Structure factor of a single linear chain of finite size

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We derive an exact expression for the structure factor $S(Q)$, at all wave numbers Q, for a single linear chain of N atoms fixed at both ends. The effect of finite size for given N on the peaks in $S(Q)$ is most pronounced for the lowest values of the quantity n^2T where $n=1,2,3,\ldots$ is the order of the peak and T the absolute temperature. For $N\gg1$, the average over the center-of-mass positions of pairs of scattering atoms is shown to be equivalent to the usual method of periodic boundary conditions with lower cutoff in wave number for the calculation of $S(Q)$. In contrast to the expression derived here for the finite system with fixed ends, the periodic-boundary-condition expression in the literature for the mean-square displacement of a single atom in the infinite chain is independent of the position of the atom in the chain. The fitted half-widths of the Lorentzian-type peaks for given N as a function of n^2T all fall on a single dipper-shaped curve which drops below the infinite-chain flat line, then approaches it from below. This dipper shape is due to the nonlinear character of the fluctuations and is understandably absent in a linearized analytic theory. A quantitative discussion is given which lends some insight into the physical mechanism responsible for the linewidths in $S(Q)$.

I. INTRODUCTION

Very few compounds exist in the solid state completely free from defects or impurities. In systems composed of linear chains of atoms, defects, impurities, or irradiation damage may cause a description of the properties of the system in terms of a finite-size theory to be more appropriate. In this paper, a study of the fluctuations and relative order between atoms on a single chain of finite size is presented, together with a physical picture of the scattering process. This is motivated in part by an x-ray scattering study due to Spal, Chen, Egami, Nigrey, and Heeger[1] of the compound $Hg_{3-\delta}AsF_6$. This unusual compound possesses linear chains[2] of Hg ions in channels created by the host AsF_6^- background. At temperatures above $T_c\simeq120$ K, the chains are independent of each other as well as of the host lattice. Spal *et al.*,[1] in an analysis of their experimental data on the one-dimensional diffraction sheets, found that for some values of n^2T, the linewidths lay below the values expected for infinitely long chains while for others it lay above. They concluded, however, that the experimental data were in agreement with the theory of independent, infinitely long chains.[3] It has been suggested,[4] however, that "shortening" of the Hg chains occurs by Hg ions from the chains occupying anion vacancies present in about 6 at.%. One consequence of this might be an alteration of the phonon spectrum and the infinite-chain dynamics.[5] We have considered here another possibility in which the system might behave as one which consists of one-dimensional (1D) "islands" of finite-length chains which are, however, long enough that surface effects are unimportant.

We present a systematic theory of N atoms free to vibrate in a chain of finite length, using both fixed and periodic boundary conditions. These two boundary conditions might, for example, approximate different physical mechanisms causing finite-size effects. In both cases, it is shown that the nth peak in the structure factor is broader or narrower than the infinite chain, depending for a given chain length, only on the quantity n^2T. This result appears to be within the reach of experimental observation even for chains as long as $\simeq1500$ Å.

In addition to its application to $Hg_{3-\delta}AsF_6$, the theory of finite chains might also be useful for systems such as Hg atoms introduced under pressure into mordenite[6] or iodine atoms in $(SN)_x$.[7] It should also act as a guideline to future experimental x-ray or neutron scattering studies done on linear-chain compounds. The remainder of the paper is divided into three parts. Sections II and III give a derivation of the fluctuations in the finite chain and structure factor together with a discussion of the effects of the boundary conditions. The results are discussed in terms of the scattering from correlated regions, in Sec. IV.

II. FLUCTUATIONS IN THE FINITE CHAIN

The static structure factor for the single chain is defined as follows:

$$S(Q)=\langle\rho(Q)\rho(-Q)\rangle\ , \tag{1}$$

where

$$\rho(Q)=\frac{1}{\sqrt{N}}\sum_l e^{iQx_l} \tag{2}$$

is the normalized longitudinal density fluctuation induced by an external probe. Q is the wave vector parallel to the chain. The angular brackets denote a thermal average. The position of the lth atom on the chain is given by

$$x_l=ld+u_l\ , \tag{3}$$

where d is the equilibrium interatomic distance and u_l the displacement of the lth atom from its equilibrium posi-

tion. Hence Eq. (1) becomes

$$S(Q)=\frac{1}{N}\sum_{l,l'=1}^{N} e^{iQ(l-l')d}\langle e^{iQu_l}e^{-iQu_{l'}}\rangle$$
$$=\frac{1}{N}\sum_{l,l'=1}^{N} e^{iQ(l-l')d}e^{-(1/2)Q^2\langle(u_l-u_{l'})^2\rangle} \quad (4)$$

for the harmonic crystal. We proceed by expanding the lattice displacements in terms of the phonons of the 1D lattice with fixed ends. In terms of the quantized lattice modes, the mean-square deviation of two atoms l and l' from their equilibrium separation is given by

$$\langle(u_l-u_{l'})^2\rangle=\frac{2\hbar}{NM}\sum_{k>0}\frac{2n_k+1}{\omega_k}\sin^2[\tfrac{1}{2}k(l-l')d]$$
$$\times[1+\cos k(l+l')d] \quad (5)$$

with

$$k=\frac{\pi m}{(N+1)d} \quad m=1,2,\ldots,N \; . \quad (6)$$

Here, n_k is the Bose distribution function and M is the atomic mass. The lower cutoff, $k_{\min}=\pi/[(N+1)d]$, appears naturally in this theory. Equation (5) shows the dependence of the fluctuations in the finite system on both the *relative* position of the two atoms and the *center of mass* of the pair along the chain. The latter is expected to be of importance only for l or l' close to either end of the chain. In the limit of $N\gg1$, we neglect the contribution of this term to Eq. (5) and also neglect the influence of the boundaries on the phonon dispersion relation

$$\omega_k=\frac{2c}{d}\,|\sin(kd/2)|\;, \quad (7)$$

where c is the phonon velocity. Alternatively, averaging over the center-of-mass coordinate $l_c\equiv(l+l')/2$ for given relative coordinate $l_r\equiv(l-l')/2$, we have

$$\frac{1}{(N+1)}\int_0^{N+1} dl_c\cos(2kl_cd)=0\;. \quad (8)$$

Thus, within the assumption of fixed boundary conditions with center-of-mass average,

$$\langle(u_l-u_{l'})^2\rangle=\frac{2\hbar}{NM}\sum_{k>0}\frac{2n_k+1}{\omega_k}\sin^2[\tfrac{1}{2}k(l-l')d]\;. \quad (9)$$

For $k_BT\gg(\hbar\omega_k)_{\max}$ (Ref. 8) this becomes

$$\langle(u_l-u_{l'})^2\rangle=\frac{\sigma^2}{N}\sum_{m=1}^{N}\frac{\sin^2[(l-l')mx]}{\sin^2(mx)}\;, \quad (10)$$

where $\sigma^2\equiv(k_BT)d^2/(Mc^2)$, k_B is Boltzmann's constant and $x\equiv\pi/[2(N+1)]$. This sum can be done exactly using the Euler-Maclaurin integration formula[9] to give

$$\sum_{m=1}^{N}\frac{\sin^2[(l-l')mx]}{\sin^2(mx)}=|l-l'|(N+1)-\frac{1}{2}\left[(l-l')^2+\sin^2\left[\frac{\pi(l-l')}{2}\right]\right] \quad (11)$$

with $(l-l')=\mathrm{mod}(2[N+1])$. This is a new result. Hence

$$\langle(u_l-u_{l'})^2\rangle=\sigma^2|l-l'|\left\{1-\frac{1}{2N}\left[|1-1'|+\sin^2\left[\frac{\pi(l-l')}{2}\right]\right]\right\} \quad (12)$$

$$\simeq\sigma^2|l-l'|\left[1-\frac{|l-l'|}{2N}\right]\;. \quad (13)$$

We now show that the averaging, Eq. (8), over the pair center-of-mass coordinate is completely equivalent for $N\gg1$, to the usual model of periodic boundary conditions with lower k cutoff. If the lattice displacements are given the form of plane waves, then the allowed values of k are

$$k=0,\ \pm\frac{2\pi m}{Nd},\quad m=1,2,3,\ldots,N\;. \quad (14)$$

Equation (5) is replaced by

$$\langle(u_l-u_{l'})^2\rangle=\frac{2\hbar}{NM}\sum_{k}\frac{2n_k+1}{\omega_k}\sin^2[\tfrac{1}{2}k(l-l')d]\;, \quad (15)$$

with k restricted to the first Brillouin zone. Excluding the $k=0$ mode we calculate the sum in Eq. (15) to give

$$\sum_{m=1}^{N/2}\frac{\sin^2[2(l-l')mx]}{\sin^2(2mx)}=|l-l'|\frac{N}{2}-\frac{1}{2}\left[(l-l')^2+-\sin^2\left[\frac{\pi(l-l')}{2}\right]\right] \quad (16)$$

with $(l-l')=\mathrm{mod}(2N)$ so that

$$\langle (u_l-u_{l'})^2\rangle=\frac{2\sigma^2}{N}\sum_{m=1}^{N/2}\frac{\sin^2[2(l-l')mx]}{\sin^2(2mx)}$$
$$=\sigma^2|l-l'|\left\{1-\frac{1}{2N}\left[|l-l'|-\sin^2\left[\frac{\pi l-l')}{2}\right]\right]\right\}, \tag{17}$$

which is exact within the assumption of periodic boundary conditions. For $N\gg 1$, Eq. (17) reduces to leading order, to

$$\langle (u_l-u_{l'})^2\rangle\simeq\sigma^2|l-l'|\left[1-\frac{|l-l'|}{2N}\right]. \tag{18}$$

This expression[10] is identical to Eq. (13), as expected, since in this limit the boundary conditions should be of little importance. In the limit $N\to\infty$, the infinite-chain relative fluctuations are given by the exact expression

$$\langle (u_l-u_{l'})^2\rangle_\infty=\langle u^2_{l-l',0}\rangle=\sigma^2|l-l'|\ , \tag{19}$$

which is easily recovered from Eq. (18).

The result in Eq. (18) can be physically interpreted as follows: From Eq. (5) we can show exactly that for the chain with fixed ends and $l'=0$,

$$\langle (u_l-u_0)^2\rangle=\langle u_l^2\rangle=\sigma^2|l|\left[1-\frac{|l|}{N+1}\right], \tag{20}$$

which has the physically reasonable behavior that the fluctuation of the lth atom about its equilibrium position, the origin, is zero at the ends of the chain. This in turn forces a maximum degree of disorder near the center of the chain. In Eq. (20) we impose the physical limitations $0<l\leq N$ corresponding to the number of atoms free to move. The factor of 2 in Eq. (18) can then be interpreted as a result of averaging over the center-of-mass coordinate of the atoms at l and $l'\neq 0$. If both atoms are allowed to move, one would expect the fluctuation in their relative deviations from equilibrium to be greater than if one of them were fixed.

Another result worth pointing out is that for periodic boundary conditions with the lower wave number cutoff, the infinite-chain expression usually seen in the literature:[11]

$$\langle u_l^2\rangle=\langle u_0^2\rangle=\lim_{N\to\infty}\left[\frac{N\sigma^2}{2\pi^2}\right] \tag{21}$$

represents the fluctuations as being independent of the atomic positions. In contrast, the $N\to\infty$ limit of Eq. (20) gives

$$\langle u_l^2\rangle=\lim_{N\to\infty}\left[\sigma^2|l|\left[1-\frac{|l|}{N+1}\right]\right]=\sigma^2|l|\ . \tag{22}$$

III. STATIC STRUCTURE FACTOR

The effect of having boundaries not at infinity means that one must be careful not to include spurious correlations, or rather to count those real correlations present carefully. We then have

$$\sum_{l,l'=-N/2}^{+N/2}f(l,l')=f(0,0)+2\sum_{l_1=1}^{N}\left[\sum_{l_2=-1}^{-N+l_1}+\sum_{l_2=0}^{N-l_1}\right]f(l_1,l_2)\ , \tag{23}$$

where $l_1=2l_r$ and $l_2=2l_c$. In the present case, Eq. (23) simplifies considerably since

$$f(l_1,l_2)=e^{-(Q^2/2)\langle (u_l-u_{l'})^2\rangle}e^{iQl_1d} \tag{24}$$

is independent of l_2 and further, $f(-l_1)=f^*(l_1)$. Hence Eq. (23) becomes

$$\sum_{l,l'=-N/2}^{+N/2}f(l,l')=N+1+2\,\mathrm{Re}\sum_{l_1=1}^{N}(N+1-l_1)f(l_1) \tag{25}$$

and the static structure factor is, using Eq. (17),

$$S(Q)=1+\frac{1}{N}+\frac{2}{N}\sum_{l_1=1}^{N}(N+1-l_1)\exp\{-(Q^2\sigma^2l_1/2)[1-(l_1-\sin^2l_1\pi/2)/(2N)]\}\cos(Ql_1d)\ . \tag{26}$$

In the limit $N\to\infty$, Eq. (26) reduces to the infinite-chain expression as expected:

$$S_\infty=D(Q)\sinh\left[\frac{Q^2\sigma^2}{2}\right],\quad Q\neq 0\ , \tag{27}$$

where

$$D(Q)\equiv\frac{1}{\cosh(Q^2\sigma^2/2)-\cos(Qd)}\ . \tag{28}$$

Close to the sheets at $Q_nd=2\pi n$, the line shapes given in Eq. (27) can be approximated by Lorentzians in the limit $Q_n\sigma^2\ll 1$, since in this limit

$$S_\infty(Q)\simeq D(Q)\kappa_nd=\frac{2\kappa_nd}{(\kappa_nd)^2+(qd)^2},\quad qd\ll 1 \tag{29}$$

where[3]

$$\kappa_n=\frac{2\pi^2}{d}\left[\frac{\sigma}{d}\right]^2n^2 \tag{30}$$

are the half-widths of the Lorentzians in Eq. (29) and $Q=Q_n+q$.

For the *finite* chain, $S(Q)$ in Eq. (26) is plotted versus Q in Fig. 1 for $N=100$ using the following experimental parameters for the Hg chains in $Hg_{3-\delta}AsF_6$,[3] $d\simeq 2.67$ Å, $c=(4.4\pm 0.8)\times 10^{-2}$ m/s, and $(\sigma/d)^2\simeq 6.4\times 10^{-4}$ at $T\simeq 300$ K. The different sheets at $Q_n=2\pi n/d$ are closer together in height as compared to the infinite chain. This behavior is most marked for the first two sheets primarily as a result of a reduction in height of the first peak to $\simeq 48\%$ of the infinite-chain value. Figure 2 shows the first peak for $N=100$ and $T=300$ K. The line shape is quite evidently flatter and broader than the infinite chain. The slight structure which is seen, another finite-size effect, is one of a series of oscillations lying further out in the tail of the line shape where they attain a periodicity of $\Delta q\simeq 2\pi/Nd$. These oscillations in the tail become weaker in intensity the further one gets from $q=0$ and are probably too weak to observe experimentally. The third peak shown at $T=300$ K in Fig. 3(a) is $\simeq 6\%$ narrower than its infinite-chain counterpart but again is broader at $T=135$ K as shown in Fig. 3(b).

To proceed further in the analytic evaluation of Eq. (26), one can proceed by neglecting the nonlinear term in the fluctuations, i.e., by linearizing. The result is

$$S^{(1)}(Q)=1+\frac{1}{N}+\frac{2}{N}\sum_{l=1}^{N}(N+1-l)e^{-(Q^2\sigma^2 l/2)}\cos(Qld) \tag{31}$$

$$=D(Q)\left\{\sinh(Q^2\sigma^2/2)\{1-D(Q)[\cos(Qd)-e^{-(Q^2\sigma^2/2)}+B(Q)]/N\}+\frac{1}{N}e^{-(Q^2\sigma^2/2)}[1-e^{-(NQ^2\sigma^2/2)}\cos(QNd)]\right\}, \tag{32}$$

with

$$B(Q)\equiv e^{-(NQ^2\sigma^2/2)}\{e^{-(Q^2\sigma^2/2)}\cos(QNd)-\cos[Q(N+1)d]\}\ . \tag{33}$$

In the limit $\kappa_n d\ll 1$ and for $qd\ll 1$, the linearized expression in Eq. (31) reduces to

$$S^{(1)}(Q)\simeq\frac{2\kappa_n d}{(\kappa_n d)^2+(qd)^2}-\frac{C_n(q)}{[(\kappa_n d)^2+(qd)^2]^2}\ , \tag{34}$$

with

$$C_n(q)\equiv\frac{2}{N}\{[1-\cos(qNd)e^{-(\kappa_n Nd)}]\times[\kappa_n^2(1+E_n)-q^2(1-E_n)]d^2+4(\kappa_n d)(qd)\sin(qNd)e^{-\kappa_n Nd}\} \tag{35}$$

and

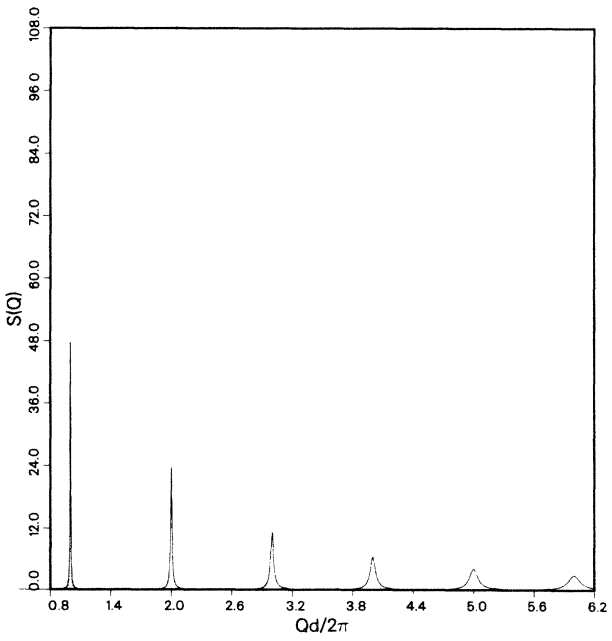


FIG. 1. The dotted line shows the infinite-chain structure factor at $T=300$ K with the first peak normalized at 100. The solid line is the structure factor for $N=100$ on the same scale. The intensity of the first peak is dramatically reduced causing a more solidlike appearance to $S(Q)$.

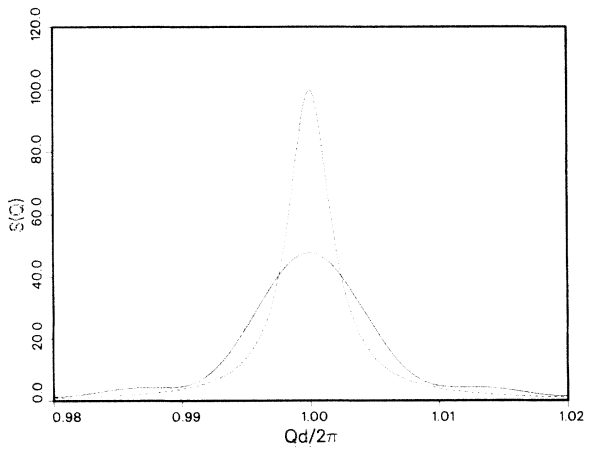
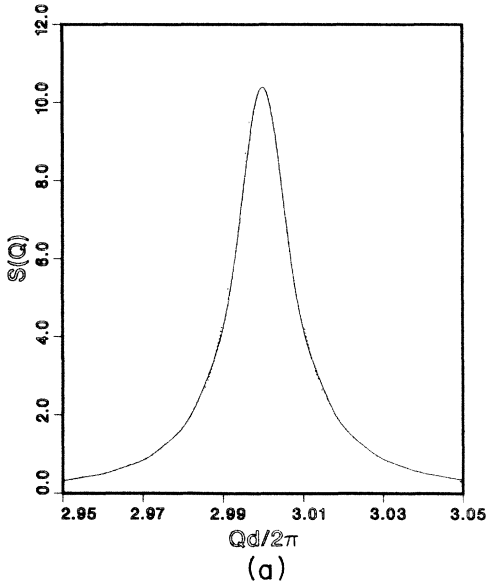


FIG. 2. The line shape for $T=300$ K at the first sheet is shown by the solid line compared to the infinite chain (dotted line) ($N=100$).



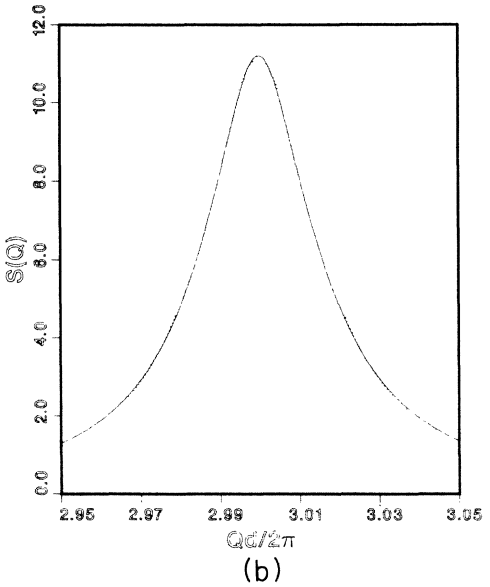


FIG. 3. (a) The line shape at the third sheet ($n=3$) for $N=100$ and $T=135$ K (solid line) is visibly broader than its infinite-chain counterpart. (b) At $T=300$ K, the situation is reversed, although the visible effect is not as obvious.

$$E_n \equiv (\kappa_n d)(1-N\kappa_n d) \ . \tag{36}$$

To leading order in $1/N$ this is just again the infinite-chain Lorentzian line shape. The appearance of terms such as $\cos(qNd)\exp(-\kappa_n Nd)\to 0$ as $N\to\infty$ in Eq. (35) helps to explain the existence of finite-size oscillations in $S(Q)$ and demonstrates their decreasing importance for $\kappa_n Nd \gg 1$. The linewidths in this linearized theory are given for $\exp(-N\kappa_n d) \ll 1$ by

$$q_n = \kappa_n d \left[\left[\frac{N\kappa_n d}{N\kappa_n d - 1} \right] \left[1 + 2\kappa_n d + \frac{3}{(N\kappa_n d)^2} \right]^{1/2} + \frac{2}{(N\kappa_n d)^2} \right]^{1/2} . \tag{37}$$

The linewidths q_n in Eq. (37) are broader than for the infinite chain, approaching κ_n monotonically from above with increasing n^2T. The linewidths are broadest compared to the infinite chain, for the lowest order sheets. This is, however, a good indication of the trend in the linewidth only for the smaller values of n^2T.

One can see clearly the effect of the *nonlinear* term in the fluctuations if the exact $S(Q)$ in Eq. (26) is least-squares fitted to a Lorentzian line shape plus a constant. We have done this in order to facilitate comparison to experiments where similar fits are made.[1] It should be noted here that the higher-order peaks become increasingly infrared shifted with a magnitude of approximately less than a few parts per thousand. The linewidths η (normalized to κ_n) for all n^2T, fall on a single dipper-shaped curve for given N, as shown in Fig. 4. This is in marked contrast to the predictions of previous theory for $N\to\infty$ where η/n^2T is a constant.[3] A test of our prediction for finite N would be of interest. For higher n^2T the line shape becomes less well described by a Lorentzian but an argument that the linewidth approaches that of the infinite chain from below is given in the next section, together with a discussion of the dipper shape.

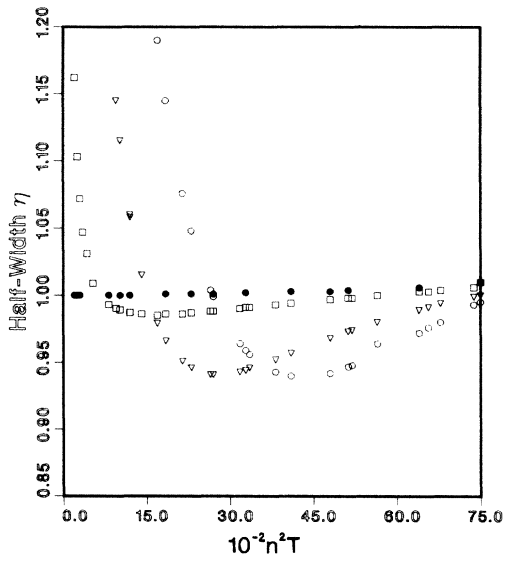


FIG. 4. The half-widths of the line shapes in Eq. (26) (normalized to κ_n) fitted to a Lorentzian plus a constant for $N=50$, 100, and 500, as depicted by the open circles, triangles, and squares. The actual half-widths of the infinite chain are depicted by the solid circles (same normalization). The characteristic dipper shape is a signature of finite-size effects.

IV. DISCUSSION

We first examine the behavior of the structure factor of the infinite chain,

$$S_\infty(Q)=1+2\lim_{N\to\infty}\left[\sum_{l=-N}^{N} e^{-(Q_n^2/2)\langle u_{l0}^2\rangle}\right], \tag{38}$$

where

$$\langle u_{l0}^2\rangle_\infty=\langle(u_l-u_{l'})^2\rangle=\langle u_{l-l',0}^2\rangle=\langle u_{l0}^2\rangle\ . \tag{39}$$

The expression Eq. (38) is like a "partition function" in that it counts the total number of "states" characterized by a given $\langle u_{l0}^2\rangle$ for given n. Each of these states contributes to the coherent peak in intensity at the reciprocal-lattice points of the 1D lattice. In this picture, $\exp(-Q_n^2\langle u_{l0}^2\rangle/2)$ is the "probability" for which two atoms separated by equilibrium distance ld and with relative mean-square fluctuation of $\langle u_{l0}^2\rangle$ scatter coherently. This probability depends on the separation of the two atoms (since the degree of disorder represented in $\langle u_{l0}^2\rangle$ depends on l) and on the wave number Q_n of the external probe (since each pair of atoms in the scattering "state" represented by a given $\langle u_{l0}^2\rangle$ will experience a mismatch in coherence which depends on Q_n).

In the ideal case of the perfect, static 1D lattice, $\langle u_{l0}^2\rangle=0$ independent of l and the coherent scattering is proportional to N:

$$S(Q_n)=N+2+\frac{1}{N},\quad \langle u_{l0}^2\rangle=0\ . \tag{40}$$

The height of the peaks is independent of Q_n.

We turn to a calculation of s_n^2 the mean value of $\langle u_{l0}^2\rangle$ set up in response to a perturbation of wave number Q_n and averaged over all the states of the 1D chain:

$$\overline{\langle u_{l0}^2\rangle}=\frac{\lim_{N\to\infty}\left[\sum_{l=-N}^{+N} e^{-(Q_n^2/2)\langle u_{l0}^2\rangle}\langle u_{l0}^2\rangle\right]}{\lim_{N\to\infty}\left[\sum_{l=-N}^{+N} e^{-(Q_n^2/2)\langle u_{l0}^2\rangle}\right]}$$

$$\equiv s_n^2\ . \tag{41}$$

The overbar denotes the average over the states (or pairs of scatterers) of the system. Thus

$$s_n=\frac{\sigma}{(1-e^{-\kappa_n d})^{1/2}} \tag{42}$$

$$\simeq\frac{\sigma}{(\kappa_n d)^{1/2}}=\frac{d}{\pi n\sqrt{2}},\quad \kappa_n d\ll 1$$

$$\simeq 0.2d \tag{43}$$

for $n=1$, independent of T to leading order.

If one can ascribe a *total* degree of disorder (at given wave number Q_n) to the correlated regions, the system would behave on average, like one in which each atom had been assigned a degree of disorder s_n^2 with respect to an arbitrary origin. Equation (43) can be written in more transparent form as

$$l_n=\frac{s_n^2}{\sigma^2}=\frac{e^{\kappa_n d}}{e^{\kappa_n d}-1} \tag{44}$$

$$\simeq\frac{1}{\kappa_n d},\quad \kappa_n d\ll 1$$

$$\simeq\frac{1}{2\pi^2}\left[\frac{d}{\sigma}\right]^2\frac{1}{n^2}\ , \tag{45}$$

where $l_n d$ is the separation of two atoms on the infinite chain corresponding to the degree of disorder s_n^2. If each atom were displaced by an amount s_n, however, this would merely correspond to a to a translation of the whole chain and the linewidths would again be perfectly sharp. In order to understand the mechanism contributing to the linewidths therefore, we must turn to an examination of the distribution of the mean-square displacements about the average value s_n^2. The dispersion in $\langle u_{l0}^2\rangle$ is given by the quantity

$$[\overline{(\langle u_{l0}^2\rangle-s_n^2)^2}]^{1/2}=[\overline{(\Delta\langle u_{l0}^2\rangle)^2}]^{1/2}$$

$$=\frac{\sigma^2 e^{\kappa_n d/2}}{e^{\kappa_n d}-1} \tag{46}$$

$$\simeq\frac{\sigma^2}{\kappa_n d},\quad \kappa_n d\ll 1\ . \tag{47}$$

Thus $\overline{(\Delta\langle u_{l0}^2\rangle)^2}\simeq s_n^2$ or equivalently

$$\Delta l=l_n\ . \tag{48}$$

The picture which emerges is one in which coherent scattering occurs from regions of correlated displacements centered, at given temperature T, with a broad dispersion around some "mean" position $l_n d\propto l/n^2$ on the chain. At this position, fluctuations have some "mean" value over the sheet of $s_n^2\propto l_n$, again with a broad dispersion $\overline{(\Delta\langle u_{l0}^2\rangle)^2}\propto\Delta l$.

The relevant scattering regions are thus roughly of length $2l_n d$. As one goes to higher-order sheets (increasing n), the size of the correlated regions decreases corresponding to increasing mismatch in coherence. This is reflected by both the decrease in peak height and the increase in linewidth with[12] n as verified analytically for the infinite chain by Eq. (47).

For the *finite* chain, the size of the correlated regions as compared to the infinite chain is expected to be greater owing to the reduced disorder in the system, but for small n's is restricted by the system size. As n increases, however, the reduced fluctuations pull the linewidth below that of the infinite chain. At still larger n's, the large mismatch in coherence should cause little difference between the finite- and infinite-chain theories and η should approach the infinite-chain linewidth from below.

We calculate the root-mean-square relative deviations $[\overline{(\Delta\langle u_{l-l',0}^2\rangle)^2}]^{1/2}$ corresponding to Eq. (46) using Eqs. (41) and (12) for $N=100$. The resulting curves, which the preceding discussion has argued are related to the

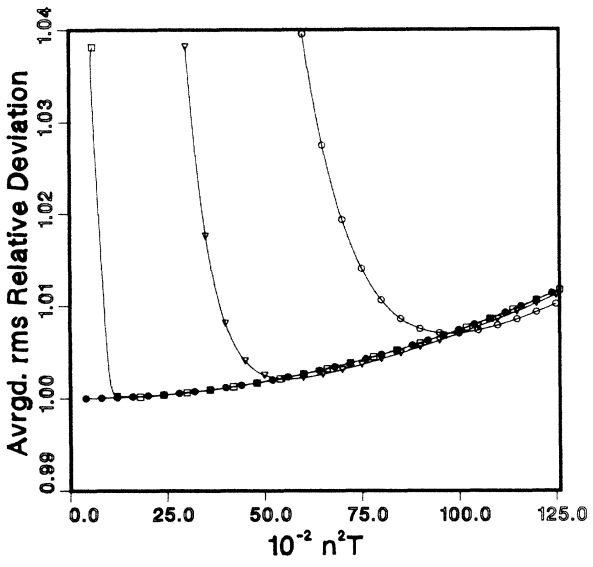


FIG. 5. The dispersion $[\overline{(\Delta\langle u_{l0}^2\rangle)^2}]^{1/2}$ (normalized to κ_n) in the degree of disorder about an average value s_n^2 induced by a perturbation of wave number Q_n for $N=50$, 100, and 500, as represented by the open circles, triangles, and squares, respectively. The solid circles are the infinite-chain expression Eq. (46), normalized to κ_n.

linewidth (with a proportionality constant possibly dependent on N), are plotted versus n^2T in Fig. 5, normalized to κ_n. It should be noted that they exhibit minima, as do the Lorentzian half-widths in Fig. 4, and approach the infinite-chain value from below as N increases. The degree of asymmetry of the Lorentzians increases with increasing n^2T, hence the curves in Fig. 4 are shown only for $n^2T \lesssim 10^4$. It should also be noted that the infinite-chain half-widths increase faster than n^2T for large values of n^2T.

To summarize, a theory for the structure factor of a linear finite chain has been presented and discussed in terms of the existing order in the system. We have used fixed boundary conditions which in the large-N limit are shown to be equivalent to periodic boundary conditions with lower wave number cutoff in the evaluation of $S(Q)$. The correlations between the displacements of pairs of atoms are a nonlinear function of the relative separation of the pair. When the half-widths (normalized to κ_n) of the peaks in $S(Q)$ are plotted versus n^2T, the resulting curve exhibits a characteristic dipper shape in contrast to the flat line predicted by infinite-chain theories in the literature.[3,11] This shape appears to be within the reach of experimental[1] observation. For chains of length $\gtrsim$ 1500 Å, the dominant effect would be the flattening of the first peak compared to subsequent peaks resulting in a more "solidlike" appearance of $S(Q)$.

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