Coherent Scattering of Slow Neutrons by a Liquid*

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The convolution approximation of Vineyard to treat the coherent scattering of slow neutrons by a monatomic liquid is extended. The correction term, which takes care of correlations between neighboring atoms, is evaluated on the basis of a "quasicrystalline" model of a liquid. In the calculation proper account is, however, taken of the geometrical arrangement and dynamical behavior of atoms in a liquid. Expression for the width of the "quasielastic" scattering is derived which exhibits a characteristic oscillatory behavior as a function of momentum transfer. Explicit numerical calculations for the width have been made for liquid argon near the triple point, which are in reasonably good agreement with experiment. An interesting feature of the basic formula of the paper is the temperature dependence of the width for a given momentum transfer, which is also in qualitative agreement with experiment. There are other features which need to be tested by further experiments, suggestions for which have been outlined.

I. INTRODUCTION

DURING recent years considerable effort, both theoretical and experimental, has been directed towards understanding the scattering of slow neutrons by an incoherent liquid. Comparatively, little experimental work has been done with a coherent liquid, despite the fact that most liquids, and particularly the simple ones, are coherent scatterers—one of the reasons being the lack of a theory on the basis of which coherent effects could be analyzed. Coherent scattering is obviously far more complex than incoherent, since the latter involves only the self-motion of an atom whereas the former involves the correlated motion of different atoms in a liquid. To treat coherent scattering, Vineyard[1] proposed his convolution approximation, which connects the coherent to the incoherent scattering through the Fourier transform of the static-pair correlation function of a liquid, which is known experimentally. The great virtue of this approximation lies in the fact that, besides being simple, it does not introduce any adjustable parameter in the theory. Unfortunately, the convolution approximation is not fully borne out by experimental facts and seems to have validity only over a limited range of momentum transfer. In fact, recently Brockhouse et al.[2] have pointed out that the oscillations in the width of the "quasielastic" scattering of 4.06-Å neutrons in liquid argon as a function of momentum transfer which they have observed, could not be explained by the convolution approximation. Earlier, Palevsky,[3] Brockhouse and Pope,[4] and others had also remarked that this approximation was not in accord with their observations.

The present paper is an attempt in the direction of improving upon the convolution approximation. This improvement is based on two basic assumptions: (a) that the convolution approximation is valid for atoms whose distance of separation is greater than a certain distance R which occurs as a parameter in the theory; and (b) that the correction term can be evaluated analogously to the case of a harmonic solid, with due care regarding the geometrical arrangement and dynamical behavior of atoms in a liquid. Both these assumptions, in particular assumption (b), are hard to justify. They are, however, made with reliance on physical intuition and should be judged by the success of the results they yield. The basic formula derived here for the scattering function $S(\kappa,\omega)$ should in general be valid for all coherent monatomic liquids for small and intermediate values of the momentum transfer κ. Explicit numerical calculations for the half-width of the "quasielastic" scattering as a function of κ have been made for liquid argon near the triple point, and are surprisingly in good agreement with experiment.[2] Our basic formula, undoubtedly quite crude, has, nevertheless, several interesting features which should be tested by future experiments.

II. CONVOLUTION APPROXIMATION

The differential scattering cross section can be written in the following form[5]:

$$d^2\sigma_{\mathrm{coh}}/d\Omega d\omega = N a_{\mathrm{coh}}^2 (k/k_0) S_{\mathrm{coh}}(\kappa,\omega), \tag{1}$$

and

$$d^2\sigma_{\mathrm{inc}}/d\Omega d\omega = N a_{\mathrm{inc}}^2 (k/k_0) S_{\mathrm{inc}}(\kappa,\omega); \tag{2}$$

where

$$S_{\mathrm{coh}}(\kappa,\omega) = \frac{1}{2\pi} \int e^{-i\omega t} F(\kappa,t) dt, \tag{3}$$

and

$$S_{\mathrm{inc}}(\kappa,\omega) = \frac{1}{2\pi} \int e^{-i\omega t} F_s(\kappa,t) dt. \tag{4}$$

The intermediate scattering functions F occurring in

[1] G. H. Vineyard, Phys. Rev. 110, 999 (1958).
[2] B. N. Brockhouse, J. Bergsma, B. A. Dasannacharya, and N. K. Pope, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 189.
[3] H. Palevsky, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 265.
[4] B. N. Brockhouse and N. K. Pope, Phys. Rev. Letters 3, 259 (1959).
[5] L. Van Hove, Phys. Rev. 95, 249 (1954).

the above equations are defined by

$$F(\kappa,t)=N^{-1}\sum_{\alpha\beta}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]$$
$$\times\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T, \quad (5)$$

and

$$F_s(\kappa,t)=N^{-1}\sum_{\alpha}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]$$
$$\times\exp[-i\kappa\cdot\mathbf{R}_\alpha(t)]\rangle_T, \quad (6)$$

and are, respectively, the space transforms of the now well known $G(\mathbf{r},t)$ and $G_s(\mathbf{r},t)$ functions introduced by Van Hove.[5] $\hbar\omega$ and $\hbar\kappa$ are, respectively, the energy and momentum transfers and are related to the incident and final wave vectors $\mathbf{k}_0$ and $\mathbf{k}$ of the neutron through the relations

$$\kappa=\mathbf{k}_0-\mathbf{k} \quad (7)$$

and

$$\hbar\omega=(\hbar^2/2m)(k_0^2-k^2), \quad (8)$$

where m is the neutron mass. The other symbols occurring in Eqs. (1)–(6) have their usual meaning. $\mathbf{R}_\beta(t)$ is the position vector of the βth atom at time t in the Heisenberg representation. We shall not discuss the properties of either the G or the F functions since they are well known.

The convolution approximation consists in writing $F(\kappa,t)$ as

$$F(\kappa,t)\rightarrow F(\kappa,0)F_s(\kappa,t), \quad (9)$$

which follows from the assumption that the bracket $\langle\cdots\rangle_T$ in (5) after introducing the identity operator $\exp[i\kappa\cdot\mathbf{R}_j(0)]\exp[-i\kappa\cdot\mathbf{R}_j(0)]$ can be broken up into a product of two factors. This amounts to assuming[1] that the motion of an atom β situated at $\mathbf{r}'$ at time zero from an atom α at the origin at time zero, is independent of the presence of the atom α. The most obvious defect of this approximation is a geometrical one. As Vineyard[1] clearly points out, it is difficult to know the error in this approximation, but qualitative considerations suggest that it may be good for small values of κ, i.e., large $\mathbf{r}$. The exact domain of κ values for which this approximation is valid is hard to know. Its merit, however, lies in the simplicity and direct way in which it connects the coherent to the incoherent scattering.

Now there are two objections against the convolution approximation. The first, and the one which is very often cited, is that it violates the moment relation

$$(\omega_{\rm coh}^2)_{\rm av}\equiv\frac{\int\omega^2 S_{\rm coh}(\kappa,\omega)d\omega}{\int S_{\rm coh}(\kappa,\omega)d\omega}=\frac{k_B T}{M}\kappa^2[1/F(\kappa,0)], \quad (10)$$

as pointed out by De Gennes.[6] From (9), however, it follows that

$$(\omega_{\rm coh}^2)_{\rm av,con}=\frac{k_B T}{M}\kappa^2=(\omega_{\rm inc}^2)_{\rm av},$$

and hence the convolution approximation violates the moment relation (10). The second objection, also first pointed by De Gennes[6] and later on more explicitly stated by Singwi and Sjölander,[7] is that in the limit $\kappa\rightarrow 0$ (case of light scattering by a liquid) the convolution approximation predicts an undisplaced Rayleigh line whose width is determined by the macroscopic self-diffusion constant, whereas in actual fact one gets three lines—the central Rayleigh line corresponding to entropy fluctuations and the two displaced Brillouin-Mandelstam components corresponding to density fluctuations. The width of the former is determined by the coefficient of heat diffusion and that of the latter by the coefficients of heat conduction and viscosity. Thus we see that the convolution approximation fails the test wherever it is possible to test it rigorously. Nevertheless, this does not preclude its usefulness, as has often been stated by the author and as will be evident in the sequel.

We mentioned earlier that for small κ and ω values, the convolution approximation might be good. This can be seen from the following argument. For small values of κ, the function $S(\kappa,\omega)$ has a very pronounced peak near $\omega=0$ and, therefore, the major contribution to the integral in the denominator of (10) comes from under this peak. In this region of κ and ω values we therefore apply the Vineyard approximation and calculate $S_{\rm coh}(\kappa,\omega)$. On the other hand, the major contribution to the integral in the numerator of (10) comes from large ω values, for which, as we know in solids, the incoherent approximation should be good. It then follows that

$$(\omega_{\rm coh}^2)_{\rm av}$$
$$=\frac{\int\omega^2 d\omega\int F_s(\kappa,t)e^{-i\omega t}dt}{F(\kappa,0)\int d\omega\int F_s(\kappa,t)e^{-i\omega t}dt}=(\omega_{\rm inc}^2)_{\rm av}\left(\frac{1}{F(\kappa,0)}\right), \quad (11)$$

which is the same as (10). Under the above-mentioned assumptions the convolution approximation, therefore, does not violate the moment relation (10). The argument is obviously approximate.

The second objection appears to us somewhat unfair in the sense that the convolution approximation was never intended to be applied to such long-range correlations—correlations which are in the "hydrodynamic" range and should indeed be calculated from the hydrodynamic equations of a liquid.

The range of κ values which one normally encounters in slow-neutron scattering by a liquid lies between $\kappa=0.2$ and 4 Å^{-1} or more. Surely, in this range interesting effects occur which are not covered by the convolution approximation. For example, it was pointed out by

[6] P. G. De Gennes, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 239.

[7] K. S. Singwi and A. Sjölander, Phys. Letters **9**, 120 (1964).

De Gennes[8] from a very general analysis of second and fourth moments of $S_{\mathrm{coh}}(\kappa,\omega)$ that for values of κ corresponding to one of the diffraction peaks in the x-ray pattern, i.e., $F(\kappa,0)$, the ratio $(\omega_{\mathrm{coh}}{}^4)_{\mathrm{av}}/3(\omega_{\mathrm{coh}}{}^2)_{\mathrm{av}}{}^2$ becomes large, since $(\omega_{\mathrm{coh}}{}^2)_{\mathrm{av}}$ becomes small, as is evident from (10). This implies for such κ values a distribution $S_{\mathrm{coh}}(\kappa,\omega)$ which is broad in the wings and narrow at the center. This narrowing effect predicted by De Gennes has unquestionably been observed by Brockhouse et al.[2] De Gennes gave a recipe for the half-width of the distribution as a function of κ which has a characteristic oscillatory behavior. However, as De Gennes himself mentions, many important questions, such as the temperature dependence of the width, the shape of $S_{\mathrm{coh}}(\kappa,\omega)$ when κ is kept constant on a maximum of $F(\kappa,0)$, and others, remain unanswered. We shall in what follows attempt to answer these questions by extending the convolution approximation of Vineyard.

III. MATHEMATICAL FORMULATION

Equation (5) can be written as

$$F(\kappa,t)=F_s(\kappa,t)$$
$$+N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T$$
$$+N^{-1}\sum_{\alpha\neq\beta}^{>R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T,\tag{12}$$

where the index $<R$ on the summation sign means that for a given α we sum over all atoms β which lie within a sphere of arbitrary radius R drawn with α as the center, and the index $>R$ means all atoms β lying outside this sphere. This is a trivial step splitting the sum into two parts. *Our first basic assumption is that for all atoms such that* $|\mathbf{R}_\alpha-\mathbf{R}_\beta|>R$, *we can apply the Vineyard approximation.* In other words, we assume that when atoms α and β are far separated, i.e., for large R, which implies κ small, the motion of β is uninfluenced by the presence of α. Equation (12) then becomes

$$F(\kappa,t)=F_s(\kappa,t)+N^{-1}\sum_{\alpha\neq\beta}^{>R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(0)]\rangle_T$$

$$\times\langle\exp[i\kappa\cdot\mathbf{R}_\beta(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T+N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T,$$

which can be rewritten as

$$F(\kappa,t)=F_s(\kappa,t)+N^{-1}\sum_{\alpha\neq\beta}^{>R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(0)]\rangle_T\langle\exp[i\kappa\cdot\mathbf{R}_\beta(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T$$

$$+N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(0)]\rangle_T\langle\exp[i\kappa\cdot\mathbf{R}_\beta(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T$$

$$+N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T$$

$$-N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(0)]\rangle_T\langle\exp[i\kappa\cdot\mathbf{R}_\beta(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T,\tag{13}$$

where we have added and subtracted the same term. Combining the second and the third terms in (13) we can write it as

$$F(\kappa,t)=[1+\Gamma(\kappa)]F_s(\kappa,t)+N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T$$

$$-N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle\exp[i\kappa\cdot\mathbf{R}_\alpha(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(0)]\rangle_T\langle\exp[i\kappa\cdot\mathbf{R}_\beta(0)]\exp[-i\kappa\cdot\mathbf{R}_\beta(t)]\rangle_T,\tag{14}$$

where

$$\Gamma(\kappa)=\int g(\mathbf{r})e^{i\kappa\cdot\mathbf{r}}d\mathbf{r}\tag{15}$$

is the Fourier transform of the static pair correlation function $g(\mathbf{r})$, which is defined by

$$g(\mathbf{r})=N^{-1}\sum_{\alpha\neq\beta}\langle\delta(\mathbf{R}_\alpha(0)-\mathbf{R}_\beta(0)-\mathbf{r})\rangle_T.\tag{16}$$

[8] P. G. De Gennes, Physica 25, 825 (1959).

In the Appendix we have defined $\Gamma(\kappa)$ through Eq. (A3), which is the same as Eq. (15) except for the term involving g_0, which gives a contribution only for $\kappa=0$.

If we neglect the last two terms in (14), we get the convolution approximation. They, therefore, represent a correction to the Vineyard approximation. We shall henceforth denote them by $H(\kappa,t)$.

$$H(\kappa,t) \equiv N^{-1} \sum_{\alpha \neq \beta}^{<R} \langle \exp[i\kappa \cdot \mathbf{R}_\alpha(0)] \exp[-i\kappa \cdot \mathbf{R}_\beta(t)] \rangle_T - N^{-1} \sum_{\alpha \neq \beta}^{<R} \langle \exp[i\kappa \cdot \mathbf{R}_\alpha(0)] \exp[-i\kappa \cdot \mathbf{R}_\beta(0)] \rangle_T$$
$$\times \langle \exp[i\kappa \cdot \mathbf{R}_\beta(0)] \exp[-i\kappa \cdot \mathbf{R}_\beta(t)] \rangle_T. \quad (17)$$

The main problem now is to evaluate $H(\kappa,t)$, and it is here that our second assumption enters. *We assume that it can be treated analogously to the case of a harmonic solid.* This is *prima facie* an ad hoc assumption; but it is based on the physical idea that the main contribution to $H(\kappa,t)$ arises from times during which the atoms have not moved far from the positions they had at time $t=0$. In fact, the essential idea behind a "quasicrystalline" model of a liquid is that the atoms do stay in their temporary equilibrium positions for a time which is greater than a few times their period of oscillation. During this time all that the atoms do is to develop their thermal cloud, and if that is so, it is not unreasonable to treat their motion as one does in a solid. In doing so, one automatically makes the assumption of a harmonic approximation, but this is the best that one can do at present.

The evaluation of $H(\kappa,t)$ now becomes a straightforward matter and we shall briefly outline the method. For the moment let us forget the index $<R$ on the summation sign in $H(\kappa,t)$ which we shall take care of later by introducing a damping factor. Consider

$$\sum_{\alpha \neq \beta} \langle \exp[i\kappa \cdot \mathbf{R}_\alpha(0)] \exp[-i\kappa \cdot \mathbf{R}_\beta(t)] \rangle_T = \sum_{\alpha \neq \beta} \langle \exp[i(\kappa \cdot \mathbf{R}_\alpha) \exp(-i\kappa \cdot \mathbf{R}_\beta)] \rangle_T$$
$$\times \exp[i\kappa \cdot \mathbf{u}_\alpha(0)] \exp[-i\kappa \cdot \mathbf{u}_\beta(t)] \rangle_T, \quad (18)$$

where $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ are the equilibrium positions, and $\mathbf{u}_\alpha(0)$ and $\mathbf{u}_\beta(t)$ are, respectively, the displacements of atoms α and β about their equilibrium positions. Now

$$\langle \exp[i\kappa \cdot \mathbf{u}_\alpha(0)] \exp[-i\kappa \cdot \mathbf{u}_\beta(t)] \rangle_T = \exp[-M_{\alpha\alpha}(0) - M_{\beta\beta}(0) + 2M_{\alpha\beta}(t)], \quad (19)$$

where

$$2M_{\alpha\beta}(t) = \langle [\kappa \cdot \mathbf{u}_\alpha(0)][\kappa \cdot \mathbf{u}_\beta(t)] \rangle_T \quad (20)$$

(see Ref. 5). The displacement $\mathbf{u}_R(t)$ can be written as

$$\mathbf{u}_R(t) = \sum_s (\hbar/2MN\omega_s)^{1/2} \mathbf{e}_s \{a_s \exp[i(\mathbf{q} \cdot \mathbf{R} - \omega_s t)] + a_s^* \exp[-i(\mathbf{q} \cdot \mathbf{R} - \omega_s t)] \}, \quad (21)$$

where the symbols have their well known meaning and the sum over s includes the sum over both wave-vector $\mathbf{q}$'s and the polarization of the vibration. Substituting (21) in (20) we have

$$2M_{\alpha\beta}(t) = \sum_s \sum_{\mu=\pm 1} g_{s\mu} \exp[i(\mathbf{q} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)) - i\mu\omega_s t], \quad (22)$$

where

$$g_{s\mu} = \frac{\hbar}{4NM} (\kappa \cdot \mathbf{e}_s)^2 \frac{1}{\omega_s} \left(\coth \frac{\hbar\omega_s}{2k_B T} - \mu \right). \quad (23)$$

μ is $+1$ for absorption and -1 for emission of a phonon. Similarly,

$$\langle \exp[i\kappa \cdot \mathbf{R}_\beta(0)] \exp[-i\kappa \cdot \mathbf{R}_\beta(t)] \rangle_T = \exp[-2M_{\beta\beta}(0) + 2M_{\beta\beta}(t)]. \quad (24)$$

The usual phonon expansion consists in writing

$$\exp[2M_{\alpha\beta}(t)] = 1 + 2M_{\alpha\beta}(t) + \tfrac{1}{2}[2M_{\alpha\beta}(t)]^2 + \cdots. \quad (25)$$

We shall in what follows retain only the first two terms of the above expansion, i.e., neglect two and higher phonon terms, which become significant only for very large values of κ. In the ω region of interest here their contribution is small.

We now write

$$N^{-1} \sum_{\alpha \neq \beta}^{<R} \langle \exp(i\kappa \cdot \mathbf{R}_\alpha) \exp(-i\kappa \cdot \mathbf{R}_\beta) \rangle_T \approx N^{-1} \sum_{\alpha \neq \beta} \langle \exp(i\kappa \cdot \mathbf{R}_\alpha) \exp(-i\kappa \cdot \mathbf{R}_\beta) \rangle_T \exp[-|\mathbf{R}_\alpha - \mathbf{R}_\beta|^2/R^2], \quad (26)$$

where we have introduced a smooth cutoff factor. We further make an approximation in which we replace $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ on the right-hand side of (26) by $\mathbf{R}_\alpha(0)$ and $\mathbf{R}_\beta(0)$. Now

$$\int e^{i\kappa\cdot\mathbf{r}}g(\mathbf{r})\exp-\frac{|\mathbf{r}|^2}{R^2}=\frac{1}{N}\int e^{i\kappa\cdot\mathbf{r}}\exp-\frac{|\mathbf{r}|^2}{R^2}\sum_{\alpha\neq\beta}\langle\delta(\mathbf{R}_\alpha(0)-\mathbf{R}_\beta(0)-\mathbf{r})\rangle_T d\mathbf{r}$$

$$=N^{-1}\sum_{\alpha\neq\beta}\langle\exp i\kappa\cdot[\mathbf{R}_\alpha(0)-\mathbf{R}_\beta(0)]\rangle_T\exp[-|\mathbf{R}_\alpha(0)-\mathbf{R}_\beta(0)|^2/R^2].\quad(27)$$

Therefore

$$N^{-1}\sum_{\alpha\neq\beta}^{<R}\langle e^{i\kappa\cdot\mathbf{R}_\alpha}e^{-i\kappa\cdot\mathbf{R}_\beta}\rangle_T\approx\int e^{i\kappa\cdot\mathbf{r}}g(\mathbf{r})\exp-\frac{|\mathbf{r}|^2}{R^2}d\mathbf{r}.\quad(28)$$

Using Eqs. (17)–(28), it follows that

$$H(\kappa,t)=e^{-2M(0)}\sum_{s,\mu}g_{s\mu}e^{-i\mu\omega_s t}\left\{\int e^{i(\kappa+\mathbf{q})\cdot\mathbf{r}}g(\mathbf{r})\exp-\frac{|\mathbf{r}|^2}{R^2}d\mathbf{r}-\int e^{i\kappa\cdot\mathbf{r}}g(\mathbf{r})\exp-\frac{|\mathbf{r}|^2}{R^2}d\mathbf{r}\right\},\quad(29)$$

where $e^{-2M(0)}$ is the usual Debye-Waller factor, which in the limit $T\gg\theta_D$ becomes

$$\exp[-2M(0)]=\exp\left(-\frac{\kappa^2\hbar^2}{2Mk_B\theta_D}\frac{6T}{\theta_D}\right),\quad(30)$$

where θ_D is the corresponding Debye temperature for a liquid.

The parameter R in Eq. (29) is unknown. It is certainly of the order of a few interatomic distances. In the following discussion we shall take the limiting case of $R\to\infty$ and shall derive the correction terms depending on R in the Appendix. As is seen from Eq. (A11) of the Appendix, to estimate the correction one needs to know the third and higher derivatives of $\Gamma(\kappa)$, which at present cannot be done with any reasonable accuracy from the x-ray data regarding $\Gamma(\kappa)$. One can, however, evaluate the term in the curly brackets in (29) numerically using formula (A17) (for details see Appendix); but then it involves an enormous numerical computation and one loses all the transparency of the final formula for $S(\kappa,\omega)$ in which we are really interested. For the present crude calculation, we shall be satisfied with the limiting case $R\to\infty$. For this case (29), on using (15), becomes

$$H(\kappa,t)=\exp[-2M(0)]$$
$$\times\sum_{s,\mu}g_{s\mu}e^{-i\mu\omega_s t}[\Gamma(\kappa+\mathbf{q}_s)-\Gamma(\kappa)].\quad(31)$$

Since we shall be interested in $\mathbf{q}\ll\kappa$, we can make Taylor's expansion of $\Gamma(\kappa+\mathbf{q}_s)$. After performing the angular average over the direction of $\mathbf{q}_s$ we have

$$\Gamma(\kappa+\mathbf{q}_s)-\Gamma(\kappa)=\tfrac{1}{6}q_s^2[\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)]$$
$$+\text{terms involving higher powers of }\mathbf{q}_s\quad(32)$$

[see Eq. (A9)]. On using (32), (31) becomes

$$H(\kappa,t)=\exp[-2M(0)]$$
$$\times\sum_{s,\mu}g_{s\mu}e^{-i\mu\omega_s t}\tfrac{1}{6}q_s^2[\Gamma''(\kappa)+(2/|\mathbf{k}|)\Gamma'(\kappa)].\quad(33)$$

We shall consider the case of phonon absorption, i.e., $\mu=1$. Also for all ω_s's of interest here $\hbar\omega_s\ll 2k_BT$, and in that case Eq. (23) simplifies to

$$g_{s,+1}\approx(k_BT/2NM)(\kappa\cdot\mathbf{e}_s)^2(1/\omega_s^2).\quad(34)$$

On using (34), (33), for an isotropic case, becomes

$$H(\kappa,t)=\exp[-2M(0)]\sum_{\mathbf{q}}\kappa^2\frac{k_BT}{12NM}\frac{q^2}{\omega_q^2}$$

$$\times\left(\Gamma''(\kappa)+\frac{2}{|\mathbf{k}|}\Gamma'(\kappa)\right)e^{-i\omega_q t}.\quad(35)$$

For a solid in the Debye approximation

$$\sum_{\mathbf{q}}\to\frac{V}{2\pi^2c^3}\int_0^{\omega D}\omega^2 d\omega,\quad(36)$$

where V is the volume and we have used the linear dispersion relation $q=\omega/c$, c being the *mean* velocity of sound. In a liquid we shall replace (36) by

$$\sum_{\mathbf{q}}\to\frac{V}{2\pi^2c^3}\int_0^\infty\omega^2\exp\left[-\frac{2\omega}{\omega_m}\right]d\omega,\quad(37)$$

where ω_m is the value of ω for which there occurs a maximum in the assumed frequency spectrum in a liquid. One might identify this spectrum with the Fourier transform of the velocity autocorrelation function in a liquid.[9] Now c is related to ω_m by

$$c=(8\pi^2n)^{-1/3}\omega_m,\quad(38)$$

where n is the number density of particles. ω_m is the parameter of our theory. Since ω_m for a liquid is much less than that for the corresponding solid, the density of states in a liquid for small ω's is very much greater than that in a solid.

[9] K. S. Singwi, A. Sjölander, and A. Rahman, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 215.

From (35) and (37) we have

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{-i\omega t}H(\kappa,t)dt=e^{-2M(0)}\frac{\kappa^2 k_B T}{24\pi^2 c^5\rho}$$

$$\times\left(\Gamma''(\kappa)+\frac{2}{|\kappa|}\Gamma'(\kappa)\right)\omega^2 e^{-2\omega/\omega_m},\quad(39)$$

where ρ is the density in g/cc of the liquid.

The total differential scattering cross section is given by the sum of Eqs. (1) and (2). Since we do not know $S_{inc}(\kappa,\omega)$ for a liquid, recourse has to be taken to models,[1,10,11] of which the simplest is the simple diffusion model. We shall use the latter in this paper. Extension to the jump diffusion model[10] is straightforward. Using Eqs. (1)–(4) and Eqs. (14), (17), and (39) and the simple diffusion model for $S_{inc}(\kappa,\omega)$, we have

$$\frac{d^2\sigma}{d\Omega d\omega}=N\frac{k}{k_0}a_{coh}^2\left[\left\{\frac{a_{inc}^2}{a_{coh}^2}+[1+\Gamma(\kappa)]\right\}\frac{\kappa^2 D}{(\kappa^2 D)^2+\omega^2}\frac{1}{\pi}\right.$$

$$\left.+e^{-2M(0)}\kappa^2\frac{k_B T}{24\pi^2\rho c^5}\left(\Gamma''(\kappa)+\frac{2}{|\kappa|}\Gamma'(\kappa)\right)\omega^2 e^{-2\omega/\omega_m}\right].$$

$$(40)$$

In writing the above equation, we have neglected the recoil term in $S_{inc}(\kappa,\omega)$, which is indeed small for our case, and have assumed as before that $\hbar\omega\ll 2k_B T$. Equation (40) is the basic equation of our paper. The second term in square brackets in (40) represents our correction to the convolution approximation. This term has a simple structure and exhibits an oscillatory behavior arising from the factor $\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)$. This factor is negative for values of κ corresponding to the peaks in $\Gamma(\kappa)$, its largest negative value occurring at the first peak. In the vicinity of the peak in $\Gamma(\kappa)$, the characteristic feature of this factor is that it rises sharply from a very small to a large positive value for a κ value below that corresponding to the peak, and then falls sharply to a negative value at the peak and rises again to a positive value, continuing this oscillatory behavior. As κ increases, the abruptness with which this function rises and falls obviously diminishes, as is apparent from the form of $\Gamma(\kappa)$ in a liquid. The above-mentioned features, as we shall see in Sec. VII, are reflected in the width of the "quasielastic" scattering as a function of κ. The other interesting feature of this factor is its temperature dependence. The temperature dependence of $\Gamma(\kappa)$ is complicated. As the temperature increases, the peaks of $\Gamma(\kappa)$ move to somewhat lower values of κ and get progressively smeared out, thus resulting in an appreciable change in the magnitude of the correction term.

[10] K. S. Singwi and A. Sjölander, Phys. Rev. 119, 863 (1960).
[11] A. Rahman, K. S. Singwi and A. Sjölander, Phys. Rev. 126, 997 (1962).

IV. WIDTH OF THE QUASIELASTIC SCATTERING

The value of ω at which the intensity falls to half its value at $\omega=0$ is, as follows from (40), determined by the equation

$$\frac{1}{2}=\frac{(\kappa^2 D)^2}{(\kappa^2 D)^2+\omega^2}+\exp[-\kappa^2 a]\kappa^2\frac{k_B T}{24\pi\rho c^5}(\kappa^2 D)$$

$$\times\frac{\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)}{a_{inc}^2/a_{coh}^2+1+\Gamma(\kappa)}\omega^2 e^{-2\omega/\omega_m},\quad(41)$$

where we have put $2M(0)=\kappa^2 a$, a being the mean-square amplitude of the thermal vibration of an atom. On putting

$$x=\omega/\kappa^2 D,\quad(42)$$

and

$$x_0=\omega_m/2\kappa^2 D,\quad(43)$$

(41) becomes

$$\tfrac{1}{2}=(1+x^2)^{-1}+\alpha(\kappa)x^2 e^{-x/x_0},\quad(44)$$

where

$$\alpha(\kappa)=\exp[-\kappa^2 a]\kappa^3\frac{\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)}{a_{inc}^2/a_{coh}^2+1+\Gamma(\kappa)}B\quad(45a)$$

and

$$B=k_B T D^3/24\pi\rho c^5.\quad(45b)$$

For every κ value, Eq. (44) has to be solved numerically to determine x.

Consider the case $x\ll x_0$. Equation (44) then becomes

$$2\alpha(\kappa)x^4-x^2[1-2\alpha(\kappa)]+1=0.\quad(46)$$

For $\alpha(\kappa)$ small enough that $[4\alpha^2(\kappa)-12\alpha(\kappa)]\ll 1$, x is given by

$$x\approx 1+2\alpha(\kappa).\quad(47)$$

We are always interested in the smallest root of Eq. (46). From (46) and (42) it follows that

$$(\Delta E-2\kappa^2 D)/2\kappa^2 D\approx 2\alpha(\kappa),\quad(48)$$

where we have put $2\omega=\Delta E$, the full width at half-height. Hence, whenever $\alpha(\kappa)$ satisfies the above-mentioned condition, the change in width relative to that given by simple diffusion is given by (48). For negative values of $\alpha(\kappa)$ there always exists a solution of Eq. (46), but for positive values of $\alpha(\kappa)$ there does not exist a solution of interest (such that $x\leqslant 2$) for

$$\alpha(\kappa)\geqslant\alpha_{max}(\kappa)=0.086.$$

Since $\alpha(\kappa)$ has both positive and negative values, it follows from (48) that the width as a function of the momentum transfer κ will oscillate around the value $2\kappa^2 D\hbar$ given by the simple diffusion formula. This result is general and holds for all coherent liquids. The magnitude of the oscillations will, however, depend on the value of $\alpha(\kappa)$. The temperature dependence of $\alpha(\kappa)$ is obviously very complicated.

From (44) we have

$$\alpha(\kappa) = \left(\frac{1}{1+x^2} - \frac{1}{2x^2}\right) \exp\frac{2\omega_{1/2}(\kappa)}{\omega_m}, \qquad (49)$$

where

$$x(\kappa) = 2\omega_{1/2}(\kappa)/2\kappa^2 D, \qquad (50)$$

and $\omega_{1/2}(\kappa)$ is the half-width.

At points of extremum in the half-width we have the condition

$$\partial\omega_{1/2}(\kappa)/\partial\kappa = 0,$$

which on using (49) gives us the following equation

$$\frac{\partial}{\partial\kappa}\ln\alpha(\kappa) = \frac{4}{|\kappa|}\left(1 - \frac{2x^2}{x^4-1}\right). \qquad (51)$$

The occurrence of the logarithmic derivative in the above equation eliminates the uncertain constant B [Eq. (45b)]. Hence, the extrema in the width function do not depend on this constant in $\alpha(\kappa)$.

V. REMARKS ABOUT SCATTERING NEAR THE CRITICAL POINT

The phenomenon of scattering at the critical point of a liquid in the limit $\kappa \to 0$ is well known by the name of critical opalescence and is studied using ordinary light. Here, we shall discuss the case of coherent neutron scattering near the critical point for not too large values of κ. The region of large κ values is not of much interest, since the structure in $\Gamma(\kappa)$ is nearly washed out with the exception of the first peak, in the vicinity of which it is still of considerable interest to study the scattering. As one approaches the critical point, the velocity of sound (because of ω_m) would diminish. The absolute value of the function $\Gamma''(\kappa) + (2/|\kappa|)\Gamma'(\kappa)$ would also decrease because of the broadening of the peak. The over-all magnitude of the correction term in (40) is hard to predict. It should, however, be kept in mind that the validity of our formula in this region is questionable. These factors put together make the experimental study of neutron scattering all the more interesting as one approaches the critical region.

It follows from the standard thermodynamic argument that very near the critical region and in the limit $\kappa \to 0$, $\Gamma(\kappa)$ has the form given by[12]

$$1 + \Gamma(\kappa) = k_B T/n(a+b\kappa^2), \qquad (52)$$

where a and b are constants and n is the number density. Even for the smallest κ values attainable in cold-neutron scattering experiments, it is very doubtful whether one could use formula (52). If, however, one uses this formula, it is a simple matter to calculate the scattering cross section using (40).

VI. APPLICATION TO LIQUID ARGON

We shall now apply the foregoing considerations to the specific case of liquid argon for the following reasons: (a) Brockhouse et al.[2] have recently made a very careful study of the "quasielastic" scattering in liquid argon near the triple point and have analyzed their data in a way suitable for the direct application of the present formulation; (b) fortunately Gingrich and Tompson[13] have also studied x-ray scattering in liquid argon near the triple point, thus making available the experimental values of $\Gamma(\kappa)$ as a function of κ; (c) liquid argon being a simple monatomic liquid with weak interatomic forces of the van der Waals type, one might expect that the self-motion of atoms would be more nearly described by the simple Langevin equation; and (d) finally, it is one of those liquids whose properties have been studied over a wide range of temperature and pressure, thus making it possible in the future, when the present theoretical considerations have been more firmly established, to make detailed and extensive neutron-scattering calculations.

Figure 1 represents a smooth curve drawn through the experimental values of $1 + \Gamma(\kappa)$ as obtained by Gingrich and Tompson.[13] Figure 2 is self-explanatory. The first derivatives of $\Gamma(\kappa)$ were obtained from the curves of Fig. 1 using the mirror method, and the same method was used to get the second derivatives from the curve for the first derivatives. Notice the behavior of the final $\Gamma''(\kappa) + (2/|\kappa|)\Gamma'(\kappa)$ curve, which will be reflected in the width of the "quasielastic" peak. The experimental accuracy of $\Gamma(\kappa)$ is such that the derived values of $\Gamma''(\kappa)$ cannot be relied on much, particularly in the region of κ where it changes abruptly from a large positive to a large negative value; but what is of significance for our present purpose is the characteristic behavior of the function $\Gamma''(\kappa) + (2/|\kappa|)\Gamma'(\kappa)$ as a function of κ.
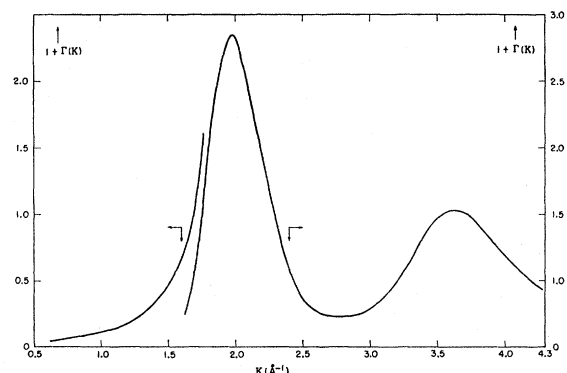

FIG. 1. $1 + \Gamma(\kappa)$ curve as a function of κ (Å^{-1}) drawn smoothly through the experimental points of Gingrich and Tompson (Ref. 13) obtained from x-ray scattering data for liquid argon at $T = 84.25°K$ and $P = 0.710$ atm.

[12] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1958), p. 369.

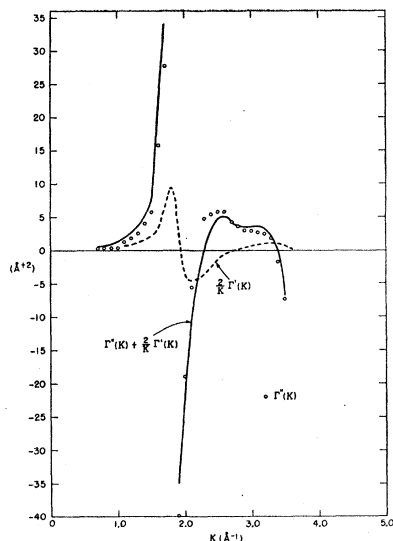[13] N. S. Gingrich and C. W. Tompson, J. Chem. Phys. 36, 2398 (1962).

FIG. 2. Dotted curve represents $(2/|\kappa|)\Gamma'(\kappa)$ (Å^{+2}) as a function of κ (Å^{-1}) obtained by the mirror method using the smooth curve of Fig. 1. Open circles denote $\Gamma''(\kappa)$ obtained from $\Gamma'(\kappa)$ using the same method. Solid curve represents $\Gamma''(\kappa)+(2/|\kappa|)$ $\times\Gamma'(\kappa)$ (Å^{+2}).

In order to calculate x and hence the half-width from (44), we need to know the value of a in the Debye-Waller factor $\exp(-\kappa^2 a)$ and ω_m. The velocity of sound c is related to ω_m through Eq. (38). The Debye temperature θ_D for solid argon is 80°K, and if we assume Mott's formula[14] we get for liquid argon at the melting point a Debye temperature of approximately 40°K, which on using formula (30) gives us $a \approx 0.2$ Å^2. In fact, calculations were made for three different values, $a = 0.1$, 0.2, and 0.25 Å^2. The parameter ω_m was chosen such that $\hbar\omega_m = 0.2k_BT$. For this choice of ω_m a reasonably good fit with experiment was obtained. It was somewhat comforting to note that this choice of ω_m was in fair agreement with the computer calculations of atomic motions in liquid argon by Rahman,[15] who finds a broad maximum in the frequency spectrum of the velocity autocorrelation function in the range given by $\hbar\omega_m \approx 0.25k_BT$. The value of the macroscopic diffusion constant $D = 2.0 \times 10^{-5}$ cm^2/sec near the triple point that we have adopted for our calculation is from a paper by Naghizadeh and Rice.[16] The value of D used by Brockhouse et al.[2] is 1.53×10^{-5} cm^2/sec. The density ρ of liquid argon at the triple point was taken as 1.4 g/cc. With the above choice of the values of the parameters and the constants, the value of the factor $B = k_BTD^3/24\pi\rho c^5$ in $a(\kappa)$ in Eq. (45) is fixed. We get a value of $B = 4 \times 10^{-52}$ (in proper units). The calculations were, however, made for three different values, $B = 3 \times 10^{-52}$, 4×10^{-52}, and 5×10^{-52}, and the best fit

[14] N. F. Mott, Proc. Roy. Soc. (London) **A146**, 465 (1934). See also L. S. Kothari, K. S. Singwi, and S. Viswanathan, Phil. Mag. **2**, 694 (1957).
[15] A. Rahman (to be published).
[16] J. Naghizadeh and S. A. Rice, J. Chem. Phys. **36**, 2710 (1962).

was obtained for the value 5×10^{-52} (in proper units). For argon[17] $a_{inc}^2/a_{coh}^2 = 0.8$.

VII. RESULTS AND DISCUSSION

In Fig. 3(a) we have plotted the calculated full width ΔE at half-height as a function of κ together with what one would get using the convolution approximation. The open circles represent the experimental values of Brockhouse et al.[2] as read from their published curve. The error bars of the experimental values are not indicated. The crosses in the figure denote the values calculated for $B = 4 \times 10^{-52}$. With the choice of the parameters $a = 0.2$ Å^2, $\hbar\omega_m = 0.2k_BT$ and $B = 5 \times 10^{-52}$ (in proper units) (solid curve), Eq. (44) does not admit the desired solution for $\kappa = 1.7$ Å^{-1}, indicating that the "quasielastic" peak has become so broad[18] that the curve for $S(\kappa,\omega)$ as a function of ω starts turning upwards before it attains half its value for $\omega = 0$. Since it is not seen in experiment, this could probably arise from (a) the uncertainty in the values of the derivatives $\Gamma'(\kappa)$ and $\Gamma''(\kappa)$ in the region of κ values (~ 1.7 Å^{-1}) where the $\Gamma(\kappa)$ curve rises very steeply, (b) the choice of the value of the parameter a, which is probably somewhat small, and (c) the neglect of the contribution of the terms involving R^2. For the choice $a = 0.25$ Å^2, $\hbar\omega_m = 0.2k_BT$, and $B = 3 \times 10^{-52}$ (in proper units), one obtains solutions for all κ values, and the calculated points are plotted in Fig. 3(b), but the agreement with experiment is not so good. On the whole, judging from the crudeness of our calculations, the agreement with experiment is surprisingly good. We do not wish to stress this quantitative agreement in view of our basic assumptions, the approximations made, and the uncertainty involved in the values of the derivatives of $\Gamma(\kappa)$; but what we do wish to stress is the characteristic oscillatory behavior of the width as a function of κ, which is in conformity with observation. This behavior is partly dynamic and partly geometric, as is revealed by a closer examination of our correction term to the convolution approximation. The precise physical nature of the effect is, however, somewhat obscure to us.

From our assumed value of ω_m, we get for the mean velocity of sound a value of 187 m/sec. The measured longitudinal velocity of sound for $\omega \to 0$ is nearly 800 m/sec. The velocity for transverse waves is always less than that for longitudinal waves. A low value of the mean velocity that we have obtained implies a large dispersion in the range $\omega \sim 10^{12}$/sec in liquid argon,

[17] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, London, 1962), 2nd ed., p. 61.
[18] From the published data of Cocking, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 234, Fig. 4(c), on the "quasielastic" scattering of 4.1-Å neutrons by liquid sodium for 75° scattering angle and $T = 198$°C, it appears to us that such a case perhaps does occur; and if our interpretation is correct, it would be interesting to repeat this experiment.
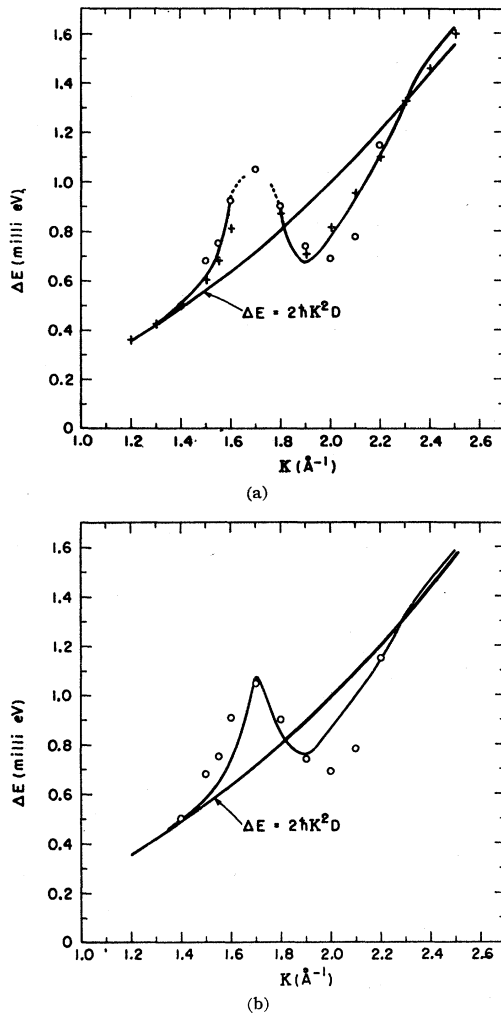
the temperature variation of the width is much less than the temperature variation of the macroscopic diffusion constant. In fact, Palevsky[3] finds that the activation energy for diffusion from his neutron measurements is almost half of that obtained from macroscopic diffusion measurements.

There are possibly two reasons for such a small width: (a) narrowing due to coherent effects and (b) that the mean-square displacement of lead atoms as a function of time is far from attaining its asymptotic value for times of importance for neutron scattering. The latter point has been discussed in detail by Rahman *et al.*[19] We shall here examine the former. For incident neutrons of wavelength 4 Å and scattering angle 90°, the κ value corresponds to the position of the main peak in the $\Gamma(\kappa)$ curve. This would mean a large negative value for the factor $\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)$ in (45). From (45) and (48), the approximate expression for the width at the peak in $\Gamma(\kappa)$ is

$$\Delta E \approx 2\kappa^2 D - \exp(-\kappa^2 a)\kappa^{10}$$

$$\times \frac{|\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)|}{a_{\text{inc}}^2/a_{\text{coh}}^2+1+\Gamma(\kappa)} \frac{k_B T D^4}{6\pi\rho c^5}. \quad (53)$$

The temperature dependence of the second term on the right-hand side of (53) is very complicated. As temperature increases both the Debye-Waller factor and the geometrical factor in the second term on the right-hand side of (53) diminish, whereas the last factor increases. It is physically reasonable to assume that since the density does not change much, and judging from the nature of these factors, the decrease is more than compensated by the increase in the value of the factor $k_B T D^4/6\pi\rho c^5$ with temperature. Thus (53) predicts a temperature dependence of ΔE which is in the right direction. We have not attempted to make, for the present, a quantitative comparison with experiment for lack of necessary data. It would be interesting to measure the temperature dependence of the width for a value of κ for which $\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)$ is large and positive. The sign of the second term in (53) is then positive. It might also be mentioned that the general behavior of $S(\kappa,\omega)$ as a function of κ in liquid Pb observed by Brockhouse and Pope[4] for not too large values of κ is what we would expect from the considerations of this paper. It is unfortunate for us that these authors have not expressed their data in terms of the width as a function of κ, but we did not venture to do this.

Recently, Cocking and Guner[20] have studied the scattering of 4.0- and 6.2-Å neutrons in liquid tin at 240°C for various scattering angles. They have been

FIG. 3(a). Full width ΔE (meV) at half-height of the "quasielastic" peak as a function of the momentum transfer κ (Å^{-1}) for liquid argon ($T=84.5°$K and $\rho=1.4$ g/cc). The solid curve is drawn through the calculated points for the values of the parameters $a=0.2$ Å^2, $B=5\times10^{-52}$ (proper units). The crosses represent the points calculated for $B=4\times10^{-52}$ (proper units). The open circles are the experimental points of Brockhouse (*et al.* Ref. 2) as read from their published curve for $T=84.5°$K and $P=550$ mm Hg. The curve $\Delta E=2\hbar\kappa^2 D$ is calculated for $D=2.0 \times10^{-5}$ cm²/sec. (b) Same as (a) except that the solid curve is now drawn for the values of the parameters $a=0.25$ Å^2, $B=3 \times10^{-52}$ (proper units), and $\hbar\omega_m=0.2k_B T$.

which might well be the case. Basically, the constant c as it occurs here should be interpreted through Eq. (38).

VIII. REMARKS ON SCATTERING IN LIQUID LEAD

Palevsky,[3] using Be-filtered neutrons ($\lambda\sim4$ Å), has studied the width of the "quasielastic" peak for 90° scattering angle as a function of temperature of liquid lead. His main conclusions are (a) that the width is much less than what one would expect for a simple diffusion model (Brockhouse and Pope[4] have also arrived at somewhat similar conclusions) and (b) that

[19] A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **122**, 9 (1961).
[20] S. J. Cocking and Z. Guner, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1963), Vol. 1, p. 237.

mainly concerned with the energy transfer region $\hbar\omega \gg 2\hbar\kappa^2 D$. Our formula can easily be extended to this case by neglecting the diffusive peak in $S_{\text{inc}}(\kappa,\omega)$ and making the usual phonon expansion for the wings. We shall defer this calculation to the future. We might mention that, in the one-phonon approximation, our formula for $S(\kappa,\omega)$ predicts in general, for small energy transfers, large coherent effects for κ values corresponding to the peaks (largest for the first peak) in the $1+\Gamma(\kappa)$ curve; these effects, however, disappear for large values of the energy transfer.

IX. CONCLUSIONS

The main conclusion of the present paper is that our extension of Vineyard's convolution approximation seems to account reasonably well for the known experimental facts regarding the coherent scattering of slow neutrons by liquid argon. The results should be applicable to all coherent monatomic liquids. The interference effects in slow-neutron scattering are, as we have seen, the result of both the dynamical behavior and the typical geometrical arrangement of atoms in a liquid, and may indeed prove to be a very sensitive test of the theories of the liquid state. It should be borne in mind that the simple diffusion model adopted in this paper for $S_{\text{inc}}(\kappa,\omega)$ is valid for only small κ values. Extension of the present considerations to more complicated models for $S_{\text{inc}}(\kappa,\omega)$ can be easily made.

Future work ought to proceed in examining more critically the basic two assumptions outlined in Sec. III, and the significance and quantitative role of the parameter R introduced here. The present considerations must be regarded as only a first step towards understanding the finer details in coherent scattering of slow neutrons by a liquid. On the experimental side one would like to have a very precise study of the "quasi-elastic" scattering in some typical monatomic liquids for different κ values at small intervals and at different temperatures. Study of the coherent scattering in the critical region is no less interesting.

APPENDIX

Define

$$W(\kappa)=\int e^{i\kappa\cdot\mathbf{r}}g(\mathbf{r})\exp(-r^2/R^2)d\mathbf{r}$$

$$=\int e^{i\kappa\cdot\mathbf{r}}(g(\mathbf{r})-g_0)\exp(-r^2/R^2)d\mathbf{r}+g_0\int e^{i\kappa\cdot\mathbf{r}}\exp(-r^2/R^2)d\mathbf{r}, \tag{A1}$$

where g_0 is the value of $g(\mathbf{r})$ for $r\to\infty$. The parameter R would be of the order of a few interatomic distances. If $g(\mathbf{r})-g_0$ becomes small for $r<R$, we can expand the exponential $\exp(-r^2/R^2)$ in the first integral in (A1). Retaining terms of order $1/R^2$, we have

$$W(\kappa)=\Gamma(\kappa)-\frac{1}{R^2}\int\exp(i\kappa\cdot\mathbf{r})[g(\mathbf{r})-g_0]r^2d\mathbf{r}+g_0\int\exp(i\kappa\cdot\mathbf{r})\exp(-r^2/R^2)d\mathbf{r}, \tag{A2}$$

where

$$\Gamma(\kappa)=\int\exp i\kappa\cdot\mathbf{r}[g(\mathbf{r})-g_0]d\mathbf{r}, \tag{A3}$$

which depends only on the magnitude of κ.

From (A3) we have

$$\frac{1}{|\kappa|}\frac{\partial^2}{\partial\kappa^2}(\kappa\Gamma(\kappa))=-4\pi\int_0^\infty r^4\frac{\sin\kappa r}{\kappa r}[g(r)-g(0)]dr. \tag{A4}$$

Using (A4) and performing the second integral in (A2), we have

$$W(\kappa)=\Gamma(\kappa)+(1/|\kappa|R^2)[2\Gamma'(\kappa)+|\kappa|\Gamma''(\kappa)]+g_0\pi^{3/2}R^3\exp(-R^2|\kappa|^2/4). \tag{A5}$$

Similarly,

$$W(\kappa+\mathbf{q})=\Gamma(\kappa+\mathbf{q})+(1/|\kappa+\mathbf{q}|R^2)[2\Gamma'(\kappa+\mathbf{q})+|\kappa+\mathbf{q}|\Gamma''(\kappa+\mathbf{q})]+g_0\pi^{3/2}R^3\exp(-R^2|\kappa+\mathbf{q}|^2/4). \tag{A6}$$

Now

$$\Gamma(\kappa+\mathbf{q})-\Gamma(\kappa)=\sum_i q_i(\partial\Gamma(\kappa)/\partial\kappa_i)+\tfrac12\sum_{ij}q_iq_j(\partial^2\Gamma(\kappa)/\partial\kappa_i\partial\kappa_j)+\cdots, \tag{A7}$$

making a Taylor expansion and retaining terms of order q^2 only, or

$$\Gamma(\kappa+q)-\Gamma(\kappa)=\frac{(\mathbf{q}\cdot\mathbf{\kappa})}{|\kappa|}\frac{\partial\Gamma(\kappa)}{\partial\kappa}+\frac{1}{2}q^2\frac{1}{|\kappa|}\frac{\partial\Gamma(\kappa)}{\partial\kappa}-\frac{1}{2}\frac{1}{|\kappa|^3}(\mathbf{q}\cdot\mathbf{\kappa})^2\frac{\partial\Gamma(\kappa)}{\partial\kappa}+\frac{1}{2}(\mathbf{q}\cdot\mathbf{\kappa})^2\frac{1}{|\kappa|^2}\frac{\partial^2\Gamma(\kappa)}{\partial\kappa^2}.\tag{A8}$$

Performing the angular average over the directions of $\mathbf{q}$ for a given κ we have

$$\Gamma(\kappa+q)-\Gamma(\kappa)=\tfrac{1}{6}q^2[\Gamma''(\kappa)+(2/|\kappa|)\Gamma'(\kappa)]+\cdots.\tag{A9}$$

Similarly

$$\Gamma''(\kappa+q)+(2/|\kappa+q|)\Gamma'(\kappa+q)-\Gamma''(\kappa)-(2/|\kappa|)\Gamma'(\kappa)=\tfrac{1}{6}q^2[\Gamma''''(\kappa)+(4/|\kappa|)\Gamma'''(\kappa)]+\cdots.\tag{A10}$$

Using (A9) and (A10) we have from (A5) and (A6)

$$W(\kappa+q)-W(\kappa)=\tfrac{1}{6}q^2\left[\Gamma''(\kappa)+\frac{2}{|\kappa|}\Gamma'(\kappa)\right]+\frac{1}{6}\frac{q^2}{R^2}\left[\Gamma''''(\kappa)+\frac{4}{|\kappa|}\Gamma'''(\kappa)\right]+\cdots$$
$$+g_0\pi^{3/2}R^3[\exp(-\kappa^2R^2/4)]\{\exp(-R^2q^2/4)[\sinh(R^2\kappa q/2)/(R^2\kappa q/2)]-1\}.\tag{A11}$$

For large R it is the first term on the right-hand side of (A11) which is important. In the text we have used the approximation $R\rightarrow\infty$. Terms containing g_0 play a part only in the neighborhood of $\kappa\approx0$ and are, therefore, unimportant for our purpose. For finite values of R, an estimate of the correction is possible only if one has the knowledge of the higher derivatives of $\Gamma(\kappa)$, which for the present cannot be estimated from x-ray data with any reliability at all. We only hope that this correction is small for reasonable values of R. A very crude estimate shows that for $R\geqslant10$ Å (a distance roughly equal to twice the interatomic distance), and for q's of interest, the second term in (A11) is small compared to the first.

A somewhat better approach, but involving a lot of numerical work, would be not to expand the exponential in (A1). We outline this procedure below. We shall forget the second term in (A1) for the reason mentioned before. We write

$$W(\kappa)=\int\exp(i\mathbf{\kappa}\cdot\mathbf{r})[g(\mathbf{r})-g_0]\exp(-r^2/R^2).\tag{A12}$$

Using the convolution theorem of the Fourier transforms we have

$$W(\kappa)=\frac{1}{(2\pi)^3}\int\Gamma(\mathbf{k})F(\kappa-\mathbf{k})d\mathbf{k},\tag{A13}$$

where

$$F(\kappa-\mathbf{k})=\int e^{i(\kappa-\mathbf{k})\cdot\mathbf{r}}\exp(-r^2/R^2)d\mathbf{r}$$
$$=\pi^{3/2}R^3\exp[-|\kappa-\mathbf{k}|^2R^2/4].\tag{A14}$$

Using (A14) in (A13) and performing the angular integration we have

$$W(\kappa)=\frac{R}{2\sqrt{\pi}}\frac{1}{|\kappa|}\int_0^\infty k\Gamma(\mathbf{k})\left\{\exp\left[-\frac{R^2}{4}(\kappa-k)^2\right]-\exp\left[-\frac{R^2}{4}(\kappa+k)^2\right]\right\}dk.\tag{A15}$$

Similarly one can show in a straightforward manner that

$$\overline{W}(\kappa+q)=\frac{R}{2\sqrt{\pi}}\frac{1}{|\kappa|}\int_0^\infty k\Gamma(\mathbf{k})dk\frac{1}{2q}\int_{|k-q|}^{k+q}\{\exp[-R^2(t-k)^2/4]-\exp[-R^2(t+k)^2/4]\}dt,\tag{A16}$$

where the bar on $W(\kappa+q)$ denotes the average over the directions of $\mathbf{q}$. Hence,

$$\overline{W}(\kappa+q)-W(\kappa)=\frac{R}{2\sqrt{\pi}}\frac{1}{\kappa}\int_0^\infty k\Gamma(\mathbf{k})dk\frac{1}{2q}\int_{-q}^{+q}\left[\left\{\exp[-\tfrac{1}{4}R^2(\kappa-k+x)^2]\right.\right.$$
$$\left.-\exp[-\tfrac{1}{4}R^2(\kappa+k+x)^2]\right\}-\{\exp[-\tfrac{1}{4}R^2(\kappa-k)^2]-\exp[-\tfrac{1}{4}R^2(\kappa+k)^2]\}\left.\right]dx.\tag{A17}$$

$\Gamma(\mathbf{k})$ is known experimentally and hence (A17) can be numerically evaluated for a given $\varkappa$ for different q's using R as a parameter. No doubt formula (A17) is valid for all R, but if we follow the above procedure we no more have an explicit formula for the width. Even formula (A17) does not circumvent the difficulty of not knowing $\Gamma(\varkappa)$ very accurately. To see this we proceed to make some approximations.

$$\overline{W}(\varkappa+\mathbf{q})-W(\varkappa)\approx\frac{R}{2\sqrt{\pi}}\frac{1}{\varkappa}\int_0^\infty k\Gamma(k)dk\,\exp\left[-\frac{R^2}{4}(\varkappa-k)^2\right]\frac{1}{2q}\int_{-q}^{+q}\left\{\exp\left[-\frac{R^2}{4}[x^2+2(\varkappa-k)x]\right]-1\right\}dx. \quad \text{(A18)}$$

Expanding the exponential in the curly brackets and integrating we have

$$\overline{W}(\varkappa+\mathbf{q})-W(\varkappa)\approx\frac{R^3}{2\sqrt{\pi}}\frac{a^2}{\varkappa}\frac{1}{12}\int_0^\infty k\Gamma(k)\,\exp\left[-\frac{R^2}{4}(\varkappa-k)^2\right][\tfrac{1}{2}R^2(\varkappa-k)^2-1]dk, \quad \text{(A19)}$$

where we have retained terms up to order q^2 only. From a scrutiny of the integrand one sees the importance of the weighting factors. It is obvious that if the function $\Gamma(\varkappa)$ is not known accurately in the region of $\varkappa$ values where the function is rising rapidly, we would introduce a large error in the value of the integral. It is also clear that one obtains a large negative value for the integral for that value of $\varkappa$ for which there occurs a peak in $\Gamma(\varkappa)$. Detailed numerical computation would be justified when more accurate experimental data are available.

Theory of the Nuclear Magnetic Resonance Chemical Shift of Xe in Xenon Gas*

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A theoretical study is made of the density-proportional paramagnetic shift of the resonant magnetic field observed in nuclear magnetic resonance studies of Xe^{129} in pure xenon gas by Streever and Carr. The theory is based on a computation of the chemical shift in "diatomic molecules" formed by colliding Xe atoms, including the effects of van der Waals and exchange interactions on the wave function of the colliding atoms. The results of this calculation show that only the exchange interactions between the colliding atoms make a significant contribution to the chemical shift. When averaged over the various types of collisions, the following value is obtained for the shift in the resonant field: $\Delta H = -2.85(10)^{-7}H\rho$, where H is the field strength and ρ is the density in amagats. This is in order-of-magnitude agreement with the observed result: $\Delta H = -4.3(10)^{-7}\rho H$.

I. INTRODUCTION

NUCLEAR magnetic resonance studies of Xe^{129} ($I=\tfrac{1}{2}$) in pure xenon gas at high pressures have yielded two interesting and related results.[1,2] First, the spin-lattice relaxation time, although inversely proportional to the density of the gas as expected,[2] was much too short to be accounted for by the relaxation mechanism of magnetic dipole-dipole interactions between the nuclei of colliding atoms.[1] Secondly, there was a paramagnetic shift of the resonant value of the magnetic field, which was proportional to the density of the gas and to the magnetic field strength.

The relation between these results was established by Torrey,[3] who pointed out that in a diatomic molecule, which may be used as an approximate representation of a pair of colliding Xe atoms, Ramsey's theory of magnetic shielding connects the chemical shift and the nuclear-spin rotational coupling constant.[4] The nuclear-spin rotational coupling is a potential relaxation mechanism because it permits the nuclear spins to exchange angular momentum with the rotational momentum of the colliding atoms. Torrey showed that if one assumed that the observed shift in the resonant field was due to chemical shifts in "diatomic molecules" of colliding Xe atoms, and used the experimental value of the shift together with Ramsey's formula to determine the nuclear-spin rotational coupling constant, then one obtained a computed value for the Xe^{129} relaxation time which was in good agreement with experiment.

Therefore, the sole remaining task in connection with this problem is to compute the chemical shift expected for a pair of colliding Xe atoms as a function of separation, and to see whether such a shift averaged over all

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