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Substrate effects on long-range order and scattering from low-dimensional systems

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Using solvable models it is shown that coupling one- and two-dimensional systems to substrates produces significant alterations in their long-range order and scattering characteristics, even if the coupling is very weak. Expressions for Peierls's long-range-order parameter, $\langle \delta_n^2 \rangle$, are obtained, with their asymptotic forms, and static structure factors, $S(\vec{Q})$, are evaluated.

Recent theoretical and experimental studies of systems of "less than three dimensions" have inspired a resurgence of interest in this subject. Among the systems reported to exhibit one-dimensional (1D) or quasi-1D behavior are some organic[1] and inorganic[2] complexes. Systems exhibiting two-dimensional (2D) or quasi-2D behavior include adsorbed layers,[3] electrons trapped on a liquid helium surface[4] and thin "soap-bubble films.[5]" Particularly intriguing are questions of ordering (degree and type) and stability in such systems.[6-10] Of special interest here is their *degree* of long-range order in light of physical arguments,[6] and rigorous proofs[7] that *true* long-range order does not exist for *strict* 1D and 2D systems. Since the physical systems mentioned above are coupled to a skeletal or substrate environment, one should expect, in general, *quasi*-1D or *quasi*-2D rather than strict 1D or 2D behavior. Such coupling effects have been observed in recent neutron-scattering studies of $Hg_{3-\delta}AsF_6$,[2,11] and of phases of CD_4 monolayer films on graphite[12] for which the scattered neutron line shapes could not be interpreted, even for the registered (commensurate) phase, on the basis of *strict* 2D theories.

Our purpose is to show that coupling to a substrate significantly affects the degree of long-range order and scattering characteristics in certain 1D and 2D model systems. To elucidate our discussion we limit our considerations to certain solvable models employing simple coupling schemes.

A measure of the long-range order in an N-particle system is provided by the function $\langle \delta_{n\hat{\kappa}}^2 \rangle \equiv \langle ((\vec{u}_n - \vec{u}_0)\cdot\hat{\kappa})^2 \rangle$ given by

$$\langle \delta_{n\hat{\kappa}}^2 \rangle = 4(Nm)^{-1} \sum_{\vec{q}} \langle |\vec{U}_{\vec{q}} \cdot \hat{\kappa}|^2 \rangle \sin^2(\tfrac{1}{2}\vec{q}\cdot\vec{R}_n)\,, \quad (1)$$

where $\vec{u}_n$ is the deviation of particle n of mass m from its equilibrium position $\vec{R}_n$, $\hat{\kappa}$ is an arbitrary direction in the lattice, and $U_{\vec{q}}$ is the normal-mode amplitude. The angular brackets denote temperature ensemble averaging. At sufficiently high temperatures, T (typically larger than the Debye temperature) equipartition can be used[6,8] to write $\langle |\vec{U}_{\vec{q}} \cdot \hat{\kappa}|^2 \rangle = k_B T \omega_q^{-2}$, where ω_q is the normal-mode frequency.

Consider first a 1D chain of atoms of lattice spacing a and interparticle nearest-neighbor (NN) force constants K. Let it be coupled via NN and next NN force constants $K_\perp$ and K_D, respectively, to a 1D parallel substrate chain of heavy masses each a distance a, for simplicity, below a lattice site of the first chain. In the harmonic approximation, and for a stationary substrate, the longitudinal normal-mode frequency (describing motions along the chain axis) is given by $\omega_q^2 = (4K/m)[R^2 + \sin^2(qa/2)]$, where $2R = K_D^2/K^2$ is a measure of the interchain relative coupling strength. Notice that this mode possesses a $q=0$ gap, equal to $4KR^2/m$. Using the high-T approximation and the above ω_q, transformation of the sum in Eq. (1) over $\vec{q}$ to an integral and converting to a contour integral in the complex plane yields the following closed-form result:

$$\langle \delta_n^2 \rangle / a^2 = \sigma\left(\frac{1 - [2R^2 + 1 - 2R(R^2+1)^{1/2}]^n}{R(R^2+1)^{1/2}}\right)$$
$$\equiv C_1(1 - e^{-\alpha n})\,, \quad (2)$$

where $\sigma = k_B T/2Ka^2$ (typically[11] of the order 10^{-3}–10^{-4}). In the limit of vanishing coupling, $R=0$, and for large n the previously known result[11] $\langle \delta_n^2 \rangle / a^2 \sim (2\sigma)n$ is recovered. With a criterion that long-range order exists when $\langle \delta_n^2 \rangle / a^2 < 1$ as $n \to \infty$, it follows that there is a long-range order if $R \gtrsim \sigma$, so that even weak coupling to a substrate restores long-range order. The modified behavior upon coupling is shown in Fig. 1(a).

Using the expression given in Eq. (2), the frequency-integrated dynamical structure factor $S(\vec{Q})$ (for $\vec{Q}$ parallel to the chain) can be evaluated, yielding

$$S'(\vec{Q}) \equiv S(\vec{Q}) - Ne^{-f^2}\delta(\vec{Q},\vec{G}) = \sum_{l=1}^{\infty} \frac{(-f)^{2l}}{l!} Z(l)\,, \tag{3a}$$

$$Z(l) = \sum_{j=0}^{l} (-1)^j \binom{l}{j} \left(\frac{e^{-\alpha j} - \cos(Qa)}{\cosh(\alpha j) - \cos(Qa)}\right), \tag{3b}$$

where $2f^2 = Q^2 C_1$ and $\vec{G}$ is a reciprocal-lattice vector. In the limit of vanishing interchain coupling[11] $S'(\vec{Q})$ [and $S(\vec{Q})$] consists of a series of narrow peaks centered upon the reciprocal-lattice vectors. For nonvanishing coupling strengths a broadening of the peaks accompanied by a pronounced asymmetry occurs as shown in Fig. 1(b) (note changes in scales). Sufficient accuracy is obtained by truncating the sum over l in Eq. (3a) typically at $l = 3-5$. The above could provide practical functional form for fitting purposes.

We turn next to the evaluation of $\langle \delta_\parallel^2(\rho)\rangle$ (where $\rho = r_\parallel/a$ and $r_\parallel$ is an interparticle distance in an arbitrary direction) for a 2D square lattice, of lattice constant a which is coupled to a stationary square substrate layer via NN and next NN force constants $K_\perp$ and K_D. Following arguments similar to the above, we obtain

$$\langle \delta_\parallel^2(\rho)\rangle/a^2 = (\sigma/2\pi)\rho^{-2}\int_0^{2\sqrt{\pi}\rho} dy\, y\, \frac{1 - J_0(y)}{R^2 + \sin^2(y/2\rho)}\,, \tag{4}$$

where the Debye cutoff has been employed and J_0 is the Bessel function of the first kind. For vanishing interplane coupling, $R = 0$, the previously[3,8] derived asymptotic logarithmic divergence of $\langle \delta_\parallel^2(\rho)\rangle$ is observed. For finite coupling asymptotic analysis yields nonlogarithmic asymptotic behavior (see Appendix).

$$\langle \delta_\parallel^2(\rho)\rangle/a^2 \sim (\sigma/\pi)\left(F(R) - \frac{\sqrt{\pi}\,J_1(2\pi\rho)/\rho}{R^2 + \sin^2\sqrt{\pi}}\right), \tag{5a}$$

where

$$F(R) = \int_0^{2\sqrt{\pi}} dy\, y(2R^2 + 1 - \cos y)^{-1}\,. \tag{5b}$$

Numerical evaluation of Eq. (4) for various values of R indicated that good fits to $\langle \delta_\parallel^2(\rho)\rangle$ are given by the form $A - B\exp(-\gamma\rho^{1/2})$ where A, B, and γ are constants dependent upon R. Sample results are shown in Fig. 2(a). Using the above form, an expression for $S'(\vec{Q})$ (for $\vec{Q}$ parallel to be plane) can be derived, yielding

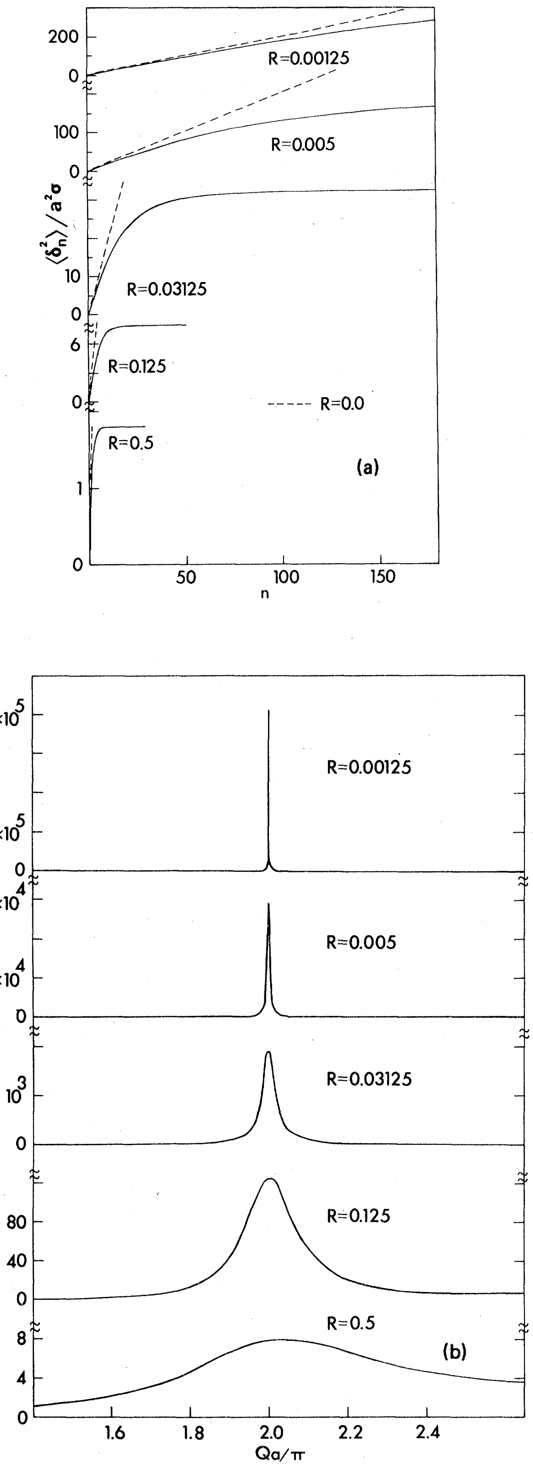

FIG. 1. 1D chain coupled to a stationary substrate chain. (a) $\langle\sigma_n^2\rangle$ vs n, for various values of relative coupling strength R. Solid lines after Eq. (2); dashed lines correspond to the $R = 0$ case. (b) Subtracted static structure factors, $S'(\vec{Q})$, around the first Bragg peak for various coupling strengths, $\sigma = 10^{-4}$. Note changes in scale.

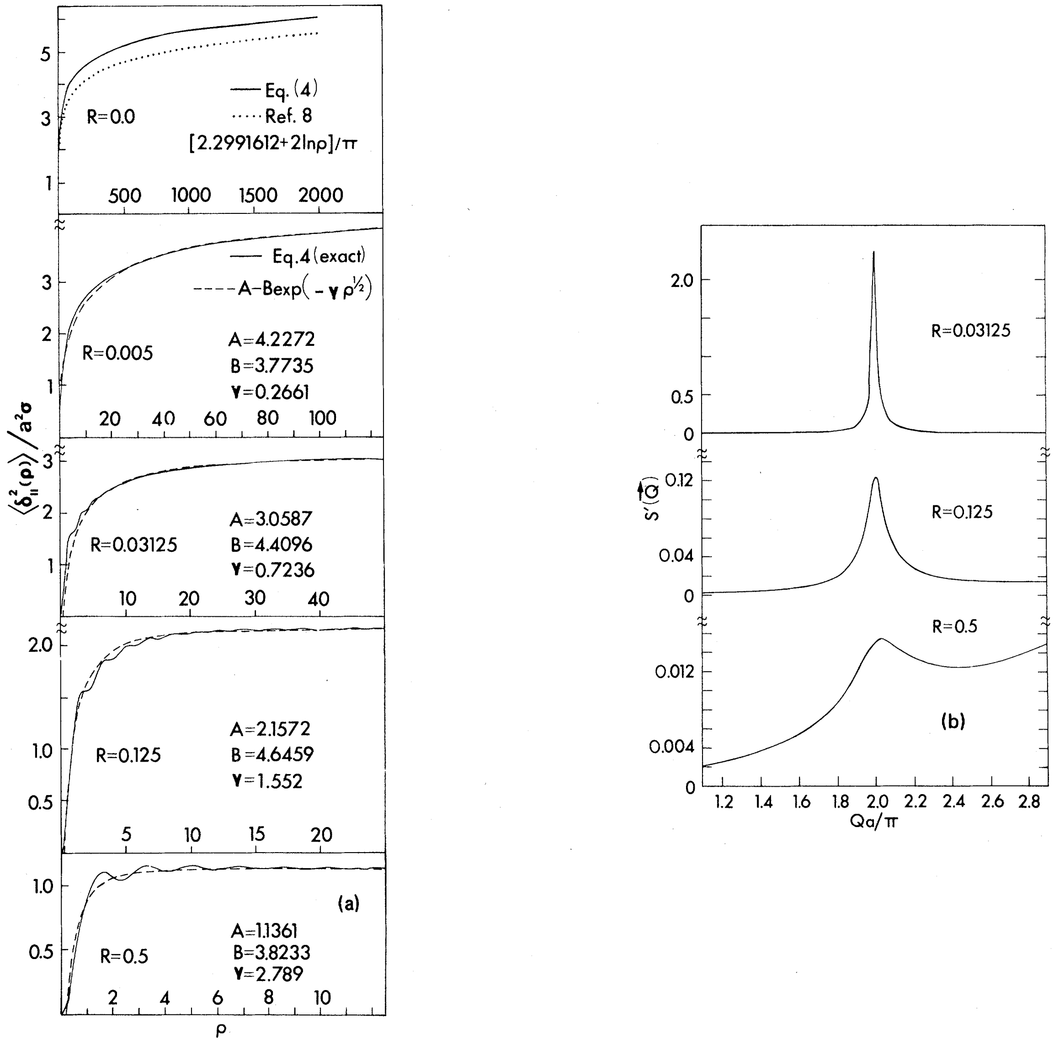

FIG. 2. 2D layer coupled to a stationary substrate layer. (a) $\langle\sigma_{\parallel}^2(\rho)\rangle$ vs $\rho = r_{\parallel}/a$ for various values of R. For $R=0$, results obtained with (dotted) and without (solid) the long-wavelength approximation are shown. For finite R values, results are shown using Eq. (4) (solid) and via the indicated fits (dashed). (b) Subtracted static structure factors, $S'(\vec{Q})$, around the (10) Bragg peak for several coupling strengths, R, $\sigma = 10^{-4}$. Note changes in scale.

$$\begin{aligned}
S'(\vec{Q}) &= S(\vec{Q}) - \delta(\vec{Q},\vec{G})\exp(-AQ^2/2) \\
&= \exp(-AQ^2/2)\Bigg(4\sum_{\mu=0}^{\infty}\sum_{\nu=0}^{\infty}\cos(Q_x\mu a)\cos(Q_y\nu a)\left[\exp\left(\tfrac{1}{2}BQ^2e^{-\gamma(\mu^2+\nu^2)^{1/4}}\right)-1\right] \\
&\qquad -2\sum_{\mu=0}^{\infty}\cos(Q_x\mu a)\left[\exp\left(\tfrac{1}{2}BQ^2e^{-\gamma\mu^{1/2}}\right)-1\right]-\sum_{\nu=0}^{\infty}\cos(Q_y\nu a)\left[\exp\left(\tfrac{1}{2}BQ^2e^{-\gamma\nu^{1/2}}\right)-1\right] \\
&\qquad +\exp\left(\tfrac{1}{2}BQ^2\right)-1\Bigg),
\end{aligned} \tag{6}$$

where A, B, and γ are the parameters defined above and $\vec{G}$ is a reciprocal-lattice vector of the 2D net. For a finite sample the summations in the above equation should extend up to $N_x/2$ and $N_y/2$, where $N_x a$ and $N_y a$ are the extensions of the 2D sample in the x and y directions. Results for $S'(\vec{Q})$ around the (10) Bragg peak, for various values of R, are shown in Fig. 2(b). It is of interest to comment that for a strict 2D lattice, i.e., $R=0$, the peaks in $S(\vec{Q})$ near reciprocal-lattice vectors

$\vec{G}$ are given by power-law singularities,[10] $S(\vec{Q}) \sim |\vec{Q}-\vec{G}|^{-2+\eta_{\vec{G}}(T)}$, where the bounded exponents $\eta_{\vec{G}}(T)$ are related to the elastic moduli of the lattice. We note that for both the 1D and 2D cases, the $\delta(\vec{Q},\vec{G})$ term has been subtracted in $S'(\vec{Q})$ [e.g., Eq. (3a)]. This term which is absent in the $R=0$ limit[11] increases with R, i.e., increasing coherent scattering intensity at $\vec{Q}=\vec{G}$. Correspondingly, the residual $S'(\vec{Q})$ decreases in amplitude and broadens upon increased coupling to the substrate [note scales in Figs. 1(b) and 2(b)].

It is important to note that for both the 1D and 2D coupled systems the long-range-order parameters exhibit an altered asymptotic behavior, deviating significantly from the uncoupled results ($R=0$) even for small substrate coupling strengths [Figs. 1(a), 2(a)]. In fact, for both cases $\langle\delta_n^2\rangle$ converges to a limit at microscopic distances even for small R values. Consequently, even for small couplings to the substrate strict 1D or 2D behavior is lost. This is due to the fact that by turning on the couplings to the substrate (finite R) the number of possible paths for linkage between any two atoms increases (the effective increase is related to the value of R). Thus the tendency to maintain long-range-order increases upon coupling. These characteristics are exhibited in the integrated scattering functions [Figs. 1(b), 2(b)], which provide possible forms for the interpretation of experimental data.

While we recognize that the above model calculations employed simplifying assumptions, such as a particular geometry, range of interaction, classical description, and a stationary substrate, the essential results pertaining to the salient effects of the *dimensionality* of the system on the *degree* of long-range-order and scattering characteristics should remain valid in more general circumstances. Moreover, the first three assumptions can be easily relaxed (for commensurate arrangements) and do not modify the main conclusions. Noncommensurate configurations and couplings to extended nonstationary substrates remain the subjects of further investigations.

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APPENDIX

In this Appendix we outline the evaluation of the asymptotic expression for $\langle\delta_\parallel^2(\rho)\rangle$ given in Eqs. (5). First, we rewrite Eq. (4) as

$$\langle\delta_\parallel^2(n)\rangle/a^2=\left(\frac{\sigma}{\pi}\right)\frac{1}{n^2}\int_0^{2n\sqrt{\pi}}dx\,x\,\frac{1-J_0(\beta x)}{2R^2+1-\cos(x/n)}\,, \tag{A1}$$

where in terms of the lattice constant, a, the distance between two lattice sites $r_\parallel$ $(=\rho a)$ is equal to $\beta a n$ (βa is the smallest distance between lattice sites in a chosen direction, and n is an integer). Owing to the large value of n with which we are concerned, the denominator of the integral in the above equation varies much more slowly than the numerator. Therefore, we partition the integral into a sum of integrals in which the denominators are almost constant,

$$\langle\delta_\parallel^2(n)\rangle/a^2=\left(\frac{\sigma}{\pi n^2}\right)\left(\sum_{m=0}^{\tilde{n}-1}\int_{m\pi}^{(m+1)\pi}dx\,x\,\frac{1-J_0(\beta x)}{2R^2+1-\cos(x/n)}+\int_{\tilde{n}\pi}^{2n\sqrt{\pi}}dx\,x\,\frac{1-J_0(\beta x)}{2R^2+1-\cos(x/n)}\right), \tag{A2}$$

where $\tilde{n}$ is the largest integer such that $\tilde{n}\pi\leq 2n\sqrt{\pi}$. Considering the denominators in the integrands in Eq. (A2) as constant over their ranges of integration and performing the remaining integration, we obtain

$$\langle\delta_\parallel^2(n)\rangle/a^2=\frac{\sigma}{\pi n^2}\left(\sum_{m=0}^{\tilde{n}}\frac{(m+\frac{1}{2})\pi^2}{2R^2+1-\cos(m\pi/n)}\right.$$
$$\left.+\sum_{m=0}^{\tilde{n}}\frac{\cos(m\pi/n)-\cos(m+1)\pi/n}{[2R^2+1-\cos(m\pi/n)]\{2R^2+1-\cos[(m-1)\pi/n]\}}\frac{m\pi J_1(\beta m\pi)}{\beta}-\frac{2n\sqrt{\pi}J_1(2\beta n\sqrt{\pi})}{\beta[2R^2+1-\cos(\tilde{n}\pi/n)]}\right). \tag{A3}$$

Consider the first sum in Eq. (A3). With negligible error (large n) the argument of the cosine in the denominator can be replaced by $y_m=(m+\frac{1}{2})\pi/n$. Converting to an integral we get to a good approximation the expression $n^2F(R)$, where $F(R)$ is given by Eq. (5b). Next, we approximate the third term in Eq. (A3) by replacing the argument of the cosine in the denominator by $2\sqrt{\pi}$ (note the above definition of $\tilde{n}$). Now, note that the first term in Eq. (A3) contributes a constant term, $(\sigma/\pi)F(R)$, to the asymptotic form of $\langle\delta^2(n)\rangle/a^2$ while the third term behaves asymptotically as $n^{-3/2}$. While we have not been able to evaluate the second sum in Eq. (A3) analysis of its terms for various ranges of m and R indicates that its contribution to $\langle\delta^2(n)\rangle/a^2$ falls off asymptotically at least as fast as n^{-2}. Consequently, retaining only the contribution from the two leading terms, we arrive at the asymptotic expression given by Eq. (5).

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