first, through a low-frequency phonon cutoff at $q_L = \pi/L$; and second, in that the sums over i and j only extend over a finite system. In the vicinity of a reciprocal-lattice vector ($\vec{K} \approx \vec{G}$) we neglect the $\vec{K}$ dependence of $f_{\vec{K}}(R)$ and write $\eta_{\vec{K}} \approx \eta_{\vec{G}} \equiv \eta$. Fourier transforming $f(R)$ in terms of momentum vector $\vec{p}$, we make the "Warren" approximation[6] for the finite lattice sums:

$$\sum_{i,j} \exp[-i(\vec{K}+\vec{p})\cdot(\vec{R}_i - \vec{R}_j)] \approx N^2 \exp[-L^2(\vec{K} - \vec{G} + \vec{p})^2/4\pi].$$

This result is not in fact obtained if the lattice sums are performed over any single domain of specified size and shape; rather, the approximation takes into account the "smearing" due to superposition of scattering from many different domains. Fourier transforming back to a real-space integral gives us

$$S(\vec{K}) = (2\pi N/L^2)\int_0^\infty dR\, J_0(qR) f(R) \exp(-\pi R^2/L^2), \tag{2}$$

where $q = |\vec{K} - \vec{G}|$. The one-dimensional integral in Eq. (2) is analogous to the two-dimensional integral given by WG, except for the radial Gaussian pair distribution which simulates the effect of a distribution of domain sizes and shapes. The use of a single "sharp-edged" model domain leads to structure factors that oscillate even in the long-range-order case $f(R) = \text{const}$ (this can be seen, for example, in the expression of WG, which is easily integrated in this limit). Experimentally, however, such oscillations are never seen; rather, diffraction line shapes from numerous systems follow the familiar Gaussian ("Warren") form $S(\vec{K}) \propto \exp(-q^2L^2/4\pi)$. (Experimental values of L, such as those quoted by WG, are determined from fits to this structure factor.) Indeed, this Gaussian line shape emerges from our expression [Eq. (2)] when $f(R) = \text{const}$.

Integrals such as Eq. (2) (or the integral given by WG) can be numerically computed only for very small q because the integrands become very oscillatory as q increases. On the other hand, the existence of an analytic solution depends on the form of $f(R)$. In Fig. 1, we have plotted $f(R)$ for $L = 200$ Å, 600 Å, and infinity. If $q_L = 0$,

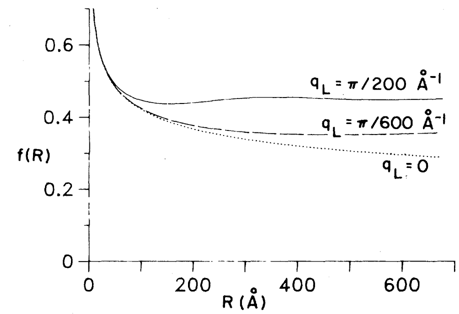

FIG. 1. $f(R)$ as defined in Eq. (1), showing the effect of a low-frequency phonon cutoff at $q_L = \pi/L$ for $L = 200$, 600, and ∞ Å. We have chosen $\eta = 0.2$.

$$f(R) = (2/\gamma q_D R)^\eta,$$

where $\gamma = 1.781\,072\,4\ldots$. Thus $f(R\to\infty) \to 0$ and there is no long-range order. [In this case Eq. (2) is fully integrable—see Eq. (4) below.] If the cutoff at $q_L = \pi/L$ is included, $f(R\to\infty) \to (a/L)^\eta$ and there is some long-range order; it is often thought that the situation is thereby substantially changed. However, the Gaussian in Eq. (2) (representing the finiteness of the lattice sums) cuts off large R values and makes the long-range behavior inconsequential; and since the effect of the cutoff on $f(R)$ is small for $R \lesssim L$ (see Fig. 1), we anticipate that it should in fact have little effect on the structure factor. To make this quantitative we expand Eq. (1) as follows (note that q_L is small):

$$\begin{aligned} f(R) &= \exp\{-\eta\int_0^{q_D} dx\, x^{-1}[1 - J_0(xR)]\}\exp\{\eta\int_0^{q_L} dx\, x^{-1}[1 - J_0(xR)]\} \\ &= (2/\gamma q_D R)^\eta\{1 + \eta\int_0^{q_L} dx\, x^{-1}[1 - J_0(xR)] + \cdots\} \\ &= (2/\gamma q_D R)^\eta\left[1 - \eta\sum_{s=1}^\infty \frac{(-\pi^2R^2/4L^2)^s}{2s(s!)^2} + \cdots\right]. \end{aligned}$$

Retaining only terms of order η is an excellent approximation for $R \lesssim L$. When $q_L = 0$, only the first term remains; the second term is the effect of the cutoff. The integral in Eq. (2) can now be performed analytically[7]:

$$S(\vec{K}) = S_0\left[\Phi(1 - \eta/2; 1; -q^2L^2/4\pi) - \eta\sum_{k=1}^\infty \frac{\Gamma(k+1-\eta/2)}{2k(k!)^2\Gamma(1-\eta/2)}\left(-\frac{\pi}{4}\right)^k \Phi\left(k+1-\frac{\eta}{2}; 1; -\frac{q^2L^2}{4\pi}\right)\right], \tag{3}$$

where Φ is the degenerate hyperbolic function ("Kummer's function")

$$\Phi(b; c; z) = \sum_{s=0}^\infty \frac{\Gamma(b+s)\Gamma(c)}{\Gamma(b)\Gamma(c+s)}\frac{z^s}{s!}$$

and $S_0 = (L/a)^{2-\eta}(2a/\gamma\sqrt{\pi})^\eta\Gamma(1-\eta/2)$ for a square lattice. For a triangular lattice there is a trivial constant factor of order unity. All sums involved in $S(\vec{K})$ converge rapidly. Clearly, when $\eta = 0$, the expected Gaussian form $S(\vec{K}) = N\exp(-q^2L^2/4\pi)$ is obtained. Moreover, from the known asymptotic form of Kummer's function, we find that at large q the term of highest order in q is independent of L and has the familiar power-law form:

$$S(\vec{K}) = 4\pi(\gamma\pi)^{-\eta}\Gamma(1-\eta/2)(qa)^{-2+\eta}/\Gamma(\eta/2). \quad (4)$$

In Fig. 2, we have plotted $S(\vec{K})$ for a triangular lattice with $a = 4.2$ Å, $L = 200$ Å, and $\eta = 0.2$, both with and without the last term in Eq. (3). As anticipated, we find that the cutoff has no qualitative effect and only a minor quantitative effect. We therefore neglect the cutoff, and Eq. (3) reduces to

$$\left(\frac{a}{L}\right)^{2-\eta} S(\vec{K}) = \Gamma\left(1-\frac{\eta}{2}\right)\left(\frac{2}{\gamma\sqrt{\pi}}\right)^{\eta}\Phi\left(1-\frac{\eta}{2};1;-\frac{q^2L^2}{4\pi}\right). \quad (5)$$

In other words, $(a/L)^{2-\eta}S(\vec{K})$ is an universal function of qL, irrespective of the value of L. This universal function is plotted in Fig. 3 for a triangular lattice and shows that the structure factors are always qualitatively similiar, differing quantitatively only by L-dependent scale factors. At large enough q ($q \gtrsim 10/L$) the structure factors always look like the infinite-size structure factor,[8] while finite-size effects round off $S(\vec{K})$ closer to the Bragg point. From Fig. 3 it can be seen that for small q, $S(\vec{K})$ contains a central peak of width $\sim L^{-1}$, as has been qualitatively predicted.[2] This is to be identified with the Bragg peak of a finite crystal, since a low-frequency phonon cutoff exists in such crystals and the Debye-Waller factor $f(\infty)$ is nonzero. However, in writing Eq. (5) we have ignored the cutoff [strictly speaking, Eq. (5) applies to the situation where a finite area of an infinite crystal is illuminated by the radiation beam]; thus the persistence of Bragg scattering may seem surprising. The fact is, however, that even if the phonons with $\lambda \gg L$ are allowed to remain, they are unimportant when the scattering is over distances smaller than L. Thus, when the lattice sums are over a finite system, for all practical purposes a cutoff exists whether it has been explicitly introduced or not.[9] Looked at in another way, in a system that extends only up to $R \sim L$, the relevant question is not whether $f(\infty)$ is nonzero but whether $f(L)$ is nonzero. Landau-Peierls systems are unique in that $f(L)$ can be appreciable ("intermediate-range order") even if $f(\infty) = 0$ (no long-range order).

Because $f(L) \propto L^{-\eta}$, $S(\vec{G}) \propto L^{2-\eta}$ [for a normal 2D Bragg peak, $S(\vec{G}) \propto L^2$]. Since η is a function of temperature, the height of the "central peak" relative to the power-law "tail" changes with temperature in a size-dependent way.[2] However, it is easily shown that the finite-size $S(\vec{K})$ [Eq. (5)] has approximately the same integrated intensity as the infinite-size $S(\vec{K})$ [Eq. (4)] between $q = 0$ and $q \sim 10/L$. [In other words finite-size effects change the shape of $S(\vec{K})$ but not the area under it.] Thus when the resolution function is wider than the central peak, one cannot discern finite-size effects in the observed line shape. This is the situation that applies in the typical x-ray or neutron diffraction experiment [resolution ~ 0.01 Å^{-1} full width at half maximum (FWHM)]

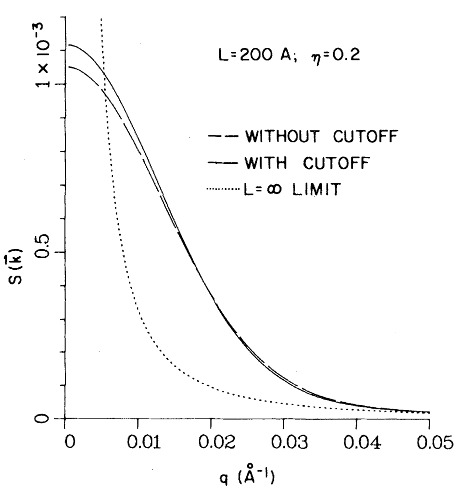

FIG. 2. $S(\vec{K})$ for $\vec{K}$ near a reciprocal-lattice vector of a triangular lattice with $a = 4.2$ Å, for a finite coherence length $L = 200$ Å, calculated with and without a low-frequency cutoff in the phonon spectrum. We have chosen $\eta = 0.2$.

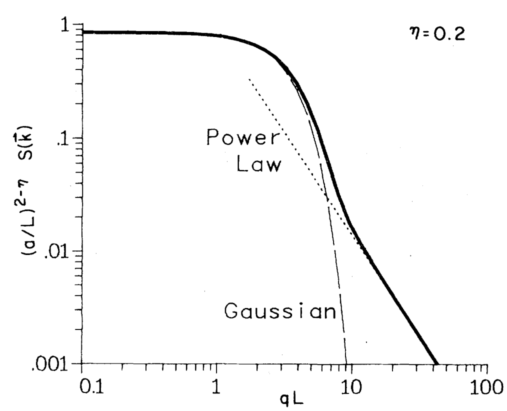

FIG. 3. "Universal curve" showing the behavior of the structure factor for any finite L. We have chosen $\eta = 0.2$ and a triangular lattice.

with use of ZYX graphite (if $L \sim 500$ Å, FWHM of central peak ~ 0.004 Å^{-1}). We have explicitly verified that for diffraction from incommensurate methane on ZYX graphite,[3] fits that use Eq. (5) cannot be distinguished from fits that use Eq. (4). (Details will be published elsewhere.) While improved resolution (such as is available when synchrotron radiation radiation is used) might make finite-size effects observable for the same value of L, our example does serve to illustrate that available surface coherence lengths are less restrictive than sometimes imagined.

[1]B. Jancovici, Phys. Rev. Lett. 19, 20 (1967).

[2]Y. Imry and L. Gunther, Phys. Rev. B 3, 3939 (1971); Y. Imry, Crit. Rev. Solid State Mater. Sci. 8, 157 (1979).

[3]P. Dutta, S. K. Sinha, P. Vora, M. Nielsen, L. Passell, and M. Bretz, in *Ordering in Two Dimensions*, edited by S. K. Sinha (North-Holland, Amsterdam, 1980), p. 169.

[4]D. E. Moncton and R. Pindak, in *Ordering in Two Dimensions*, edited by S. K. Sinha (North-Holland, Amsterdam, 1980), p. 83; J. Als-Nielsen, R. J. Birgeneau, M. Kaplan, J. D. Litster, and C. R. Safinya, Phys. Rev. B 21, 312 (1980).

[5]F. Weling and A. Griffin, Phys. Rev. Lett. 46, 353 (1981).

[6]B. E. Warren, Phys. Rev. 59, 693 (1941).

[7]See, e.g., I. S. Gradshteyn and I. W. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1965), Sec. 6.631.

[8]Equation (5) (like the power-law structure factor) is valid only in the continuum approximation for the lattice sums. It was pointed out to us by A. Griffin that the error made by this approximation increases with qa and not with qL. Thus for very small L, when q is so large that finite-size effects are negligible, $S(\vec{K})$ may still deviate observably from a power law—this time because of the inadequacy of the continuum approximation.

[9]Y. Imry, private communication.