$$B^{(+)}(s,t)=g_r^2\left(\frac{1}{m^2-s}+\frac{1}{m^2-\bar{s}}\right)$$

$$+\frac{1}{\pi}\int ds'\ \mathrm{Im}B^{(+)}(s',t)\left(\frac{1}{s'-s}-\frac{1}{s'-\bar{s}}\right),\quad(B6)$$

$$A^{(-)}(s,t)=\frac{1}{\pi}\int ds'\ \mathrm{Im}A^{(-)}(s',t)\left(\frac{1}{s'-s}-\frac{1}{s'-\bar{s}}\right),\quad(B7)$$

and

$$B^{(-)}(s,t)=g_r^2\left(\frac{1}{m^2-s}+\frac{1}{m^2-\bar{s}}\right)$$

$$+\frac{1}{\pi}\int ds'\ \mathrm{Im}B^{(-)}(s',t)\left(\frac{1}{s'-s}+\frac{1}{s'-\bar{s}}\right).\quad(B8)$$

Comparing these equations, it becomes clear that the subtraction is necessary only for the $A^{(+)}$ amplitude. This is the reason why the charge-exchange scattering amplitude was successfully explained.[2]

Evaluation of the Van Hove Correlation Functions for Certain Physical Systems*

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The space and time Fourier transforms of the Van Hove correlation function are evaluated for the cases of coherent scattering from simple crystals and, in a "quantum hydrodynamics" approximation, from liquid HeII. A compact approximate expression for the one-phonon part of the crystal correlation function transform is given, and the contribution of the two-phonon term is considered. A new method of obtaining quantum-mechanical corrections to the classical expression for the Van Hove self-correlation function is discussed.

I. INTRODUCTION

IT has been shown that the energy-transfer-dependent differential cross section for the coherent scattering of cold neutrons[1] or gamma rays[2] from an assembly of N identical atoms is given by

$$\frac{d^2\sigma}{d\Omega d\epsilon}=N\frac{d\sigma_A}{d\Omega}Z(\mathbf{q},\epsilon),$$

where

$$Z(\mathbf{q},\epsilon)\equiv\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\ \exp(-i\epsilon t)\Gamma(\mathbf{q},t)\quad(1)$$

and

$$\Gamma(\mathbf{q},t)$$

$$\equiv N^{-1}\left\langle\sum_{j=1}^{N}\exp[-i\mathbf{q}\cdot\mathbf{r}_j(0)]\sum_{j'=1}^{N}\exp[i\mathbf{q}\cdot\mathbf{r}_{j'}(t)]\right\rangle_T.\quad(2)$$

Here $d\sigma_A/d\Omega$ is the appropriate scattering cross section for a single atom, $\mathbf{q}$ is the momentum transfer of the scattered particle, ϵ is the initial energy of the scattered particle minus its final energy, and $\mathbf{r}_j(t)$ is

the Heisenberg position operator for the jth atom at time t. The operator $\langle\ \rangle_T$ denotes an ensemble average over the states of the target system at constant temperature T; thus we have

$$\langle O\rangle_T=\mathrm{Tr}[\exp(-2\beta H)O]/\mathrm{Tr}[\exp(-2\beta H)],\quad(3)$$

where O is any Heisenberg operator pertaining to the system, H is the system Hamiltonian, and

$$\beta\equiv1/2K_BT,$$

where K_B is the Boltzmann constant. Unless otherwise indicated, units with $\hbar=1$ will be used throughout this paper.

The evaluation of these functions and their counterparts for incoherent scattering has been undertaken by several authors[1-6]; the work of Van Hove[1] and Visscher[3] on crystals and of Vineyard,[4] Schofield,[5] and especially Rahman, Singwi, and Sjölander[6] on nearly classical fluids is of special interest here. We derive improved approximate expressions for $Z(\mathbf{q},\epsilon)$ and its three- and four-dimensional Fourier transforms for the cases of liquid HeII, idealized crystal lattices, and nearly classical fluids.

¹ L. Van Hove, Phys. Rev. 95, 249 (1954).
² K. S. Singwi and A. Sjölander, Phys. Rev. 120, 1093 (1960).
³ W. M. Visscher, Ann. Phys. (N. Y.) 9, 194 (1960).
⁴ G. H. Vineyard, Phys. Rev. 110, 999 (1958).
⁵ P. Schofield, Phys. Rev. Letters 4, 239 (1960).
⁶ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. 126, 986 (1962).

I. LIQUID HeII

The exact particle density function is

$$\rho(\mathbf{r},t) \equiv \sum_{j=1}^{N} \delta[\mathbf{r}-\mathbf{r}_j(t)]. \qquad (4)$$

Then from (2) and (4):

$$\Gamma(\mathbf{q},t) = N^{-1} \int\int d^3r\, d^3r'$$

$$\times \exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')]\langle\rho(\mathbf{r}',0)\rho(\mathbf{r},t)\rangle_T. \qquad (5)$$

From elementary "quantum hydrodynamics" arguments,[7] approximate representations for the particle density function $\bar{\rho}(\mathbf{r},t)$ and Hamiltonian $\tilde{H}$ may be obtained. In this model, there is a continuous fluid that sustains plane wave excitations of momentum $\mathbf{k}$ and energy $\omega(\mathbf{k})$. The expressions are

$$\bar{\rho}(\mathbf{r},t) = N/V + i(N/2MV^2)^{1/2}\sum_{\mathbf{k}} k[\omega(\mathbf{k})]^{-1/2}$$

$$\times [a_{\mathbf{k}}\exp\{i(\mathbf{k}\cdot\mathbf{r}-\omega(\mathbf{k})t)\}$$

$$-\text{Hermitian conjugate}], \qquad (6)$$

$$\tilde{H} = \tfrac{1}{2}\sum_{\mathbf{k}}\omega(\mathbf{k})(a_{\mathbf{k}}a_{\mathbf{k}}{}^\dagger + a_{\mathbf{k}}{}^\dagger a_{\mathbf{k}}), \qquad (7)$$

with

$$[a_{\mathbf{k}},a_{\mathbf{k}'}]=[a_{\mathbf{k}}{}^\dagger,a_{\mathbf{k}'}{}^\dagger]=0, \quad [a_{\mathbf{k}},a_{\mathbf{k}'}{}^\dagger]=\delta_{\mathbf{k}\mathbf{k}'}. \qquad (8)$$

Here V is the system volume, M is the particle mass, and $a_{\mathbf{k}}$ is an annihilation operator for an excitation of momentum $\mathbf{k}$.

By direct evaluation we find that

$$\langle\rho(\mathbf{r},t)\rangle_T = \langle\bar{\rho}(\mathbf{r},t)\rangle_T.$$

It is not so obvious, however, that the relation

$$\langle\rho(\mathbf{r}',0)\rho(\mathbf{r},t)\rangle_T \approx \langle\bar{\rho}(\mathbf{r}',0)\bar{\rho}(\mathbf{r},t)\rangle_T$$

is a reasonable approximation. On the other hand, this type of substitution has been fairly successful in other treatments of liquid HeII, and will be assumed here. This immediately gives

$$\Gamma(\mathbf{q},t) = \frac{q^2}{2M\omega(\mathbf{q})}\{\langle a_{\mathbf{q}}a_{\mathbf{q}}{}^\dagger\rangle_T \exp[i\omega(\mathbf{q})t]$$

$$+\langle a_{\mathbf{q}}{}^\dagger a_{\mathbf{q}}\rangle_T \exp[-i\omega(\mathbf{q})t]\}. \qquad (9)$$

Since $\langle a_{\mathbf{q}}{}^\dagger a_{\mathbf{q}}\rangle_T$ is the expectation value of the number operator for the excitation state of momentum $\mathbf{q}$, and the excitations obey Bose-Einstein statistics, we find that

$$\langle a_{\mathbf{q}}{}^\dagger a_{\mathbf{q}}\rangle_T = \tfrac{1}{2}\{\coth[\beta\omega(\mathbf{q})]-1\}. \qquad (10)$$

Upon using (8) and (10), we get

$$\langle a_{\mathbf{q}}a_{\mathbf{q}}{}^\dagger\rangle_T = \tfrac{1}{2}\{\coth[\beta\omega(\mathbf{q})]+1\}, \qquad (11)$$

which gives

$$\Gamma(\mathbf{q},t) = \frac{q^2}{2M\omega(\mathbf{q})}[\tfrac{1}{2}\{\coth[\beta\omega(\mathbf{q})]+1\}\exp[i\omega(\mathbf{q})t]$$

$$+\tfrac{1}{2}\{\coth[\beta\omega(\mathbf{q})]-1\}\exp[-i\omega(\mathbf{q})t]]. \qquad (12)$$

The $Z(\mathbf{q},\epsilon)$ corresponding to (12) is

$$Z(\mathbf{q},\epsilon) = \frac{q^2}{2M\omega(\mathbf{q})}\tfrac{1}{2}\{\coth[\beta\omega(\mathbf{q})]+\text{sgn}(\epsilon)\}$$

$$\times \delta[|\epsilon|-\omega(\mathbf{q})], \qquad (13)$$

where

$$\begin{aligned}\text{sgn}(x) &\equiv \;\;1, \quad x>0\\ &\equiv\;\;0, \quad x=0\\ &\equiv -1, \quad x<0.\end{aligned}$$

If $q^2/2M\omega(\mathbf{q})$ is replaced by its free-particle value of unity, the result for $Z(\mathbf{q},\epsilon)$ is just that for ideal He gas. This indicates that our results are quite crude, and that any support for the approximate validity of (13) must be of an empirical nature. Such a check could be obtained from measurements of the amplitude of the cross section integrated over energy transfers in the neighborhood of the peak indicated by (13).

III. SIMPLE CRYSTALS

A very general expression for $\Gamma(\mathbf{q},t)$ for the case of simple crystals has already been derived by Van Hove[1]; the expression he obtains is, however, somewhat complicated. We obtain a somewhat more transparent result for $\Gamma(\mathbf{q},t)$ and give simple approximations for the coherent part of $Z(\mathbf{q},\epsilon)$ corresponding to one-phonon processes. The contributions of the coherent second-order processes are also discussed. (The incoherent cases have been considered in detail by Visscher,[3] and will not be treated here.)

For completeness, we shall indicate the procedure of derivation starting from Eq. (2). The development follows the well-known approach of Zemach and Glauber[8] and Van Hove.[1] First, we make the normal mode expansion:

$$\mathbf{r}_j(t) = \mathbf{l}_j + \sum_{\lambda}\hat{\mathbf{e}}_{\lambda j}u_{\lambda j}(t), \qquad (14)$$

where $\mathbf{l}_j \equiv \langle\mathbf{r}_j(t)\rangle_T$ is the average position of the jth atom and $\hat{\mathbf{e}}_{\lambda j}$ and $u_{\lambda j}(t)$ are the direction (polarization) and amplitude of its displacement in the λth normal mode.

We shall need the exponential combination rule: If $[\alpha,[\alpha,\beta]]=[\beta,[\alpha,\beta]]=0$, then

$$\exp(\alpha)\exp(\beta) = \exp(\tfrac{1}{2}[\alpha,\beta])\exp(\alpha+\beta). \qquad (15)$$

We shall also make use of the Bloch theorem[9]: If L is a linear combination of harmonic oscillator displacements,

[7] K. R. Atkins, *Liquid Helium* (Cambridge University Press, New York, 1959), pp. 70–73.

[8] A. C. Zemach and R. J. Glauber, Phys. Rev. **101**, 118 (1956).
[9] F. Bloch, Z. Physik **74**, 295 (1932).

then

$$\langle \exp(L) \rangle_T = \exp(\tfrac{1}{2}\langle L^2 \rangle_T). \tag{16}$$

If we combine (2) and (14), and use (15) and (16), it is easy to show that

$$\Gamma(\mathbf{q},t) = N^{-1} \sum_{ii'} \exp(-i\mathbf{q}\cdot\mathbf{l}_{jj'})$$

$$\times \exp[-\tfrac{1}{2}\sum_{\lambda}\{(\mathbf{q}\cdot\hat{\mathbf{e}}_{\lambda j})^2 + (\mathbf{q}\cdot\hat{\mathbf{e}}_{\lambda j'})^2\}\langle u_{\lambda}{}^2(0)\rangle_T]$$

$$\times \exp[\sum_{\lambda}(\mathbf{q}\cdot\hat{\mathbf{e}}_{\lambda j})(\mathbf{q}\cdot\hat{\mathbf{e}}_{\lambda j'})\langle u_{\lambda j}(0)u_{\lambda j'}(t)\rangle_T], \tag{17}$$

where

$$\mathbf{l}_{jj'} \equiv \mathbf{l}_j - \mathbf{l}_{j'}$$

and

$$\langle u_{\lambda j}{}^2(0)\rangle_T \equiv \langle u_{\lambda}{}^2(0)\rangle_T.$$

A representation of the $u_{\lambda j}(t)$ is

$$u_{\lambda j}(t) = i(2NM)^{-1/2} \sum_{\mathbf{k}} [\omega_{\lambda}(\mathbf{k})]^{-1/2}$$

$$\times [a_{\lambda\mathbf{k}} \exp\{i[\mathbf{k}\cdot\mathbf{l}_j - \omega_{\lambda}(\mathbf{k})t]\} - \text{Hermitian conjugate}].$$

Here $a_{\lambda\mathbf{k}}$ is an annihilation operator for a phonon of momentum $\mathbf{k}$ and energy $\omega_{\lambda}(\mathbf{k})$ in the λth mode. The $a_{\lambda\mathbf{k}}$ satisfy the relations:

$$[a_{\lambda\mathbf{k}},a_{\lambda'\mathbf{k}'}] = [a_{\lambda\mathbf{k}}{}^{\dagger},a_{\lambda'\mathbf{k}'}{}^{\dagger}] = 0,$$

$$[a_{\lambda\mathbf{k}},a_{\lambda'\mathbf{k}'}{}^{\dagger}] = \delta_{\lambda\lambda'}\delta_{\mathbf{k}\mathbf{k}'}.$$

Upon using these expressions in (17) and noting that the phonon excitations corresponding to the operators $a_{\lambda\mathbf{k}}$ obey Bose-Einstein statistics, we obtain

$$\Gamma(\mathbf{q},t) = N^{-1} \sum_{ii'} \exp(-i\mathbf{q}\cdot\mathbf{l}_{jj'}) \exp\left\{-\tfrac{1}{2}\sum_{\lambda}\left[(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})^2\right.\right.$$

$$\left. + (\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})^2\right]\frac{1}{N}\sum_{\mathbf{k}}F_{\lambda}{}^0(\mathbf{k})\right\} \exp\left\{\sum_{\lambda}(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})\right.$$

$$\left. \times (\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})\frac{1}{N}\sum_{\mathbf{k}}[F_{\lambda jj'}{}^{+}(\mathbf{k})+F_{\lambda jj'}{}^{-}(\mathbf{k})]\right\}, \tag{18}$$

where

$$F_{\lambda}{}^0(\mathbf{k}) \equiv \frac{q^2}{2M\omega_{\lambda}(\mathbf{k})}\coth[\beta\omega_{\lambda}(\mathbf{k})],$$

$$F_{\lambda jj'}{}^{\pm}(\mathbf{k}) \equiv \frac{q^2}{2M\omega_{\lambda}(\mathbf{k})}\tfrac{1}{2}\{\coth[\beta\omega_{\lambda}(\mathbf{k})]\pm 1\}$$

$$\times \exp\{\mp i[\mathbf{k}\cdot\mathbf{l}_{jj'} - \omega_{\lambda}(\mathbf{k})t]\}. \tag{19}$$

This expression is a generalization of a result obtained by Schiff[10] in connection with the theory of bremsstrahlung from crystals.

If the process described by (18) is to be coherent, then the phases of all the terms in the sum over (j,j') must be the same, which implies that, in such a case, the

[10] L. I. Schiff, Phys. Rev. **117**, 1394 (196).

summand must be essentially independent of $\mathbf{l}_{jj'}$. The condition for this independence is just over-all momentum conservation. Equation (18) can now be rewritten:

$$\Gamma(\mathbf{q},t) = N^{-3} \sum_{ii'} \exp[-\tfrac{1}{2}\sum_{\lambda}\{(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})^2 + (\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})^2\}$$

$$\times \frac{1}{N}\sum_{\mathbf{k}}F_{\lambda}{}^0(\mathbf{k})] \sum_{JJ'} \exp(-i\mathbf{q}\cdot\mathbf{l}_{JJ'})$$

$$\times \exp[\sum_{\lambda}(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})$$

$$\times \frac{1}{N}\sum_{\mathbf{k}}\{F_{\lambda JJ'}{}^{+}(\mathbf{k})+F_{\lambda JJ'}{}^{-}(\mathbf{k})\}]. \tag{20}$$

Equation (20) is a rather formidable expression. It appears difficult to proceed much further in the evaluation of $\Gamma(\mathbf{q},t)$ for crystals without resorting to special cases and other approximations. Fortunately, the results of greatest interest are special cases which can be presented in fairly simple form.

If the third exponential term in (20) is expanded in a Taylor's series, the nth-order term will correspond only to n-phonon processes. For the moment, we confine our attention to the one-phonon processes, since they are the ones of greatest interest for the practical purpose of evaluating $\omega_{\lambda}(\mathbf{k})$. In this case, the scattering is effectively a two-body process, and $\omega_{\lambda}(\mathbf{k})$ can be obtained directly from the relation:

$$\omega_{\lambda}(\mathbf{q}) = |\epsilon|.$$

The one-phonon part of $\Gamma(\mathbf{q},t)$ is

$$\Gamma_1(\mathbf{q},t) = N^{-3} \sum_{\lambda}[\sum_{ii'}(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})\exp\{-\tfrac{1}{2}\sum_{\lambda'}[(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda' j})^2$$

$$+ (\hat{q}\cdot\hat{\mathbf{e}}_{\lambda' j'})^2]\frac{1}{N}\sum_{\mathbf{k}}F_{\lambda'}{}^0(\mathbf{k})\}][\sum_{JJ'}\exp(-i\mathbf{q}\cdot\mathbf{l}_{JJ'})$$

$$\times \frac{1}{N}\sum_{\mathbf{k}}\{F_{\lambda JJ'}{}^{+}(\mathbf{k})+F_{\lambda JJ'}{}^{-}(\mathbf{k})\}].$$

This leads to the following expression for $Z_1(\mathbf{q},\epsilon)$:

$$Z_1(\mathbf{q},\epsilon) = \frac{q^2}{2M|\epsilon|}\tfrac{1}{2}[\coth(\beta|\epsilon|)+\text{sgn}(\epsilon)]$$

$$\times \sum_{\lambda}\left[\frac{1}{N^2}\sum_{ii'}(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})\right.$$

$$\times \exp\left\{-\tfrac{1}{2}\sum_{\lambda'}[(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda' j})^2 + (\hat{q}\cdot\hat{\mathbf{e}}_{\lambda' j'})^2]\right.$$

$$\left.\left. \times \frac{1}{N}\sum_{\mathbf{k}}F_{\lambda'}{}^0(\mathbf{k})\right\}\right]\sum_{\mathbf{Q}}\delta[|\epsilon| - \omega_{\lambda}(\mathbf{q}-\mathbf{Q})], \tag{21}$$

where $\mathbf{Q}$ is a reciprocal lattice vector.

Equation (21) can be simplified further by making the Debye approximation in the argument of the exponential term. In many cases this exponential term, which is just the Debye-Waller factor, will be only slightly different from unity; when this is the case, this approximation should entail little error. We then obtain

$$Z_1(\mathbf{q},\epsilon) \approx \exp[-\gamma R(T/\Theta)]\frac{q^2}{2M|\epsilon|}\tfrac{1}{2}[\coth(\beta|\epsilon|)+\mathrm{sgn}(\epsilon)]$$

$$\times\sum_\lambda \frac{1}{N^2}\sum_{jj'}(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j})(\hat{q}\cdot\hat{\mathbf{e}}_{\lambda j'})\sum_Q \delta[|\epsilon|-\omega_\lambda(\mathbf{q}-\mathbf{Q})],$$

where Θ is the Debye temperature,

$$\gamma \equiv q^2/2MK_B\Theta$$

and

$$R(x) \equiv 3\int_0^1 t\coth(t/2x)dt.$$

For most purposes, the contributions of the higher order phonon processes to $Z(\mathbf{q},\epsilon)$ are dominated by the two-phonon term. We have evaluated $Z_2(\mathbf{q},\epsilon)$ in Debye approximation; the result is

$$Z_2(\mathbf{q},\epsilon) \approx \tfrac{1}{2}\exp[-\gamma R(\alpha)][\gamma R(\alpha)]^2(vq)^{-1}\theta\!\left(1-\frac{vq}{2K_B\Theta}\right)$$

$$\times\theta\!\left(1-\frac{|\epsilon|}{2K_B\Theta}\right)\tfrac{1}{2}[\coth(\beta|\epsilon|)+\mathrm{sgn}(\epsilon)]$$

$$\times\left[\frac{3\alpha}{R^2(\alpha)}\right]\!\left[\theta\!\left(\frac{|\epsilon|}{vq}-1\right)G_2\right.$$

$$\left.+\theta\!\left(1-\frac{vq+|\epsilon|}{2K_B\Theta}\right)(G_1-G_2)\right],$$

where

$$G_1 \equiv \ln\{\sinh[\tfrac{1}{2}\beta(|\epsilon|+vq)]\,\mathrm{csch}[\tfrac{1}{2}\beta(|\epsilon|-vq)]\},$$
$$G_2 \equiv \ln\{\sinh(1/2\alpha)\,\mathrm{csch}[\beta|\epsilon|-1/2\alpha]\}.$$

Here v is the speed of sound,

$$\alpha \equiv T/\Theta, \quad \theta(x) \equiv [1+\mathrm{sgn}(x)]/2,$$

and we have suppressed the reciprocal lattice vector sum.

In the limit of zero temperature, the background arising from two-phonon creation processes in the range of energy and momentum transfers corresponding to one-phonon excitations is

$$Z_2(\mathbf{q},\epsilon) \to \tfrac{3}{4}\gamma^2\exp(-\tfrac{3}{2}\gamma)\theta(\epsilon-vq)/(K_B\Theta),$$

which is independent of ϵ for $\epsilon > vq$.

IV. NEARLY CLASSICAL FLUIDS

Much of the theoretical work on cold neutron scattering from matter has concerned the evaluation

of the quantity:

$$\Gamma_s(\mathbf{q},t) \equiv N^{-1}\sum_{j=1}^N \langle\exp[-i\mathbf{q}\cdot\mathbf{r}_j(0)]\exp[i\mathbf{q}\cdot\mathbf{r}_j(t)]\rangle_T \quad (22)$$

and its corresponding Fourier transform $Z_s(\mathbf{q},\epsilon)$ for nearly classical fluids. To a great extent, this research has been concerned with the development of approximation techniques for the use of classical results to obtain $Z_s(\mathbf{q},\epsilon)$.[4,6] Two of the most fruitful of these approximations have been the Gaussian approximation[4] and the use of the Schofield theorem.[5]

The Gaussian approximation, proposed by Vineyard, is based on the observation that in several cases of physical interest $\Gamma_s(\mathbf{q},t)$ has the form:

$$\Gamma_s(\mathbf{q},t) = \exp[-\tfrac{1}{6}q^2 s(t)]. \quad (23)$$

Here $s(t)$ is a time-dependent width function, so that the Van Hove self-correlation function:

$$G_s(\mathbf{r},t) \equiv (2\pi)^{-3}\int d^3q\,\exp(-i\mathbf{q}\cdot\mathbf{r})\Gamma_s(\mathbf{q},t), \quad (24)$$

$$\lim_{\hbar\to0}G_s(\mathbf{r},t) = N^{-1}\sum_{j=1}^N \langle\delta\{\mathbf{r}-[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle_T \quad (25)$$

is a Gaussian function of the form:

$$G_s(\mathbf{r},t) = [\tfrac{2}{3}\pi s(t)]^{-3/2}\exp\left[-\frac{3}{2}\frac{r^2}{s(t)}\right]. \quad (26)$$

In this approximation, $s(t) = \int d^3r\, r^2 G_s(\mathbf{r},t)$.

For example, the exact result for a perfect gas is

$$s(t) = -3i\hbar M^{-1}t + 3K_B T M^{-1}t^2, \quad (27)$$

where M is the particle mass. Similarly, the form of $s(t)$ for the *classical* Langevin equation is

$$s(t) = (6K_B T/\eta^2 M)[\eta|t|-1+\exp(-\eta|t|)], \quad (28)$$

where η is the viscous damping coefficient.

Vineyard[4] suggested the direct substitution of classical forms of $s(t)$ into (23), but, as pointed out by Schofield,[5] this procedure leads to a result which fails to satisfy the detailed balance requirement, and implies zero momentum transfer. To remedy this difficulty, Schofield suggested the replacement of $G_s(\mathbf{r}, t+i\hbar\beta)$, which can be shown to be real,[5] by $G_s(\mathbf{r},t)|_{\text{classical}}$, and showed that this substitution satisfies the detailed balance requirement.

Two more recent papers give expressions for $G_s(\mathbf{r},t)$ which satisfy the detailed balance principle and take some of the recoil corrections into account. Aamodt et al.[11] obtain the expression:

$$Z_s(\mathbf{q},\epsilon) \approx \exp(\beta\epsilon)\exp(-\beta q^2/4M)Z_s(\mathbf{q},\epsilon)|_{\text{classical}}, \quad (29)$$

where $Z_s(\mathbf{q},\epsilon)|_{\text{classical}}$ is the four-dimensional Fourier transform of $G_s(\mathbf{r},t)|_{\text{classical}}$. In a paper by Rahman

[11] R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. 126, 1165 (1962).

et al.,[6] the generalized $s(t)$ function:

$$\frac{1}{6}s(t) \equiv \gamma_1(t) \equiv -\frac{i\hbar t}{2M} + \frac{1}{3}\int_0^t dt' \ (t-t')\langle \mathbf{v}(0)\cdot\mathbf{v}(t')\rangle_T, \quad (30)$$

where $\mathbf{v}(t)$ is the particle velocity operator, is first obtained. It is then used in the expression:

$$H_s(\mathbf{q},t) \equiv \Gamma_s(\mathbf{q},\ t+i\hbar\beta), \quad H_s(\mathbf{q},t) \approx \exp[-q^2\gamma_1(t+i\hbar\beta)],$$

which is substituted into the exact formula:

$$Z_s(\mathbf{q},\epsilon) = \exp(\beta\epsilon)\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt \ \exp\!\left(-\frac{i}{\hbar}\epsilon t\right)H_s(\mathbf{q},t). \quad (31)$$

We shall now derive quantum-mechanical corrections for $G_s(\mathbf{r},t)\vert_{\text{classical}}$ using an approach somewhat different from that of reference (6). Let V denote a smoothly-varying dimensionless parameter which vanishes when the coupling between the particles is zero, and let Δ be a similar dimensionless parameter which vanishes when $G_s(\mathbf{r},t)$ has the Gaussian form. For example, V might be a coupling constant while Δ might be the relative deviation of $G_s(\mathbf{r},t)$ from its best Gaussian fit. Imagine $G_s(\mathbf{r},t)$ to be expanded in the series:

$$G_s(\mathbf{r},t) \approx \sum_{m=0}^{\infty} (a_m + Vb_m + V\Delta c_m)\hbar^m. \quad (32)$$

The dimensions of $\hbar^m$ are to be compensated by appropriate combinations of $\hbar$-independent variables forming parts of the coefficients a_m, b_m, c_m. No terms proportional to Δ alone appear, since the expression obtained for zero interaction is already a Gaussian represented by the sum over the "a" terms. This series is only intended to be used as an aid in understanding different approximations to $G_s(\mathbf{r},t)$; it is of no value otherwise.

All the approximations presently made correspond to truncations of the series (32). Obviously, the Vineyard classical approximation has errors proportional to $\hbar$, while the original Schofield approximation has errors proportional to $\hbar^2$. On the other hand, the approximations given in references (6) and (11) yield the correct result in the limit of no interaction, and are certainly correct to zero order in $\hbar$; their errors are, thus, at worst proportional to $V\hbar$.

Since $G_s(\mathbf{r},\ t+i\hbar\beta)$ is real, and

$$G_s(\mathbf{r},t) = \exp[-i\hbar\beta\delta/\delta t]G_s(\mathbf{r},\ t+i\hbar\beta),$$

we have by inspection the Schofield relation.[5]

$$\text{Im}[G_s(\mathbf{r},t)] = -\tan(\hbar\beta\delta/\delta t)\ \text{Re}[G_s(\mathbf{r},t)].$$

If (26) is applicable, we can also write:

$$\text{Im}[s(t)] = -\tan(\hbar\beta\delta/\delta t)\text{Re}[s(t)].$$

We also note that the real parts of the correlation functions contain only even powers of $\hbar$, and that, for a perfect gas,

$$\text{Re}[s(t)] = s(t)\vert_{\text{classical}}.$$

Suppose for the moment that $G_s(\mathbf{r},t)$ has the Gaussian form. Then

$$\begin{aligned}
s(t) &= \text{Re}[s(t)] + i\ \text{Im}[s(t)], \\
&= [1 - i\ \tan(\hbar\beta\delta/\delta t)]\ \text{Re}[s(t)], \\
&= [1 - i\ \tan(\hbar\beta\delta/\delta t)]s(t)\vert_{\text{classical}} + O(V\hbar^2).
\end{aligned}$$

Our result is easily extended to include more general forms of $G_s(\mathbf{r},t)$. It is convenient to use $\Gamma_s(\mathbf{q},t)$ in the development of these expressions. We write

$$\begin{aligned}
\Gamma_s(\mathbf{q},t) &\approx \exp[-\tfrac{1}{6}q^2 s(t)], \\
&= \exp[\tfrac{1}{6}iq^2 \tan(\hbar\beta\delta/\delta t)\ \text{Re}\{s(t)\}]\exp[-\tfrac{1}{6}q^2\ \text{Re}\{s(t)\}], \\
&\approx \exp[\tfrac{1}{6}iq^2 \tan(\hbar\beta\delta/\delta t)s(t)\vert_{\text{classical}}] \\
&\qquad\qquad\qquad \times \exp[-\tfrac{1}{6}q^2 s(t)\vert_{\text{classical}}].
\end{aligned}$$

In addition, we have

$$\begin{aligned}
H_s(\mathbf{q},t) &\equiv \Gamma_s(\mathbf{q},\ t+i\hbar\beta), \\
&\approx \exp[\tfrac{1}{6}iq^2 \tan(\hbar\beta\delta/\delta t)\exp(i\hbar\beta\delta/\delta t)s(t)\vert_{\text{classical}}] \\
&\qquad \times \exp[-\tfrac{1}{6}q^2\exp(i\hbar\beta\delta/\delta t)s(t)\vert_{\text{classical}}], \\
&= \exp[-\tfrac{1}{6}q^2\{\sec(\hbar\beta\delta/\delta t) - 1\}s(t)\vert_{\text{classical}}] \\
&\qquad\qquad\qquad \times \exp[-\tfrac{1}{6}q^2 s(t)\vert_{\text{classical}}].
\end{aligned}$$

Define $\bar{s}(t)$ by:

$$\bar{s}(t) \equiv \int d^3r\ r^2 G_s(\mathbf{r},t)\vert_{\text{classical}}. \quad (33)$$

Then it is evident that the following approximations correspond to $G_s(\mathbf{r},t)$ functions having errors: $O(V\hbar^2) + O(V\Delta\hbar)$ and $O(V\hbar^2) + O(V\Delta\hbar^2)$, respectively.

$$\Gamma_s(\mathbf{q},t) \approx \exp\left[\frac{i}{6}q^2\hbar\beta\bar{s}'(t)\right]$$
$$\times \int d^3r\ \exp(i\mathbf{q}\cdot\mathbf{r})G_s(\mathbf{r},t)\vert_{\text{classical}}, \quad (34)$$

$$H_s(\mathbf{q},t) \approx \exp[-\tfrac{1}{12}q^2\hbar^2\beta^2\bar{s}''(t)]$$
$$\times \int d^3r\ \exp(i\mathbf{q}\cdot\mathbf{r})G_s(\mathbf{r},t)\vert_{\text{classical}}. \quad (35)$$

In the special case where $G_s(\mathbf{r},t)\vert_{\text{classical}}$ has the Gaussian form (26), we have the following simple approximations of error $O(\hbar^2 V)$:

$$\Gamma_s(\mathbf{q},t) \approx \exp[-\tfrac{1}{6}q^2\{\bar{s}(t) - i\hbar\beta\bar{s}'(t)\}], \quad (36)$$

$$H_s(\mathbf{q},t) \approx \exp[-\tfrac{1}{6}q^2\{\bar{s}(t) + \tfrac{1}{2}\hbar^2\beta^2\bar{s}''(t)\}]. \quad (37)$$

The expression (37) is not really new, for it can be derived easily from Eq. (77) of reference 6, which can be written in the form:

$$\gamma_1(t+i\hbar\beta) = \gamma_1(i\hbar\beta) + \frac{1}{3}\int_0^t dt' \ (t-t')\ \sec\!\left(\hbar\beta\frac{\partial}{\partial t'}\right)$$
$$\times \text{Re}[\langle\mathbf{v}(0)\cdot\mathbf{v}(t')\rangle_T].$$

(37) is not, however, equivalent to Eq. (81) of reference 6, which can be obtained by replacing $\bar{s}''(t)$ in (37) by its value for a perfect gas. The reason for this is that the derivation of (81) from (77) in reference 6 did not consistently take into account all the terms of order $\hbar^2$. For practical purposes the influence of terms $O(V\hbar^2)$ is negligible, and the improved results do not play an important role for classical fluids.

Let us apply (36) and (37) to the Langevin equation result (28) for $s(t)|_{\text{classical}}$. If we let $s(t)$ and $s(t+i\hbar\beta)$ denote the new forms of the width functions thus obtained, we find:

$$s(t) \approx (6K_BT/\eta^2M)[\eta|t| - 1 + \exp(-\eta|t|)]$$
$$- (3i\hbar/\eta M)[1 - \exp(-\eta|t|)]\operatorname{sgn}(t), \quad (38)$$

and

$$s(t+i\hbar\beta) \approx (6K_BT/\eta^2M)[\eta|t| - 1$$
$$+ \{1 + \tfrac{1}{2}(\hbar\eta/2K_BT)^2\} \exp(-\eta|t|)]. \quad (39)$$

The most general form of the Gaussian approximation admits just the kind of results we have obtained. To see this, we note that if the Gaussian result is exact, then

$$s(t) = \bar{s}(t) = -\nabla_q^2 \Gamma_s(\mathbf{q},t)|_{q=0},$$

$$= \langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle_T - \sum_{l=1}^{3} \langle[x_l(0),x_l(t)]\rangle_T,$$

$$= 2\int_0^t dt' \, (t-t')\langle\mathbf{v}(0)\cdot\mathbf{v}(t')\rangle_T$$

$$- \sum_{l=1}^{3} \int_0^t dt' \, \langle[x_l(0),v_l(t')]\rangle_T, \quad (40)$$

where x_l and v_l are components of the position and velocity operators, respectively. We have used the definition (2) of $\Gamma_s(\mathbf{q},t)$ to obtain the second line of this result from the first. Notice that this expression gives us:

$$s(t)|_{\text{classical}} = 2\int_0^t dt' \, (t-t')\langle\mathbf{v}(0)\cdot\mathbf{v}(t')\rangle_T|_{\text{classical}}$$

which is a result obtained in reference 6.

Now it is easy to show by using the invariance of $\langle\mathbf{v}(t)\cdot\mathbf{v}(t')\rangle_T$ under time translations that $2\int_0^t dt'(t-t')$ $\times\langle\mathbf{v}(0)\cdot\mathbf{v}(t')\rangle_T$ is even in time and is equal to $s(t)|_{\text{classical}}$ with error $O(V\hbar^2)$. Evidently (40) is in agreement with (36) if $\mathbf{v}(t)$ satisfies the "consistency condition":

$$\langle\mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T = -\frac{i}{\hbar}K_BT \sum_{l=1}^{3} \langle[x_l(0),v_l(t)]\rangle_T. \quad (41)$$

The solution of (41) is:

$$\mathbf{v}(t) = \mathbf{v}(0)f(t) + \mathbf{F}(t),$$

where $f(t)$ and $\mathbf{F}(t)$ are c numbers and $\mathbf{F}(t)$ is uncorrelated with $\mathbf{v}(0)$. This leads to $-3i\hbar M^{-1}K_BTf(t)$ for the "nonclassical" part of $s(t)$, which is exactly of the form we have found.

It is interesting to note that (38) is not actually a new result, but is equivalent to an expression derived by Vineyard[4] in 1958. His procedure involved the evaluation of $\Gamma_s(\mathbf{q},t)$ from first principles, treating the displacements $\mathbf{r}(t)$ as solutions of a "quantum-mechanical" Langevin differential equation involving the operator $\mathbf{v}(t)$. In view of (41), it is not strange that the final results should agree.

Unfortunately, the corrections we have obtained are very small for the cases of scattering for which many experimental data are available.[12,13] In any case where the perfect gas correction $q^2/8MK_BT$ is significant, however, the new factors may also be quite important, especially if the viscosity is reasonably large and the mass of the particles is low.

[12] See, for example, A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 997 (1962).
[13] B. N. Brockhouse and N. K. Pope, Phys. Rev. Letters **3**, 259 (1959).