Anharmonic Effects in Bulk Smectic Liquid Crystals and Other "One-Dimensional Solids"

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Anharmonic corrections to the familiar harmonic description of "one-dimensional solids" (i.e., liquids which develop a one-dimensional mass-density wave) are calculated by analytic renormalization-group methods in three dimensions. The elastic constants describing the compressional and undulational modes respectively vanish and diverge logarithmically at small wave vectors. Density correlations decay as r^{-x} with $x=\eta(T)(\ln r)^{\tilde{\eta}}$, where the exponent $\tilde{\eta}$ assumes the universal value $\frac{1}{5}$.

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It has been understood theoretically for some forty years that one-dimensional (1D) solids —systems whose mass density varies in one spatial direction but is uniform (liquidlike) in the other two—ought not to occur in nature: Fluctuations destroy the long-range density order in such structures, restoring the uniform density of the liquid state.[1] The existence of smectic liquid crystals, composed for all intents and purposes of layers, uniform in density, of organic molecules stacked in a uniform 1D array, is nevertheless undeniable.[2] The resolution of this apparent contradiction was provided by Caille,[3] who argued that while the density in a smectic is indeed uniform, density correlations fall off very slowly —algebraically—with distance. These strong correlations simulate, in all but the most excruciatingly precise experiments, the existence of true long-range density order. Experimental verification of this prediction has recently been furnished by the high-resolution x-ray measurements of Als-Nielsen *et al.*[4] Their static structure factor data for a smectic-A liquid crystal demonstrated the absence of long-range order and was, in agreement with Caille,[3] consistent with power-law decay of density correlations.

The calculations which rule out long-range order and produce algebraic decay can be summarized as follows: From symmetry considerations[1-3] one deduces the form of the quadratic Hamiltonian[1] appropriate to the description of the 1D solid (the quadratic theory is, alternatively, called the harmonic or Gaussian spin-wave approximation). The density-density correlation function $G(\vec{x})$ is then simply computed; the results[3]

$$G(z, x_\perp = 0) \sim |z|^{-\eta(T)}, \quad G(z = 0, x_\perp) \sim x_\perp^{-2\eta(T)},$$

valid at large $|\vec{x}|$, follow, where η is a continuous function of the temperature T. (Here z is taken as the direction of the 1D density wave.[5]) In the terminology of the renormalization group (RG) the continuously varying exponent η arises from the existence of a fixed line in the harmonic (Gaussian spin-wave) approximation.[6,7]

Terms of higher than quadratic order in the spin-wave Hamiltonian are of course allowed (in fact demanded) by symmetry. In this note we point out that the fixed line of the harmonic theory is marginally *unstable*[8] with respect to two such terms. We show, in consequence, that $G(z, x_\perp = 0) \sim |z|^{-x}$ with $x = \eta(T)(\ln z)^{\tilde{\eta}}$ at large z (a similar result holding in the $x_\perp$ direction), the exponent $\tilde{\eta}$ assuming the universal value $\frac{1}{5}$. In addition, the elastic constants B and K_1 (here we adopt the notation conventionally used[2] to describe smectics A) which characterize the 1D quasisolid are respectively shown to vanish and diverge logarithmically at very small momenta (that is, in the regime where hydrodynamics is usually valid).

Consider any isotropic system whose density, $n(\vec{x})$, tends to order at wave vectors $\vec{q}$ for which $|\vec{q}| = q_0 \neq 0$. The gradient (elastic) terms of the free-energy functional that describes such a system take the form

$$H = \tfrac{1}{2}K \int d^3x [-2q_0^2(\nabla m)^2 + (\nabla^2 m)^2 + O((\nabla^3 m)^2)], \tag{1}$$

for some parameter K, $m(\vec{x})$ being the spatially varying part of the density: $n(\vec{x}) = n(\vec{0}) + m(\vec{x})$. Writing

$m(\vec{x}) = \mathrm{Re}\psi(\vec{x})$, where $\psi(\vec{x})$ describes a 1D density wave, $\psi(\vec{x}) = A(\vec{x})\exp iq[z + u(\vec{x})]$, and ignoring fluctuations[9] in the amplitude $A(\vec{x})$ [i.e., taking $A(\vec{x}) = A$, a constant] one arrives at the spin-wave[10] Hamiltonian

$$H_{sw} = (2t)^{-1}\int d^3x\{C(\partial u/\partial z) + \tfrac{1}{2}C(\nabla u)^2 + \lambda^2(\nabla^2 u)^2 + (\partial u/\partial z)^2 + (\partial u/\partial z)(\nabla u)^2 + \tfrac{1}{4}[(\nabla u)^2]^2\}; \quad (2)$$

here $t \equiv [4K(Aq^2)^2]^{-1}$, $C \equiv q^{-2}(q^2 - q_0^2)$, the wave number q is chosen to ensure that the expectation value $\langle \partial u/\partial z\rangle = 0$, and λ is proportional[11] to q^{-1}.

Consider first only terms of (2) quadratic in u. Clearly then to obtain $\langle \partial u/\partial z\rangle = 0$ one must choose $C = 0$ (or $q = q_0$), whereupon, for small $\vec{k}$,

$$H_{sw} \sim (2t)^{-1}\int [d^3k/(2\pi)^3][k_z^2 + \lambda^2(k_\perp^2)^2]|u(\vec{k})|^2, \quad (3)$$

where $k_\perp^2 \equiv k_x^2 + k_y^2$. This is the form of the Hamiltonian typically used to show[1] that $\langle m(\vec{x})\rangle = 0$ and that $G(\vec{x})$ decays algebraically: A simple calculation with (3) yields[3] $G(x) \sim x^{-q^2 t/4\pi\lambda}$. These results can, alternatively, be obtained through a RG treatment of (3), which has a fixed line for all positive t.[7]

Next consider the cubic and quartic terms of (2). These are conveniently treated perturbatively in powers of t via the loop expansion; (3) is used as the noninteracting Hamiltonian and each loop gives rise to a factor of t.[12] Before using this expansion to generate a RG equation for $G(\vec{x})$ we comment on the rotational symmetry of the problem: At the quadratic (zero-loop) level [Eq. (3)], the correlation function $g^{-1}(\vec{k}) \equiv \langle|u(\vec{k})|^2\rangle^{-1}$ is simply $t^{-1}(k_z^2 + \lambda^2 k_\perp^4)$. The absence of a $k_\perp^2$ term in g^{-1} is a well-known consequence[1] of the spatial isotropy of Hamiltonian (1); we arbitrarily chose the 1D density wave in the z direction but any other direction must produce identical physics. This symmetry naturally holds to all orders in t. The coefficient of $k_\perp^2$ in g^{-1} must therefore vanish to all orders as well. In each order of the series in t one must choose C so that $\langle \partial u/\partial z\rangle = 0$. In the same order, this choice for C guarantees the vanishing of the coefficient of $k_\perp^2$ in g^{-1}. It is straightforward to verify this mechanism in $O(t)$.

It is convenient to treat the cubic and quartic terms of (2) with the field theoretic RG techniques of Brézin *et al.*[12] Since the calculation is, except for the presence of the $(\partial u/\partial z)(\nabla u)^2$ term here, identical to the RG treatment[7] of the $m = 2$ Lifshitz point model,[13] we sketch only the main ideas. Elementary power counting shows that only the $(\partial u/\partial z)(\nabla_\perp u)^2$ and $[(\nabla_\perp u)^2]^2$ terms need be considered as these are marginal[7,8] with respect to the fixed line of the quadratic theory. Terms like $(\partial u/\partial z)^3$, $(\partial u/\partial z)^2(\nabla_\perp u)^2$, and $(\partial u/\partial z)^4$ are *irrelevant*[8]; they cannot alter the long-distance behavior of any correlation function and so can be dropped from Hamiltonian (2).

We find the following RG flow equations for the couplings t and λ:

$$\frac{dt(l)}{dl} = \frac{t(l)w(l)}{16\pi}[1 + O(w(l))], \quad (4a)$$

$$\frac{d\lambda(l)}{dl} = \frac{3\lambda(l)}{64\lambda}w(l)[1 + O(w(l))], \quad (4b)$$

where $l \equiv \ln\Lambda$, the inverse length Λ is the ultraviolet cutoff of the theory, and the dimensionless combination $w \equiv t\lambda^{-3}$ satisfies the RG equation

$$\frac{dw(l)}{dl} = \frac{-5w^2(l)}{64\pi}[1 + O(w(l))]. \quad (4c)$$

Using dimensional analysis to write the correlation function $g^{-1}(k_\perp, k_z = 0, t, \lambda)$ as $k_\perp^4 f(\Lambda/k_\perp, w)$ we obtain an RG scaling equation for f:

$$f(\Lambda/k_\perp, w) = f(1, w(l^*))\exp[(3/32\pi)\int_0^{l^*} w(l')\,dl'], \quad (5)$$

with $l^* \equiv \ln(\Lambda/k_\perp)$. Note that $w(l)$ is a nonuniversal function of w in that it depends on the details of the ultraviolet cutoff prescription employed. Equations (5) and (4c) yield

$$g^{-1}(k_\perp, k_z = 0, t, \lambda) \sim \lambda^2 t^{-1} k_\perp^4 \left(1 + \frac{5w\ln(\Lambda/k_\perp)}{64\pi}\right)^{2/5}. \quad (6)$$

Similarly,

$$g^{-1}(k_z, k_\perp = 0, t, \lambda) \sim t^{-1}k_z^2 \left(1 + \frac{5w\ln[\Lambda(\lambda/k_z)^{1/2}]}{64\pi}\right)^{-4/5}, \quad (7)$$

and the density-density correlation function scales as

$$G(x_\perp, z=0) \sim \exp\left\{-\frac{8}{3}\left[\left(1+\frac{5w}{64\pi}\ln(x_\perp\Lambda)\right)^{6/5}-1\right]-R\left(1+\frac{5w}{64\pi}\ln(x_\perp\Lambda)\right)^{2/5}\right\}. \quad (8)$$

Here R is a nonuniversal positive coefficient. When $x_\perp = 0$, $z \neq 0$, $G(z)$ is given by (8) with $x_\perp$ replaced by $(z\lambda)^{1/2}$.

Equations (6) and (8) imply the existence of a length scale

$$x_\perp^* \equiv k_\perp^{*-1} \equiv \Lambda^{-1}\exp(64\pi/5w), \quad (9)$$

at which the system crosses over from the familiar Gaussian behavior to the asymptotic behavior governed by the full Hamiltonian (2). In the Gaussian regime, $k_\perp \gg k_\perp^*$ or $x_\perp \ll x_\perp^*$, $g^{-1}(k_\perp) \sim k_\perp^4$ and $G(x_\perp) \sim x_\perp^{-q^2 t/4\pi\lambda}$. For $k_\perp \ll k_\perp^*$, however,

$$g^{-1}(k_\perp) \sim k_\perp^4[\ln(\Lambda/k_\perp)]^{2/5}, \quad (10a)$$

$$G(x_\perp) = x_\perp^{\eta} \text{ with } \eta = -(8/3)(q\lambda)^2(5t\lambda^{-3}/64\pi)^{6/5}[\ln(x_\perp\Lambda)]^{1/5}. \quad (10b)$$

When $z \neq 0$, $x_\perp = 0$, the analogous crossover length scale is given by $z^* = \lambda^{-1}(x_\perp^*)^2$. For $k_z \ll k_z^* \equiv (z^*)^{-1}$, (7) yields

$$g^{-1}(k_z) \sim k_z^2\{\ln[\Lambda(\lambda/k_z)^{1/2}]\}^{-4/5}, \quad (11)$$

while $G(z)$ is given by (10b) with $x_\perp\Lambda$ replaced by $\Lambda(\lambda z)^{1/2}$.

In the conventional language of smectic liquid crystals,[2] the coefficients of $(\partial u/\partial z)^2$ and $(\nabla_\perp^2 u)^2$ in (2) are, respectively, B/k_BT and K_1/k_BT, where B and K_1 are the bare elastic constants. That is, $B/k_BT = t^{-1}$ and $K_1/k_BT = \lambda^2 t^{-1}$. Defining renormalized elastic constants $B^R(k)$ and $K_1^R(k)$ as the coefficients of k_z^2/k_BT and $k_\perp^4/k_BT$ in $g^{-1}(k)$, respectively, one sees from Eqs. (10a) and (11a) that $B^R(k)$ and $K_1^R(k)$ respectively vanish and diverge logarithmically at small k. This nonanalytic dependence of B^R and K^R on k at small k implies that the gradient expansion, whose existence is the central assumption of hydrodynamics, is not valid[14] in 1D solids such as smectic-A liquid crystals.

We now consider the feasibility of observing these corrections to the harmonic approximation experimentally. For a typical smectic-A liquid crystal, $T \sim 350$ °K,[15] $\lambda \sim 13$ Å,[15] and $K_1 \sim 5\times10^{-7}$ dyne,[2] whereupon $w \equiv t\lambda^{-3} = k_BT/\lambda K_1 \sim 0.7$. Since these numbers are typically obtained through experiments done at wave vectors[15] $\Lambda \sim 10^{-3}$ Å^{-1}, we substitute this value for Λ in Eq. (6),[16] obtaining

$$K_1^R(k_\perp) = K_1(\Lambda)[1 - 0.017\ln(10^3 k)]^{2/5}, \quad (12)$$

where $k_\perp$ is measured in reciprocal angstroms and $K_1(\Lambda) \sim 5\times10^{-7}$ dyne is the value of K_1^R at $k_\perp \sim \Lambda \sim 10^{-3}$ Å^{-1}. K_1 can be measured by light scattering with an accuracy of about[17] 3%. The logarithmic correction term in (12) therefore becomes observable at $k_\perp$'s sufficiently small that $K_1^R(k_\perp)$ and $K_1(\Lambda)$ differ by more than 3%, that is, when $k_\perp \sim 10^{-5}$ Å^{-1}. In light-scattering experiments[18] k's of $\sim 10^{-5}$ Å^{-1} are obtainable.[19] In deriving this estimate for $k_\perp$ we have assumed $w \ll 1$, a criterion not obviously satisfied by $w \sim 0.7$. An explicit calculation of $O(w(l))$ corrections in (4) and (5) would improve the estimate. Note that this estimate for $k_\perp$ is rather sensitive to the value of w which characterizes the material. If, for example, a smectic-A with $w = 4$ can be found,[20] then the effect becomes manifest at $k_\perp \sim 10^{-4}$ Å^{-1}. More detailed consideration of this and other experiments where the corrections might be visible (e.g., x-ray measurements[4] of the static structure factor [Eq. (8)], and second-sound measurements[21]) is clearly warranted.

Results analogous to those obtained here can be derived for any isotropic 3D system that develops a pseudo-1D condensate. Systems other than smectics-A and -C and cholesterics[2] may well have this character. For example, discussions of pion condensation in neutron stars[22] often assume that the condensate has a 1D character. If this assumption is correct the pion-condensed state cannot have long-range order but rather correlations whose spatial decay is given by (7).

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[4]See, e.g., J. Als-Nielsen, J. D. Litster, R. J. Birgeneau, M. Kaplan, C. R. Safinya, A. Lindegaard-Andersen, and S. Mathiesen, Phys. Rev. B 22, 312 (1980).

[5]Note that the problem is cylindrically symmetric about the (here the z) direction of the 1D structure.

[6]A similar fixed line occurs in the Gaussian spin-wave approximation to the 2D XY model. See, e.g., J. José, L. P. Kadanoff, S. Kirkpatrick, and D. R. Nelson, Phys. Rev. B 16, 1217 (1977).

[7]G. Grinstein, J. Phys. A 13, L201 (1980), and Phys. Rev. B 23, 4615 (1981).

[8]See, e.g., F. J. Wegner, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1976), Vol. 6, for a clear discussion of this terminology.

[9]We have not proved that this approximation does not affect our results, though the analogous approximation in the 2D XY model has been proven innocuous. See J. Toner, Ph.D. thesis, Harvard University, 1981 (unpublished).

[10]The spin-wave approximation neglects topological defects—dislocation loops—which presumably play no role in determining the properties of the 1D solid though they may well be relevant to the smectic-A–nematic transition. See, e.g., D. R. Nelson and J. Toner (unpublished).

[11]Using only the terms shown explicitly in (1) one concludes that $\lambda = (2q)^{-1}$. The higher-order terms represented by $O((\nabla^3 m)^2)$ in (1) would, however, result in $\lambda = (aq)^{-1}$ for some $a \neq 2$.

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[16]Since the arguments of the logarithms in (6) and (7) involve $k_\perp$ and $k_z^{1/2}$, respectively, the corrections in (6) (i.e., to K_1) should be more readily observable than those in (7) (i.e., to B).

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[18]See, e.g., M. Delaye and P. Keller, Phys. Rev. Lett. 37, 1068; M. Delaye, J. Phys. (Paris), Colloq. 40, C3-350 (1979).

[19]It is unlikely, given the slow growth of the logarithmic function, that one can probe experimentally the asymptotic region (defined by $k_\perp < k^*$) where the logarithmic correction term in (12) dominates the leading term. For $w \sim 0.7$, e.g., $k_\perp^* \sim 10^{-27}$ Å^{-1}, a hopelessly immeasurable wave vector. One can nonetheless hope to observe the beginnings of the crossover to this asymptotic region; we have just argued that one may well observe the evolution of the logarithm to 3% of the leading term. The value of k^* is, moreover, extremely sensitive to the parameter w: if $w \sim 7$, e.g., $k_\perp^* \sim 3 \times 10^{-6}$ Å^{-1}.

[20]Measurements by Delaye, Ref. 18, suggest that the smectic-A p-nonyloxybenzoate-p-butyloxyphenol has an unusually small λ, i.e., a relatively large w.

[21]See, e.g., Y. Liao, N. A. Clark, and P. S. Pershan, Phys. Rev. Lett. 30, 639 (1973); M. R. Fisch, L. B. Sorensen, and P. S. Pershan, Phys. Rev. Lett. 47, 43 (1981); L. Ricard and J. Prost, J. Phys. (Paris) 42, 861 (1981).

[22]See, e.g., G. A. Baym, in *Proceedings of the Les Houches Summer Institute on Nuclear Physics with Heavy Ions and Mesons, Grenoble, France, 1977*, edited by R. Balian, M. Rho, and G. Ripka (North-Holland, Amsterdam, 1978), Vol. 2, pp. 745–836; G. A. Baym, B. Friman, and G. Grinstein (unpublished).