

Fluctuations and Freezing in a One-Dimensional Liquid:  $\text{Hg}_{3-6}\text{AsF}_6$

J. D. Axe

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FLUCTUATIONS AND FREEZING IN A ONE-DIMENSIONAL LIQUID:  $\text{Hg}_{3-\delta}\text{AsF}_6$ 

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## INTRODUCTION

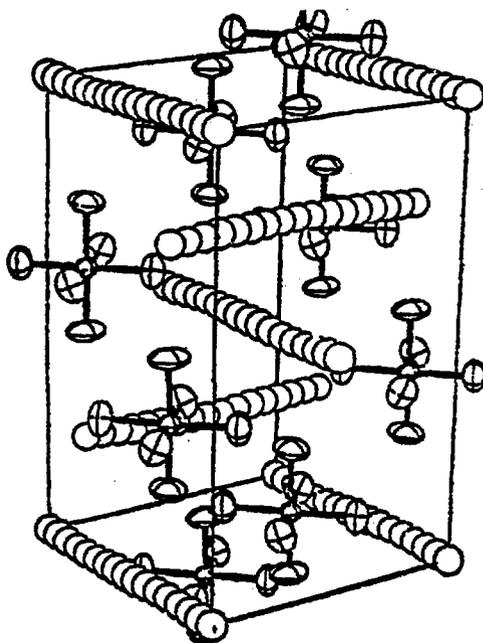
Many of the papers of this conference deal quite properly with systems at their critical dimensionality,  $d^*$ . (See, for example, the contributions of Young, Villain, Als-Nielsen, Litster, and Weeks.) In such systems the competing forces between organization and disorder are nearly equally balanced and the analysis of the resulting situation requires some subtlety. Not surprisingly, the situation is somewhat simplified when the dimensionality falls below  $d^*$ . For ordinary translational ordering of fluids (i.e. crystallization),  $d^*=2$ . In this paper we explore the properties of certain quasi-one-dimensional systems, which since they are effectively below  $d^*$ , resist the conventional crystalline order until abnormally low temperatures, and assume instead a state which we liken to a 1-dimensional liquid.

The circumstances which promote this unusual state arise in solids composed of two (or more) interpenetrating sublattices with spacings which are incommensurate one with another. The reason to suspect something out of the ordinary is shown by the following simple considerations. Imagine the two sublattices to be perfectly periodic and write their interaction energy as a product of the charge density,  $\sigma_A(\vec{r})$ , of one times the potential,  $\phi_B(\vec{r})$ , of the other,

$$\begin{aligned}
 V_{AB} &= \int \sigma_A(\vec{r}) \phi_B(\vec{r}) d\vec{r} \\
 &= \sum_{GG'} \sigma_A(\vec{G}) \phi_B(\vec{G}') \int e^{i(\vec{G}-\vec{G}') \cdot \vec{r}} d\vec{r} \\
 &= \sum_{GG'} \sigma_A(\vec{G}) \phi_B(-\vec{G}') \delta_{G,G'}
 \end{aligned}
 \tag{1}$$

This shows that the two sublattices interact only by virtue of common reciprocal lattice vectors. Suppose that both sublattices can be thought of as two-dimensional arrays of chains arranged on a common rectangular lattice, but with different and incommensurate interatomic spacings along the common chain direction,  $z$ . It then follows trivially that the only common reciprocal lattice vectors have  $G_z = G'_z = 0$  and the resulting forces, while constraining the chains in the  $x, y$  plane, do not fix the relative positions of the two sublattices along  $z$ . (In fact, the system can gain additional interaction energy by a mutual modulation of the natural period of one chain type with the period of the other. But this is a small effect and does not change the qualitative conclusion that the forces which act to localize the atoms on their chains are, at best, abnormally weak.)

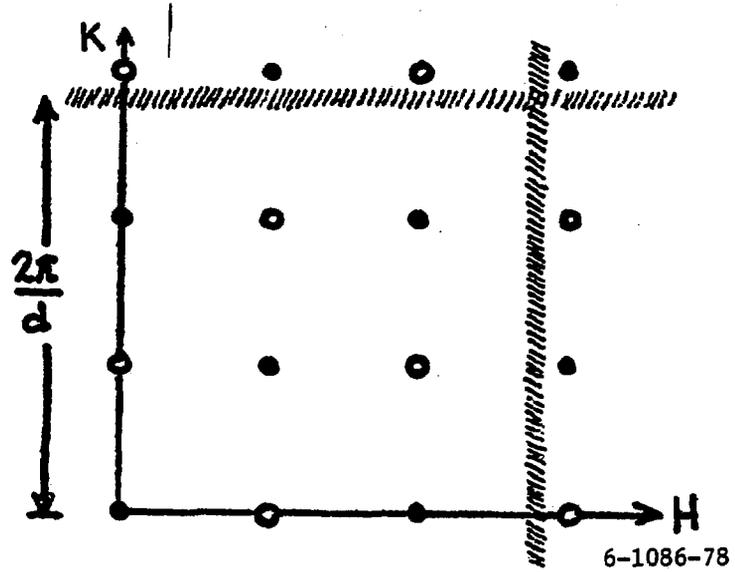
Perhaps the best studied example to date of the type of structure we have in mind is the mercury chain compound  $\text{Hg}_{3-\delta}\text{AsF}_6$ . It consists of an ordered body-centered tetragonal (bct) lattice of  $\text{AsF}_6^-$  anions (the host lattice) through which pass linear chains of polymercury cations arranged in two identical perpendicular nonintersection arrays, one parallel to  $\vec{a}_L$ , the other to  $\vec{b}_L$ . See Fig. 1. These will be referred to as the  $x$ - and  $y$ -arrays, respectively. Room temperature diffraction studies have shown in addition to the expected Bragg reflections, strong diffuse scattering arranged into series of thin sheets in reciprocal space [1-3]. Fig. 2 is a sketch of the (HKO) scattering plane. It is established that the diffuse sheets arise from the Hg-atoms and the narrow width of the sheets shows that the intrachain Hg-Hg distance,  $d$ , is well defined, and the nearly uniform distribution of intensity within a sheet shows that there is little or no interference between scattering from different chains [3,4]. Thus positions of the atoms along the chains are virtually uncorrelated from one chain to the next. Finally, from the spacing of the diffuse sheets, the interchain Hg distance,  $d = 2.67 \text{ \AA}$ , which is incommensurate with  $a_L = 7.53 \text{ \AA}$ . This results from a non-stoichiometric composition  $\text{Hg}_{3-\delta}\text{AsF}_6$  with  $3-\delta = (a_L/d) = 2.82$ . (A puzzling fact is that chemical analyses consistently find  $\delta = 0$ . Whether this is due to "pools" of excess Hg, to random vacancies on the host lattice, or neither, is at present unresolved.)



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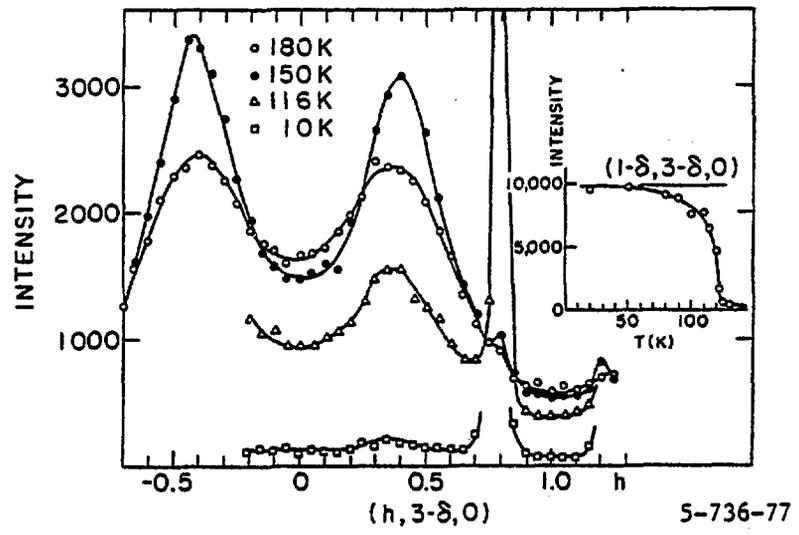
**Fig. 1.** Structure of  $\text{Hg}_{3-\delta}\text{AsF}_6$ . The octahedral  $\text{AsF}_6$  groups carry one negative charge. The Hg-atoms on the chains are shown schematically. Above  $T_c = 120$  K the average Hg density is uniform along the chains. After A. J. Schultz et al. (Ref. 3).

Further work by Hastings et al. [4] extended the diffraction study to low temperatures and concentrated on the behavior of the diffuse scattering in the  $m = 1$  sheets. Fig. 3 shows that what is essentially a uniform distribution of intensity within a sheet at room temperature evolves into a pronounced modulation at 180 K. The modulation was interpreted as arising from short range correlations between the position of Hg atoms on nearby parallel chains. In the vicinity of  $T_c = 120$  K sharp Bragg peaks grow out of the sheet of diffuse scattering with a temperature dependence typical of a continuous second order transformation (see inset, Fig. 3) and which must be associated with interchain ordering. Very peculiar, however, is the fact that the Bragg peaks do not develop at the positions on the sheets where the modulated diffuse intensity is strongest, but grow instead from regions of low intensity, i.e. the Bragg peaks are preceded by little or no "critical" scattering. The nature of the resulting ordering was deduced by Hastings et al. by noting that the positions of the Bragg peaks on the sheets were such that a reciprocal lattice vector from the x-array coincided with one from the y-array (at a point on the intersection of the two  $m = 1$  sheets). This fact, in conjunction with the theorem of the first paragraph, strongly implicates interactions between perpendicular chains as the dominant factor in the ordering. Unexplained, however, was the



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**Fig. 2.** A schematic representation of the diffraction pattern of  $Hg_{3-\delta}AsF_6$  at room temperature. The straight lines represent the intersection of sheets of diffuse scattering lying perpendicular to the figure with the  $HK0$  scattering plane.



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**Fig. 3.** Temperature dependent evolution of short and long range order as seen by the modulation of the  $m=1$  diffuse sheet. Parallel chain interactions are responsible for the broad peaks at  $h \approx \pm 0.4$ . The long range order appears in the sharp Bragg peaks at  $h = (1-\delta) \approx 0.82$ . The inset shows the temperature dependent growth of the Bragg scattering below  $T_c$ . After J. M. Hastings et al. (Ref. 4).

apparent sudden reversal of the relative importance of the parallel chain interactions, responsible for the short range order, and perpendicular chain interactions responsible for the long range order.

At high temperatures Hastings et al. also found that emanating from all points of the diffuse scattering sheets are inelastic scattering surfaces with linear dispersion depending only upon the component,  $Q$ , of momentum along the chain direction. That is  $\omega = \pm v |Q - Q_m|$  and  $Q_m = 2\pi m/d$  specifies the position of the  $m$ 'th diffuse sheet. They ascribed this scattering to 1-d longitudinal phonons propagating along the independent Hg chains and found that  $v = 4.4 \times 10^5$  cm/sec.

The remainder of this talk is devoted to a discussion of a simple model developed and analyzed by Emery and Axe [5] for  $\text{Hg}_{3-\delta}\text{AsF}_6$  (although with little modification it should be useful in thinking about other linear incommensurate phases as well). It incorporates competing parallel and perpendicular chain interactions, predicts correctly the long range order and clarifies the apparent failure of the system to anticipate this ordering in the fluctuations above  $T_c$ . In addition, it treats carefully the effects of one-dimensional fluctuations, and predicts that the Hg chains at high temperatures behave as a one-dimensional liquid. The subsequent phase transformation can be thought of as a freezing of the 1-d Hg liquid, and can be discussed in terms of self-consistent solutions of the sine-Gordon Hamiltonian.

#### THE MODEL HAMILTONIAN

The Hamiltonian is the sum of intra- and inter-chain contributions.  $\mathcal{H}_{\text{intra}}$  assumes harmonic interactions,  $\mathcal{H}_{\text{intra}} = \sum_{l_x} \mathcal{H}_{l_x}^0$  where for example

$$\mathcal{H}_{l_x}^0 = \frac{1}{2} \sum_{\alpha=1}^N \frac{\Pi^2(l_x, \alpha)}{m} + K(x(l_x, \alpha+1) - x(l_x, \alpha-d))^2 \quad (2)$$

where  $(\Pi(l_x, \alpha), x(l_x, \alpha))$  are the components of the momentum and position vectors of the  $\alpha$ 'th particle on the  $l_x$ 'th chain. (The subscript  $i = x, y$  is to be used to specify the x- or y-array of chains.) The effective near-neighbor stiffness constant  $K = mv^2/d^2$  is chosen to give the measured 1-d phonon velocity.  $m$  is the bare Hg atom mass.

The configuration of the  $l_x$ 'th chain is specified by the particle density operators, for example

$$\rho_{l_x}(x) = \sum_{\alpha} \delta(x - x(l_x, \alpha)). \quad (3)$$

In the disordered (high temperature) phase the Hg density is uniformly distributed along the chains, i.e. the thermodynamic averages  $\langle \rho_{lx}(x) \rangle = \langle \rho_{ly}(y) \rangle = \text{constant}$ . In terms of the Fourier transformed variables,  $\langle \rho_{lx}(Q) \rangle = \langle \rho_{ly}(P) \rangle = 0$  except for  $P = Q = 0$ . The quantities  $\langle \rho_{lx}(Q_m) \rangle$ ,  $\langle \rho_{ly}(P_m) \rangle$  for  $(P_m, Q_m) = 2\pi m/d$  can be taken as a complete set of order parameters specifying the chain ordering transformation. We will see that the instability is associated with the primary order parameters  $(\langle \rho_{lx}(Q_1) \rangle, \langle \rho_{ly}(P_1) \rangle)$ . Note that we have retained the notion of a local chain variable by Fourier transforming only the position along the chain direction. Although it is useful in what follows to introduce wave vector components perpendicular to the chain directions as well, it is still important to distinguish between parallel and perpendicular components, as the latter are conjugate to discrete chain positions and can be restricted to the first Brillouin zone, whereas the former is associated with a continuous distribution along the chains and are thus unrestricted.

We introduce coupling between chains of the form

$$\mathcal{H}_{\text{inter}} = \mathcal{H}_{xx} + \mathcal{H}_{yy} + \mathcal{H}_{xy} \text{ where}$$

$$\mathcal{H}_{xx} = \frac{1}{2} \sum_{lx, lx'} \int dx \int dx' v_{lx, lx'}^{xx}(x-x') \rho_{lx}(x) \rho_{lx'}(x') \quad (4a)$$

$$\mathcal{H}_{xy} = \frac{1}{2} \sum_{lx, ly} \int dx \int dy v_{lx, ly}^{xy}(x-x^o, y-y^o) \rho_{lx}(x) \rho_{ly}(y) \quad (4b)$$

These equations can be rewritten in terms of their Fourier transforms, e.g.

$$\rho_{lx}(Q) = N^{-1/2} \sum_{\alpha} e^{-iQx(l_x, \alpha)}$$

and for example

$$\mathcal{H}_{xx} = \frac{1}{2} \sum_Q v_{lx, lx'}(Q) \rho_{lx}(Q) \rho_{lx'}(-Q) \quad (4c)$$

where  $N$  is the number of atoms per chain.

1. Range of Interactions. We find that only rather near-neighbor coupling is necessary to explain the observed behavior of  $\text{Hg}_{3-\delta}\text{AsF}_6$ . The short range of the interchain coupling is understandable. If we associate a charge density,  $\sigma_{lx}(x) = e^* \rho_{lx}(x)$  with

the atomic density and calculate the Coulomb coupling between two parallel chains ( $\ell x, \ell x'$ ) separated by a distance R, we find

7

$$v_{x,x'}^{\parallel}(Q) = \frac{2e^*2}{d} \int_{-\infty}^{\infty} \frac{\cos Q(x-x')}{[(x-x')^2 + R^2]^{1/2}} dx = \frac{2e^*2}{d} K_0(QR) \quad (5a)$$

$$\approx \frac{2e^*2}{d} \left(\frac{\pi}{2QR}\right)^{1/2} e^{-QR} \quad (QR \gg 1) \quad (5b)$$

where  $K_0(z)$  is a Bessel function. This shows that the coupling between charge modulations on parallel chains is exponentially small if the wave vector of the modulation is large compared to the inverse interchain spacing,  $R^{-1}$ . The coupling between perpendicular chains shows similar behavior. The important charge fluctuations are at multiples of  $Q_1 = (2\pi/d)$  and for near-neighbor parallel chains  $Q_1 R = 2\pi(a_L/d) = 2\pi(3-\delta)$ . Although neighbor perpendicular chains are closer, we are justified not only in neglecting interactions between widely separated chains, but also in neglecting interactions involving harmonics of the fundamental chain spacing even on nearby chains. That is, the secondary order parameters  $\langle \rho_{\ell x}(Q_m) \rangle$ , etc. with  $m > 1$  play a vanishingly small role in the interchain coupling.

#### HIGH TEMPERATURE PROPERTIES ( $T > T_c$ )

We discuss the thermodynamics using a generalized mean field theory in which the interchain coupling is approximated by a mean field but the resulting one-dimensional chain problem is solved exactly [6]. At low temperatures, where the full nonlinear response of the chains is important, this formulation leads to a sine-Gordon Hamiltonian, and thus is of most direct relevance for this conference. It is worthwhile, however, to sketch some results for  $T > T_c$  since they display several unusual features of this system and establish much of the necessary justification for the model itself. For  $T > T_c$  we need only the linear response,  $\chi^0$ , of the harmonic chain, so that

$$\langle \rho_x(\vec{q}) \rangle = \chi^0(\vec{q}) h^{\text{eff}}(\vec{q}) \quad (6a)$$

$$h^{\text{eff}}(\vec{q}) = h^0(\vec{q}) - v_{\parallel}^{\parallel}(\vec{q}) \langle \rho_x(\vec{q}) \rangle - \sum_{\vec{p}} v_{\perp}^{\perp}(-\vec{q}, \vec{p}) \Delta(\vec{p}-\vec{q}) \langle \rho_y(\vec{p}) \rangle \quad (6b)$$

where we have now introduced Fourier components perpendicular to the chain directions, so that for the x-array  $\vec{q} \equiv (Q, q_y, q_z)$  and for the y-array  $\vec{p} \equiv (p_x, P, p_z)$ . The notation emphasizes the mixed nature of the momentum variables, with the components represented by lower

case symbols being defined modulo a reciprocal lattice vector and thus reducible to the first Brillouin zone. This mixed momentum representation is also in evidence through the function

$$\Delta(\vec{p}-\vec{q}) \equiv 1 \text{ if } \vec{p}_x = \vec{Q}(\text{mod } \vec{G}); \vec{q}_y = \vec{P}(\text{mod } \vec{G}'); \vec{p}_z = \vec{q}_z;$$

$$\equiv 0 \text{ otherwise.}$$

where  $\vec{G}(\vec{G}')$  is a reciprocal lattice vector of the x(y)-array.

Eq. (6), together with a similar set defining  $\langle \rho_y(\vec{p}) \rangle$  are to be solved for the coupled response  $\chi(\vec{q}) \equiv \langle \rho_x(\vec{q}) \rangle / h^0(\vec{q})$ , or equivalently the pair correlation functions  $\langle \rho_x(\vec{q}) \rho_x(-\vec{q}) \rangle = kT\chi(\vec{q})$ . (We will justify shortly the use of the classical form of the fluctuation-dissipation theorem.) Because of the umklapp momentum terms, the solutions can only be developed perturbatively. Their character depends upon the relationship of the momenta components along the two chain directions.

1. Uncoupled Solutions. In regions of reciprocal space such that P and Q are not approximately equal the two chain arrays are effectively decoupled, and for the x-array

$$\langle \rho_x(\vec{q}) \rho_x(-\vec{q}) \rangle = \frac{S^0(Q)}{1 + \beta v^2 \|\vec{q}\| S^0(Q)} \quad (7)$$

where  $\beta \equiv (kT)^{-1}$  and a similar expression holds for the y-array.  $S^0(Q) = kT\chi^0(Q)$  is the pair correlation function for an independent one-dimensional harmonic chain. It is given by

$$S^0(Q) = \sum_{\alpha} e^{iQ(x_{\alpha}^0 - x_0^0)} \langle e^{iQu_{\alpha}} e^{iQu_0} \rangle = \sum_{\alpha} e^{iQd\alpha} e^{-\frac{1}{2}Q^2 \langle (u_{\alpha} - u_0)^2 \rangle} \quad (8)$$

and  $\langle (u_{\alpha} - u_0)^2 \rangle$  may be evaluated as an ensemble average over the single chain Hamiltonian,  $\mathcal{H}_0$

$$\langle (u_{\alpha} - u_0)^2 \rangle = \frac{d^2 kT}{4\pi m v^2} \int_{-\pi/a}^{\pi/a} dq \frac{(1 - \cos qd)}{\sin^2(\frac{qd}{2})} \equiv |\alpha| \sigma^2 \quad (9)$$

where  $\alpha^2 = \frac{kT}{mv^2} d^2$  is the mean square fluctuation in nearest neighbor distance. As is well known, even though there is a well-defined average spacing,  $\alpha d$ , for  $\alpha$ 'th neighbors, the harmonic 1-d chain lacks long range order since the mean square fluctuation about  $\alpha d$  increases linearly with  $|\alpha|$ . Substituting (9) into (8) yields a geometric series which can easily be summed to give

$$S^0(Q) = \frac{\sinh(\frac{1}{2}\sigma^2 Q^2)}{\cosh(\frac{1}{2}\sigma^2 Q^2) - \cos(Qd)} \quad (10)$$

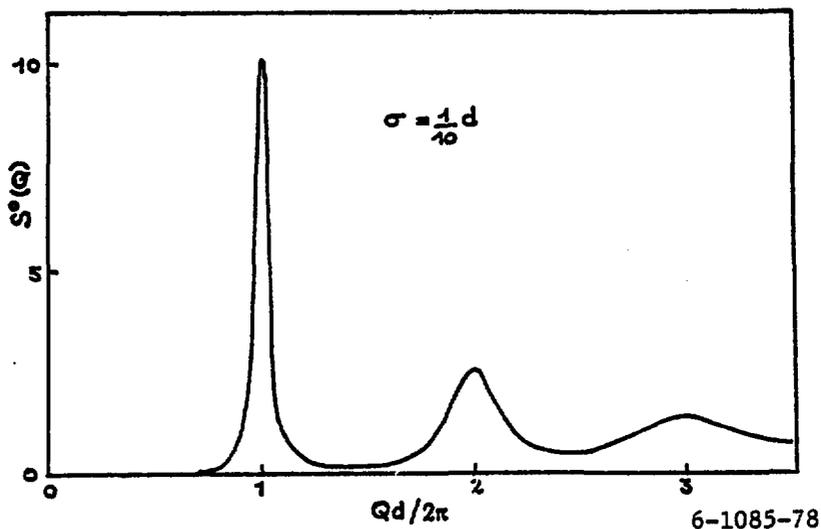
This is a typical liquid-like scattering function (see Fig. 4). Using the measured phonon velocity, we find for  $\text{Hg}_{3-\delta}\text{AsF}_6$ ,  $(\sigma/d)^2 = 6.4 \times 10^{-4}$  at room temperature, which justifies the use of the harmonic approximation within the chain.

In the high temperature limit (somewhat above room temperature for  $\text{Hg}_{3-\delta}\text{AsF}_6$ ) that we may set the denominator of (7) to unity and we recover the independent chain limit. For  $Qd \gg (\sigma/d)^2$  which is easily fulfilled in this case,  $S^0(Q)$  consists of a series of nearly Lorentzian peaks (the sheets of scattering) centered at  $Q_m = 2\pi m/d$  with a half width at half maximum,  $\kappa_m$ , given by  $\kappa_{m,d} = 2\pi^2 (\sigma/d)^2 m^2$ .

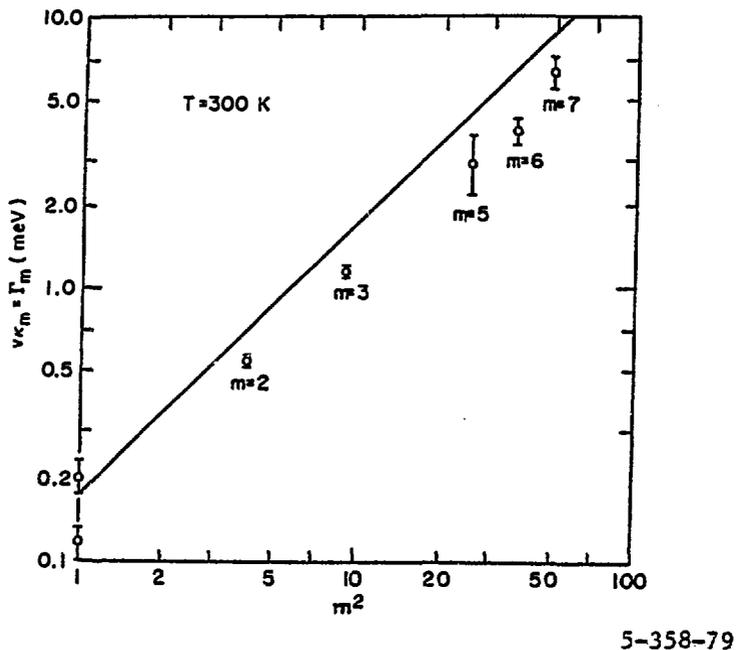
The above prediction, one of several made by this model, was put to the test in a second series of neutron scattering experiments by Heilmann, et al. [7]. Figure 5, taken from their paper, shows that the measured linewidth  $\kappa_m$  does increase as  $m^2$ . Furthermore, the absolute value of  $\kappa_m$  is quite close to that calculated in the preceding paragraph. (Much of the  $\sim 20\%$  discrepancy arises from a downward revision of  $v$  from  $4.4$  to  $3.6 \times 10^5$  cm/sec, based upon more careful measurements and resolution corrections. But considering the residual uncertainty in  $v$ , it is by no means clear that the apparent discrepancy is to be taken seriously. Measurements of the temperature dependence of  $\kappa_m$  for  $m=3$  also verify the predicted linear behavior for  $120 \text{ K} < T < 300 \text{ K}$ . It thus appears that to a very good approximation, the high temperature thermal behavior of the Hg-chains is that of a 1-d harmonic liquid.

As the temperature is lowered, the form of (7) and (8) shows that the effect of parallel chain interaction is first evidenced near  $Q = Q_1$  since successive maxima in  $S^0(Q_m) = S^0(Q_1)/m^2$ . (This explains the failure to observe modulation on the  $m=2$  sheet at temperatures where such modulation was pronounced at  $m=1$ .) The modulation along the sheet is determined by  $v^{\parallel}(Q)$  and the existing data can be fit semiquantitatively with contributions from near neighbor and next near neighbor chains only, with  $v_{nnn} \approx -2v_{nn} \approx 0.14 \text{ K}$ . (The interaction seems other than direct Coulomb as  $v_{nn}$  is the wrong sign and both are  $\sim 50$  too large.) Although the interactions are weak, they are sufficiently enhanced by the long coherence length within a chain as to tend toward an ordered state only a few degrees below  $T_c = 120 \text{ K}$ .

2. Coupled Solutions. The character of the solutions of (6), together with the corresponding ones for  $\rho_y(\vec{p})$  are of a different character if the momenta along the two chains are nearly equal,



**Fig. 4.** The scattering function,  $S^0(Q)$ , for a 1-d harmonic model (see Eq. (10) shows a typical liquid-like pattern. For this case,  $\sigma/d = 1/10$ , the correlations are weak.



**Fig. 5.**  $Q$  width ( $\kappa_m = \Gamma_m/v$ ) of successive planes of 1-d scattering in  $\text{Hg}_{3-8}\text{AsF}_6$ . The solid line represents the theoretical value based upon the independently measured phonon velocity,  $v$ .

$P = Q$ . For these momenta, the x- and y-arrays are strongly coupled, giving rise to new fluctuation modes,  $\rho^\pm(\vec{q}) = [\rho_x(\vec{q}) \pm \rho_y(\vec{q})]$  and the fluctuation scattering is proportional to

$$\sum_{i,j} \langle \rho_i(\vec{q}) \rho_j(-\vec{q}) \rangle = \frac{S^0(Q)}{1 + \beta(v^{\parallel}(\vec{q}) + v^{\perp}(\vec{q})) S^0(Q)} \quad (11)$$

which for reasons discussed above is enhanced for  $Q = Q_m$ , that is along the line of intersection of the m'th sheets (a reflection of the simple physics of (1)) and most enhanced for  $m=1$ . Whether an instability first arises on the  $m=1$  sheet at  $(Q_1, Q_1, q_2)$  due to perpendicular chain coupling or at a more general position  $(Q_1, q_y, q_2)$  due to parallel chain coupling depends upon whether the denominator is smaller in (11) or (7); the former is the case for  $\text{Hg}_{3-\delta}\text{AsF}_6$ . We believe that the apparent failure to observe critical scattering above  $T_c$  is the result of the fact that the region of enhanced scattering is restricted to a linear dimension of order  $2\kappa_1$  in the  $(a_T, b_T)$  plane. Since this width is below the existing experimental resolution, the basal plane scans should have the appearance of weak Bragg scattering persisting above  $T_c$ . Just such scattering has been observed, and it should be possible to establish its true character by determining whether the scattering is broad or narrow in the  $z$  direction, perpendicular to both chain arrays. In both sense (repulsive) and magnitude  $v^{\parallel}$  seems roughly consistent with Coulombic interactions.

The fact that the instability occurs exclusively on the  $m=1$  sheet means that the long range order first appears as a weak purely sinusoidal modulation of the otherwise uniform average mass density of a Hg-chain,  $\langle \rho_{lx}(x) \rangle$ . A similar sinusoidal mass density wave also breaks the continuous translation symmetry of a liquid crystal in the nematic-smectic transformation, as discussed by Litster in this conference. Indeed much of the physics is the same, although there are also differences connected with the fact that the liquid crystal system is at its critical dimensionality,  $d^*=3$ .

#### LONG RANGE ORDER

As usual, we associate the order parameter with the mode giving rise to the divergent fluctuations (i.e. with the coupled mode solutions discussed above) and thus define a complex order parameter,  $\eta_1 e^{i\psi} = \langle \rho_x(\vec{q}_c) \rangle = \pm \langle \rho_y(\vec{q}_c) \rangle$ . The arbitrary phase factor  $e^{i\psi}$  plays no role in determining the energetics of the system and is associated with a zero energy "sliding mode," familiar in incommensurate systems. For convenience, we set  $\psi = 0$ .  $\eta_1$  specifies the amplitude of the sinusoidal modulation of the mean atomic density on a chain, e.g.  $\langle \rho_{lx}(Q_1) \rangle = \eta_1 e^{i\phi^0} l_x$ , where  $\phi^0$  is a phase associated with the perpendicular components of  $\vec{q}_c$  and can be made to vanish by an appro-

private choice of origin for each chain. Using this convention the mean field potential  $\bar{v}$ , obtained by replacing one of the density operators in (4) by its mean value, is identical for each chain. This allows us in what follows to suppress the chain index  $l_1$ , and we are left with the problem of a 1-d harmonic chain in a (commensurate) staggered field,

$$\bar{v}(\eta_1) = \sum_{\alpha} \left\{ \frac{K}{2} (u_{\alpha+1} - u_{\alpha})^2 + \eta_1 h \cos Q_1 u_{\alpha} \right\} \quad (12)$$

where  $h = 2(v^H(\vec{q}_c) + v^L(\vec{q}_c))$ . To discuss the evolution of the low temperature phase we must calculate the growth of all of the Fourier components of the atomic density on a chain. This can be done classically using transfer matrix techniques [8] since except at very low temperatures the effect of zero point fluctuations are negligible. The long intrachain coherence length,  $\kappa_1^{-1} \approx 200 d$ , allows us to pass to the continuum limit ( $(u_{\alpha+1} - u_{\alpha}) \rightarrow d(\partial u(x)/\partial x)$ ) and (12) reduces to the classical sine-Gordon potential and we must calculate

$$\eta_m = \langle \sum_{\alpha} \cos Q_m u_{\alpha} \rangle = \sum_{\alpha} \int du_1 \dots du_N \cos(Q_m u_{\alpha}) e^{-\beta \bar{v}} \quad (13a)$$

$$= \langle \phi_0 | \cos Q_m u | \phi_0 \rangle / \langle \phi_0 | \phi_0 \rangle \quad (13b)$$

where  $\phi_0 \equiv ce(q, v)$  is the lowest eigen vector of the transfer matrix and satisfies the Mathieu equation.

$$\left[ \frac{d^2}{dv^2} + (a_0 - 2q \cos 2v) \right] \phi_0(v) = 0 \quad (14a)$$

$$q = \frac{4K\beta^2 h \eta_1}{Q_1^2} = -2 \left( \frac{\beta}{\beta_c} \right)^2 \eta_1 \quad (14b)$$

where  $2v = Q_1 u$ . The transformation temperature  $T_c = (k\beta_c)^{-1} = [-2Kh]^{1/2} / kQ_1$  is obtained by setting the denominator of (9) to zero for  $\vec{q} = \vec{q}_c$ . Note that  $T_c^2$  is the geometric mean of the harmonic stiffness,  $K$ , and the ordering field,  $h$ .

Eq. (13) can be readily evaluated by developing  $\phi_0(v)$  in a Fourier series. When  $m=1$  (13) must be solved self-consistently with (14b). The temperature dependence of the first three Fourier components of the atomic density are shown in Fig. 6. For small  $\eta_1$  ( $T \approx T_c$ )

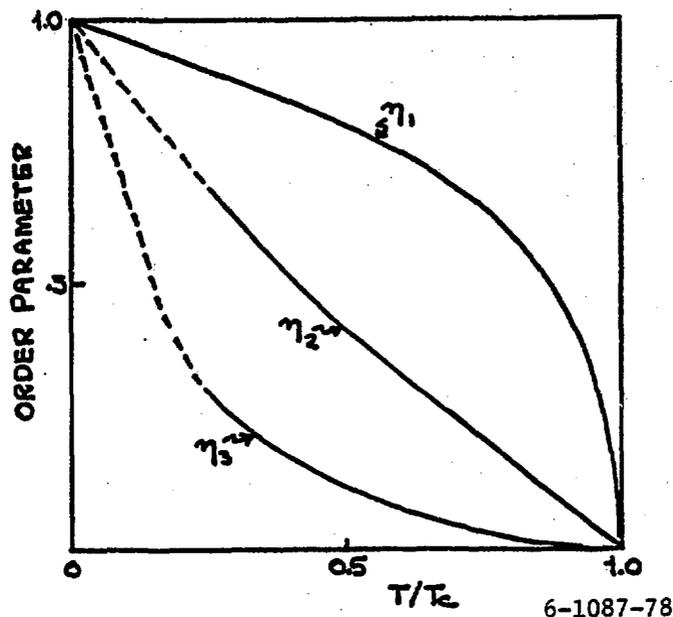


Fig. 6. Self-consistent solutions of the sine-Gordon Hamiltonian for the order parameter,  $\eta_m$ , associated with the first three density wave components.

$$\eta_1^2 \approx \frac{16}{7} \left[ 1 - \frac{T}{T_c} \right] \quad (15)$$

and  $\eta_m$  is proportional to  $\eta_1^m$ , while near  $T = 0$

$$\eta_m = \eta_1^{m^2} \approx 1 - \frac{m^2}{\sqrt{8}} \left( \frac{T}{T_c} \right).$$

As  $T \rightarrow 0$ , the density distribution on the chain approaches that of a sum of Gaussians centered at  $x_\alpha = nd$  with a mean square fluctuation  $\langle (x-x_\alpha)^2 \rangle = (T/\sqrt{2} Q_1^2 T_c)$ .

The temperature dependence of the Bragg scattering associated with  $Q_1$  as studied by Hastings et al. (see inset Fig. 3), rises much more quickly than predicted by (15). We believe that the reason for this is that the fluctuations associated with  $v''$  may not be neglected for  $T \approx T_c$  because they are divergent at  $T = T_1$  a few degrees below  $T_c$ . The coupling of the two types of order parameters not only has the effect of promoting a more rapid growth in  $\eta_1(T)$  but also in suppressing the  $v''$  fluctuations below  $T_c$ , a feature which is very noticeable in Fig. 3. As this aspect of the theory is specialized to  $\text{Hg}_{3-\delta}\text{AsF}_6$  we will not pursue it further here.

We conclude with a brief discussion of the dynamical properties that are to be expected in a system of loosely coupled harmonic chains. The dynamics are readily susceptible to calculation and contain several novel features which one can compare with neutron scattering experiments in progress.

In the high temperature limit, it is possible to redo the calculations summarized in (8) and (9) for the time dependent pair correlations

$$S^0(Q, \omega) = (2\pi)^{-1} \int dt e^{i\omega t} \sum_{\alpha} \langle e^{iQx_{\alpha}(t)} e^{iQx_0(0)} \rangle \equiv kT\chi^0(Q, \omega)$$

The result, in the vicinity of the  $m$ 'th diffuse sheet (i.e.  $|\Delta Q_m| = |Q - Q_m| \ll d^{-1}$ ) is

$$S^0(\Delta Q_m, \omega) = \frac{4}{\pi d v} \left\{ \frac{\kappa_m}{(\Delta Q_m - \frac{\omega}{v})^2 + \kappa_m^2} \right\} \left\{ \frac{\kappa_m}{(\Delta Q_m + \frac{\omega}{v})^2 + \kappa_m^2} \right\} \quad (16)$$

Eq. (16) deserves several comments.

1. The unusual product-of-Lorentzian form is characteristic of correlation functions of one-dimensional problems [9].

2. In deriving (16) one cannot proceed through the familiar separation into a product of a time dependent and time independent parts, as the latter (Debye-Waller) term vanishes while the time dependent fluctuations diverge. Similarly, there is no separation into one- and multiphonon terms. Eq. (16) represents the total density response.

3. When (16) is integrated over frequency one recovers (10), and, as with a 3-d liquid, there is no truly elastic scattering (i.e. no term proportional to  $\delta(\omega)$ ).

It is possible to extend the above results to include interchain coupling in the random phase approximation. The dynamical analogs of (7) and (11) are obtained by replacing  $\langle \rho_i(\vec{q}) \rho_j(\vec{q}) \rangle$  by

$$S_{ij}(\vec{q}, \omega) \equiv (2\pi)^{-1} \int dt e^{i\omega t} \langle \rho_i(\vec{q}, t) \rho_j(-\vec{q}, 0) \rangle$$

and  $S^0(Q)$  by  $S^0(Q, \omega)$  in those expressions.

Below  $T_c$  the dynamics can be discussed in terms of weakly coupled sine-Gordon systems. For an individual chain there are two sorts of excitations to consider [10]. The first are free solitons for which

$$\omega_s^2 = \Delta_s^2 + v^2 Q^2; \Delta_s^2 = \frac{16 \pi v^2 \hbar \eta_1}{(\pi \hbar)^2}$$

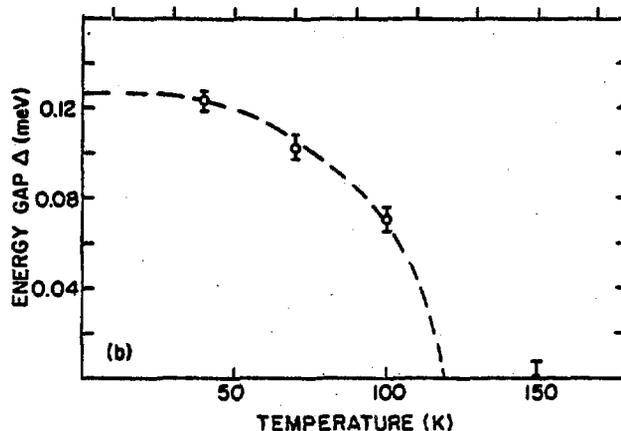
At low temperatures, the minimum energy necessary to create a soliton is so large ( $\hbar \Delta_s / k \sim 700$  K) that these are not important thermal excitations, but the gap vanishes as  $\eta_1^{1/2}$  near  $T_c$ . It may be possible to directly excite these soliton defect pairs with neutrons, or at least to observe the scattering from the thermally excited pairs near  $T_c$ . This latter experiment would be directly analogous to the experiments described by Steiner in this volume on the 1-d ferromagnetic system  $\text{CsNiF}_3$ . The second kind of excitations can be described as bound soliton-antisoliton pairs or doublets for which

$$\omega_v^2 = \Delta_v^2 + v^2 Q^2; \Delta_v^2 = 4\Delta_s^2 \sin^2\left(\frac{\pi \theta v}{2}\right)$$

where  $v = 1, 2, \dots, \theta^{-1}$  and  $\theta = (\pi \hbar / 2\pi v d)$ . The maximum value of  $v$  is the boundary of stability for breakup into a free soliton-antisoliton pair, whereas for small  $v$ ,  $\omega_v \approx \pi \left(\frac{4\hbar \eta_1}{m d^2}\right)^{1/2} v$  and the excitations can be thought of as ordinary phonons near the bottom of the sinusoidal potential. These single-chain excitations form the basis for coupled collective modes which satisfy the lattice translational symmetry. (In particular there will still be a collective gapless Goldstone mode representing motion of the chains without change of the relative phase relation between them.) The appearance of a gap in the 1-d phonon spectrum below  $T_c$  has been recently observed [11]. As shown in Figure 7, the gap drops rapidly as  $T \rightarrow T_c$ , in at least qualitative agreement with the prediction,  $\Delta \sim \eta_1^{1/2}$ . Further inelastic neutron scattering experiments are planned.

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**Fig. 7.** Temperature dependence of energy gap in Hg-chain spectrum induced by long range order. The dashed curve is merely a guide to the eye.

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