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A DIFFUSIVE SLOW NEUTRON SCATTERING LAW

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A DIFFUSIVE SLOW NEUTRON SCATTERING LAW

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ABSTRACT

The diffusive center of mass motion of particles is derived by assuming that the particles are coupled to a heat bath by a dipole interaction. Both the particles and the bath are treated as quantum mechanical systems. The equations of motion are obtained by using a perturbation method which describes dissipative effects in quantum mechanics. The diffusive slow neutron scattering law for the center of mass motion of particles in a liquid is then derived in the incoherent approximation. The scattering law satisfies the principle of detailed balance and the zeroth and first energy transfer moment theorems. The scattering law is expressed as a series of incomplete gamma functions and is evaluated in that form.

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INTRODUCTION

The cross section for scattering of slow neutrons by a system of atoms depends only in a minor way on the actual interaction of a neutron with the individual atoms of the system; rather, the cross section depends primarily on the positions of the atoms and their motions within the structure of the system. If the scattering system is a gas, it is a reasonable approximation to assume that the center of mass motion of each molecule is completely free. For a crystalline solid the lowest order approximation is to regard the molecules as harmonically bound in a regular array. In the intermediate case of a liquid, the molecules may be imagined to move either singly or in clusters, but this motion is expected to be diffusive rather than free.

In the original work of Vineyard,[1] the diffusive motion of a molecule in a liquid is described by a Langevin equation. In this report diffusion is described by this same equation, but both the diffusing particle and the surrounding medium with which it interacts are treated as quantum mechanical systems.

$$m \frac{d^2 x_i}{dt^2} = - f \frac{dx_i}{dt} + F_i(t) \tag{1}$$

where the x_i are quantum mechanical operators that correspond to the coordinates of the particle, and the F_i are also operators which belong to the particle's environment. The friction coefficient f is given in terms of the diffusion coefficient D by the Einstein relation

$$f = \frac{T}{D} \tag{2}$$

where T is the temperature of the liquid in energy units.

In Equation (1) the liquid environment yields two forces:

(1) The first term on the right is a dissipative force. It is given in hydrodynamics by Stoke's law. Hydrodynamics treats the fluid medium as a continuum, and this force represents an average effect.

(2) The second term is a fluctuating force. It represents the instantaneous electric field which would exist at the position of the particle in the absence of the perturbing effect of the particle at that point. The dissipative force can be regarded as a reaction of the particle to its own effect on the surrounding liquid.

This report derives a slow neutron scattering law which corresponds to the diffusive center of mass motion of particles in a scattering system. All of the particles are assumed to have the same constitution. The internal degrees of freedom of the particles are considered to show how the center of mass contribution is separated out. The origin of the Langevin equation and the fluctuation-dissipation theorem which relates the two forces appearing in this equation is discussed in terms of a perturbation method introduced by Senitzky.[2] This discussion should clarify the physical assumptions made in describing the liquid.

The differential cross section for scattering of slow neutrons by an atomic system can be written[3,4]

$$\frac{d^2\sigma}{d\Omega dE} = \frac{1}{\hbar}\ \frac{k}{k_o}\ S(\underset{\sim}{\kappa},\omega) \tag{3}$$

where the Fourier transform* is defined as

$$S(\underset{\sim}{\kappa},\omega) = \frac{1}{2\pi}\sum_{\nu,\nu'}\left\langle a_\nu a_{\nu'}\right\rangle_{Av}\int_{-\infty}^{+\infty} e^{-i\omega t}\,\chi_{\nu\nu'}(\underset{\sim}{\kappa},t)\,dt \tag{4}$$

and the correlation function as

$$\chi_{\nu\nu'}(\underset{\sim}{\kappa},t) = \left\langle e^{i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_\nu(t+t')}\quad e^{-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}_{\nu'}(t')}\right\rangle_T \tag{5}$$

In these expressions, the quantity

$$\hbar\underset{\sim}{\kappa} = \hbar\ (\underset{\sim}{k} - \underset{\sim}{k}_o) \tag{6}$$

is the neutron momentum transfer, and

$$\hbar\omega = E - E_o \tag{7}$$

is the neutron energy transfer. The bound scattering length of the νth atom is denoted by a_ν, and $\underset{\sim}{r}_\nu(t)$ is the position operator of the νth atom in the Heisenberg representation. The scattering system is assumed to be in thermal equilibrium, and the symbol $\langle\qquad\rangle_T$ denotes an average over a thermal distribution of

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* For a discussion of the physical interpretation of $S(\underset{\sim}{\kappa},\omega)$, see Appendix A.

initial states. If correlations between the spins of different atomic nuclei of the scattering system are neglected, all orientations of these nuclear spins can be assumed to be equally probable in the initial state. Alternatively, the incident neutrons can be assumed to be unpolarized. In either case, the average products of scattering lengths in Equation (4) can be written as

$$\left\langle a_\nu a_{\nu'} \right\rangle_{Av} = A_\nu A_{\nu'} + C_\nu^2 \delta_{\nu\nu'} \qquad (8)$$

where A_ν and C_ν are the coherent and incoherent scattering lengths of the νth atom, respectively.

The position of the νth atom of a particle* (molecule or cluster) can be written as

$$\underset{\sim}{r}_\nu = \underset{\sim}{r} + \underset{\sim}{b}_\nu + \underset{\sim}{u}_\nu \qquad (9)$$

where $\underset{\sim}{r}$ is the position of the center of mass of the particle, $\underset{\sim}{b}_\nu$ is the equilibrium position of the atom relative to the center of mass, and $\underset{\sim}{u}_\nu$ is its displacement from equilibrium. The center of mass coordinates describe the translational motion of the particle as a whole. The vectors $\underset{\sim}{b}_\nu$ and $\underset{\sim}{u}_\nu$ describe rotational and vibrational motions, respectively. Isolation of the translational motion of a liquid particle from its other motions will be considered in the first section of the Discussion.

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* Henceforth the basic constituents of the liquid, whether they are molecules or clusters of molecules, will be called "particles."

SUMMARY

A general formalism of Van Hove,[3] and Zemach and Glauber[4] was used in this report to derive the slow neutron cross section for a monatomic liquid in the incoherent approximation. An electric dipole interaction was assumed for the particles of the liquid. The electric field experienced by a particle of the liquid was expanded to first order using a perturbation method introduced by Senitzky. This procedure yielded a Langevin equation of motion for a liquid particle in which the resistance (which is in general a function of frequency) was taken to be a constant. A fluctuation-dissipation theorem was derived for the liquid field, and the resistance was seen to be proportional to the photon spectrum of the field. The time correlation function, whose Fourier transformation gives the cross section, was determined in the Gaussian approximation by consistently applying Senitzky's perturbation treatment of the liquid field. The cross section was expressed in terms of dimensionless quantities in the form of a scattering law as defined by Egelstaff and Schofield.[5,6]

The width function which appears in the expression for the scattering law depends upon a frequency distribution $f(\omega)$ which characterizes the motion of a liquid particle. This distribution is determined by (but is not equal to) the photon spectrum of the surrounding environment. In the case of simple diffusion with constant resistance, this frequency distribution is a Lorentzian function. However, the diffusing-particle model does not restrict $f(\omega)$ to a Lorentzian form, because the only a priori condition on the photon spectrum $R(\omega)$ is that it be a real, positive function of frequency.

The scattering law was written as a series of incomplete gamma functions. Diffusive scattering laws based on classical width functions have been expressed in terms of incomplete gamma functions previously by Singwi and Sjolander[7] and by Gibbs and Ferziger.[8] In addition to the momentum and energy transfer parameters alpha and beta, the diffusive scattering law depends upon a resistance parameter λ. The computer code which was written to evaluate the scattering law is applicable only for values of λ which lie in a range between 0 and 2π (and not too close to either 0 or 2π). This range is adequate for water in the temperature range 0° to 100°C.

DISCUSSION

MOTION IN A LIQUID

The liquid environment of a particle is accounted for by assuming a dipole interaction of its atoms with a time-dependent electric field. This interaction is valid because the wavelengths represented in the field are all large compared with atomic dimensions. To obtain the form of the interaction, the dipole moment of a liquid particle is first considered. This moment consists of two terms; one associated with its equilibrium configuration, and the second due to elastic stretching.

$$\underset{\sim}{M} = \underset{\sim}{M}_o + \sum_{\nu} f_{\nu} \, \underset{\sim}{u}_{\nu} \tag{10}$$

A charge e_{ν} is associated with the νth atom such that

$$\underset{\sim}{M}_o = \sum_{\nu} e_{\nu} \, \underset{\sim}{b}_{\nu} \tag{11}$$

$$\sum_{\nu} e_{\nu} = 0 \tag{12}$$

Let $\underset{\sim}{E}_{\nu}(t)$ be the electric field at the νth atom. The ν-dependence of the field means that the field varies from atom to atom. However, all $\underset{\sim}{E}_{\nu}(t)$'s are assumed to have the same average properties in that they all represent the same field energy density. The interaction between the particle and the surrounding liquid is

$$V = \sum_{\nu} e_{\nu} \, \underset{\sim}{E}_{\nu} \cdot (\underset{\sim}{r} + \underset{\sim}{b}_{\nu}) + \sum_{\nu} f_{\nu} \, \underset{\sim}{E}_{\nu} \cdot \underset{\sim}{u}_{\nu} \tag{13}$$

The total Hamiltonian for the scattering system is then

$$H = H_p + H_B + V \tag{14}$$

where H_p is the Hamiltonian for the particle, H_B is the Hamiltonian for all the other particles of the system (which will be referred to as the "heat bath"), and V is the interaction between the one particle and the heat bath.

The Hamiltonian H_p can be written as the sum of two terms; one for the center of mass motion, and the second for the internal (rotational-vibrational) degrees of freedom. Similarly, Equation (13) can be separated into center of mass and internal terms.

Therefore, the correlation function Equation (5) can be written as a product

$$\chi_{\nu\nu'}(\underset{\sim}{\kappa},t) = \chi(\underset{\sim}{\kappa},t)\ \chi^{i}_{\nu\nu'}(\underset{\sim}{\kappa},t) \tag{15}$$

where the center of mass term is

$$\chi(\underset{\sim}{\kappa},t) = \left\langle e^{i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}(t+t')}\ e^{-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}(t')} \right\rangle_T \tag{16}$$

and the internal term is

$$\chi^{i}_{\nu\nu'}(\underset{\sim}{\kappa},t) = \left\langle e^{i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}^{i}_{\nu}(t+t')}\ e^{-i\underset{\sim}{\kappa}\cdot\underset{\sim}{r}^{i}_{\nu'}(t')} \right\rangle_T \tag{17}$$

where the internal coordinates are

$$\underset{\sim}{r}^{i}_{\nu} = \underset{\sim}{b}_{\nu} + \underset{\sim}{u}_{\nu} \tag{18}$$

By allowing the index ν to enumerate the atoms of a single liquid particle, coherent scattering by atoms belonging to different particles is effectively neglected, i.e., an incoherent approximation is made.

The following natural assumptions were made for the heat bath:

(1) In the absence of any perturbation, the heat bath has a uniform temperature.

(2) The influence that the single particle exerts on the heat bath is a small perturbation.

In contrast to assumption (2), the bath may have a considerable influence on the motion of the single particle. Therefore, in a perturbation expansion of the electric fields of the heat bath, the coordinates of the particle must appear in the Heisenberg (exact) representation, while the electric fields will appear in the interaction (unperturbed) representation. Furthermore, the first order term of the expansion will be averaged using a Boltzmann distribution of initial states for the heat bath. This is the essence of Senitzky's[2] perturbation method.

The interaction of the center of mass of the particle with the bath is

$$V_p = \underset{\sim}{E} \cdot \underset{\sim}{r} = \sum_{i=1}^{3} E_i \, x_i \qquad (19)$$

where

$$\underset{\approx}{E} = \sum_{\nu} e_\nu \, \underset{\sim}{E}_\nu \qquad (20)$$

Let a superscript (o) denote the interaction representation, and no superscript denote the Heisenberg representation. The connection between these representations is given by a unitary transformation

$$E_i(t) = U^{-1}(t) \; E_i^{(o)}(t) \; U(t) \qquad (21)$$

which satisfies the equation of motion

$$i\hbar \frac{dU}{dt} = V_p^{(o)} \; U \qquad (22)$$

A perturbation expansion of the electric field components can be generated by using the integral equation

$$E_i(t) = E_i^{(o)}(t) + \frac{1}{i\hbar} \sum_j \int_0^t U^{-1}(t_1) \left[E_i^{(o)}(t), \; E_j^{(o)}(t_1) \right]$$

$$\times \; U(t_1) \; x_j(t_1) \; dt_1 \qquad (23)$$

which follows from Equations (19), (21), and (22). The square bracket in this equation denotes a commutator of the enclosed field operators. With Equation (23) the field components can be approximated while leaving the particle coordinates in the Heisenberg representation. If the unitary operators are set equal to unity in Equation (23), the approximate equation is

$$E_i(t) \approx E_i^{(o)}(t) + \frac{1}{i\hbar} \sum_{j=1}^{3} \int_o^t \left[E_i^{(o)}(t), E_j^{(o)}(t_1)\right] x_j(t_1)dt_1 \quad (24)$$

To complete the approximation, the commutator in the first order term is replaced by its thermal average

$$E_i(t) \approx E_i^{(o)}(t) + \int_o^t B(t-t_1)\ x_i(t_1)dt_1 \qquad (25)$$

where

$$B(t-t_1)\ \delta_{ij} = \frac{1}{i\hbar} \left\langle \left[E_i^{(o)}(t), E_j^{(o)}(t_1)\right] \right\rangle_T \qquad (26)$$

The Kronecker delta symbol on the left side of Equation (26) means that the field is assumed to be isotropic and that different field components are not correlated. The unperturbed field can now be identified with the fluctuating force of Equation (1)

$$-E_i^{(o)} = F_i \qquad (27)$$

and the equation of motion for the particle takes the form

$$m\frac{d^2x_i}{dt^2} = F_i(t) - \int_o^t B(t-t_1)\ x_i(t_1)dt_1 \qquad (28)$$

The zeroth order (fluctuating) term in Equation (25) is not averaged because it represents the direct effect of the unperturbed heat bath. Its average value in an isotropic bath would be zero. In the next section, the function B(t) is related to the resistance of the liquid medium and this resistance is determined by the photon spectrum of the fluctuating electric field.

RESISTANCE AND THE PHOTON SPECTRUM

The resistance in the equation of motion (28) and also the photon spectrum of the unperturbed field may both be defined in terms of the spectral density of the field. Let the Fourier transform of the field be taken over a finite time interval $(-\tau, \tau)$

$$E_i^{(o)}(\omega) = \frac{1}{2\pi} \int_{-\tau}^{+\tau} E_i^{(o)}(t)\, e^{-i\omega t}\, dt \tag{29}$$

Because the field does not necessarily vanish for large times, its transform over an infinite interval will not in general exist. The spectral density matrix of the unperturbed field components is then

$$G_{ij}(\omega) = \lim_{\tau \to \infty} \frac{\pi}{\tau} \left\langle E_i^{(o)}(\omega)\, E_j^{(o)}(-\omega) \right\rangle_T \tag{30}$$

From this definition the Wiener-Khintchine[9,10,11] theorem can be established

$$\left\langle E_i^{(o)}(t+t')\, E_j^{(o)}(t') \right\rangle_T = \int_{-\infty}^{+\infty} G_{ij}(\omega)\, e^{i\omega t}\, d\omega \tag{31}$$

Equation (30) can also be used to derive the symmetry relation

$$G_{ji}(-\omega) = e^{\hbar\omega/T}\, G_{ij}(\omega) \tag{32}$$

and from this relation it follows that the averaged commutator of the fields is

$$\left\langle \left[E_i^{(o)}(t+t'),\, E_j^{(o)}(t') \right] \right\rangle_T = \int_{-\infty}^{+\infty} (1 - e^{\hbar\omega/T})\, G_{ij}(\omega)\, e^{i\omega t}\, d\omega \tag{33}$$

The resistance responsible for the dissipative effect of the heat bath is

$$R_{ij}(\omega) = \frac{\pi}{\hbar\omega} \left(e^{\hbar\omega/T} - 1\right) G_{ij}(\omega) \tag{34}$$

This resistance is related to the fluctuating field by the fluctuation-dissipation (Nyquist) theorem[12,13]

$$\left\langle \left\{ E_i^{(o)}(t+t'),\ E_j^{(o)}(t') \right\} \right\rangle_T = \frac{2}{\pi} \int_{-\infty}^{+\infty} R_{ij}(\omega)\ E(\omega,T)\ e^{i\omega t}\ d\omega \tag{35}$$

where the curled bracket denotes an anticommutator, and $E(\omega,T)$ is the average thermal energy of a harmonic oscillator with natural frequency ω,

$$E(\omega,T) = \frac{\hbar\omega}{2} \coth \frac{\hbar\omega}{2T} \tag{36}$$

A modified version of the theorem is

$$\left\langle E_i^{(o)}(t)\ E_j^{(o)}(t) \right\rangle_T = \frac{1}{\pi} \int_{-\infty}^{+\infty} R_{ij}(\omega)\left(E(\omega,T) - \frac{\hbar\omega}{2}\right) d\omega \tag{37}$$

which removes the zero point energy from $E(\omega,T)$. Equation (37) is a frequency analysis of the energy in the fluctuating field.

Because of the previous assumptions that the field is isotropic and that the fluctuations of different field components are uncorrelated

$$R_{ij}(\omega) = R(\omega)\ \delta_{ij} \tag{38}$$

The resistance $R(\omega)$ is proportional to the density of field oscillators in the frequency range $(\omega,\ \omega + d\omega)$. The Fourier transform of the function $B(t)$ defined by Equation (26) is given in terms of the resistance by

$$B(\omega) = \frac{1}{\pi}\ \omega\ R(\omega) \tag{39}$$

The resistance can be shown to be positive and an even function of ω. It follows that $B(t)$ is a real, odd function of t. The equation of motion (28) takes the form of the simple Langevin equation if

$$B(t) = f \frac{d}{dt} \left(\delta(t+\epsilon) + \delta(t-\epsilon) \right) \tag{40}$$

where f is the friction coefficient. The parameter ϵ gives the integral of Equation (28) an unambiguous meaning and is allowed to tend to zero after the integration. The resistance in this case is a constant

$$R(\omega) = f \tag{41}$$

which implies that the density of field oscillators is the same for all frequencies. This is sometimes referred to as a white spectrum.

THE CORRELATION FUNCTION

When the solution of Equation (1) is considered, the particle is assumed to have been in contact with the heat bath for essentially an infinite time so that transients associated with its motion have vanished. In that case the solution is

$$x_i = (x_i^o + \frac{1}{m\gamma} p_i^o) + \int_o^t A_i(t-t_1)\ g(t_1) dt_1 \tag{42}$$

where x_i^o and p_i^o are respectively, the initial position and momentum of the particle, and

$$\begin{aligned} \gamma &= f/m \\ A_i &= F_i/m \end{aligned} \tag{43}$$

In the integral of Equation (42) the following kernel function was introduced

$$g(t) = \frac{1}{\gamma} (1 - e^{-\gamma t}) \tag{44}$$

To evaluate the correlation function Equation (16), use the relation

$$e^P e^Q = e^{P + Q + \frac{1}{2} [P,Q]} \tag{45}$$

where P and Q are operators which commute with their commutator. In this case

$$P = i\underset{\sim}{\kappa} \cdot \underset{\sim}{r}\ (t+t') \tag{46}$$

$$Q = -i\underset{\sim}{\kappa} \cdot \underset{\sim}{r}\ (t') \tag{47}$$

and the desired commutator is

$$\begin{aligned} \frac{1}{2} [P,Q] = \frac{1}{2} \sum_{i,j=1}^{3} \kappa_i \kappa_j \int_o^{t+t'} \int_o^{t'} \Big[A_i(t+t'-t_1), A_j(t'-t_2)\Big] \\ \times\ g(t_1) g(t_2) dt_1 dt_2 \end{aligned} \tag{48}$$

Equation (48), as it stands, is not expected to commute with P or Q. The equation of motion (1) was derived by averaging the commutator of the fields. Expressions for the coordinate and momentum operators of the particle contain the effect of this average, and they satisfy the correct commutation relations only if products of the field components are averaged whenever they appear.* It is therefore consistent with the approximate treatment of the heat bath to perform a thermal average of the commutator of the fields which appears in Equation (48) by using Equations (26) and (40).

$$\frac{1}{2}\left\langle\left[P,Q\right]\right\rangle_T = \pm\frac{\hbar\kappa^2}{2im}\,g(|t|) \tag{49}$$

where the plus sign is used if t is positive, and the minus sign if t is negative. The Fourier integral representation of this commutator

$$\frac{1}{2}\left\langle\left[P,Q\right]\right\rangle_T = \frac{\hbar\kappa^2}{2im}\int_{-\infty}^{+\infty}\frac{f(\omega)}{\omega}\sin\omega t\,d\omega \tag{50}$$

will be used, where the Lorentzian function $f(\omega)$ is

$$f(\omega) = \frac{\gamma}{\pi}\frac{1}{(\omega^2+\gamma^2)} \tag{51}$$

which is normalized to unity.

Now consider the exponential of the sum P + Q. If the average value of the fluctuating field is zero, the first order expansion is

$$e^{P+Q} \approx 1 - \sum_{i,j=1}^{3}\kappa_i\kappa_j\left[T_{ij}(t+t',t+t') + T_{ij}(t',t') - 2\,T_{ij}(t+t',t')\right] \tag{52}$$

where

$$T_{ij}(\tau_1,\tau_2) = \frac{1}{4}\int_0^{\tau_1}\!\!\int_0^{\tau_2}\left\langle\left\{A_i(\tau_1-t_1),A_j(\tau_2-t_2)\right\}\right\rangle_T g(t_1)g(t_2)\,dt_1dt_2 \tag{53}$$

Here the anticommutators of the fields have been averaged in keeping with the general treatment of the heat bath. This average is given by Equation (35). The result for a constant resistance is

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* For a discussion of the commutation relations between the coordinate and momentum operators of the particle, see Appendix B.

$$\frac{1}{4}\sum_{i,j}\kappa_i\kappa_j\left\langle\left\{A_i(t+t'),A_j(t')\right\}\right\rangle_T = \frac{\gamma\kappa^2}{2\pi m}\int_{-\infty}^{+\infty} E(\omega,T)\; e^{i\omega t}\, d\omega \qquad (54)$$

When the integrals over t_1 and t_2 in Equation (52) are evaluated, the limit as t' tends to infinity is taken to give the first order result.

$$e^{P + Q} \approx 1 - \frac{\kappa^2}{m}\int_{-\infty}^{+\infty} E(\omega,T)\,\frac{f(\omega)}{\omega^2}\,(1 - \cos\omega t)\, d\omega \qquad (55)$$

In the perturbation treatment of the heat bath, the products of two components of the unperturbed field have been accounted for but not products of three or more. Therefore, the expansion Equation (55) cannot be extended by direct calculation without introducing some conventions for performing averages of these higher order products. Instead of introducing such conventions, the complete expansion is assumed to be represented by the Gaussian function

$$e^{P + Q} = e^{-\frac{\kappa^2}{2}\Gamma_c(t)} \qquad (56)$$

This procedure is suggested by the form that the correlation function takes when the scattering system is a gas or a polycrystalline material. In particular, it is consistent with the isotropy property which a liquid shares with these other systems. The first two terms of the expansion imply

$$\Gamma_c(t) = \frac{2}{m}\int_{-\infty}^{+\infty} E(\omega,T)\,\frac{f(\omega)}{\omega^2}\,(1 - \cos\omega t)\, d\omega \qquad (57)$$

By combining Equation (57) with the result of Equation (50), the complete correlation function Equation (16) can now be written in the Gaussian form

$$\chi(t) = e^{-\frac{\kappa^2}{2}\Gamma(t)} \qquad (58)$$

where the dispersion is

$$\Gamma(t) = \frac{\hbar}{m}\int_{-\infty}^{+\infty}\frac{f(\omega)}{\omega}\left[i\sin\omega t + \coth\frac{\hbar\omega}{2T}\,(1 - \cos\omega t)\right] d\omega \qquad (59)$$

This dispersion has the same form as the dispersion function for a crystal, where $f(\omega)$ takes the place of the phonon spectrum. It also gives the ideal gas dispersion when $f(\omega)$ is replaced by a delta function.

THE SCATTERING LAW AND WIDTH FUNCTION

The differential cross section for scattering of slow neutrons by a monatomic liquid has the form of Equation (3). Under the conditions of the foregoing argument the Fourier transform in Equation (3) is now given by

$$S(\underset{\sim}{\kappa},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}\, e^{-\frac{\kappa^2}{2}\Gamma(t)}\, dt \qquad (60)$$

It is desirable to express this in terms of dimensionless parameters

$$\alpha = \frac{\hbar^2\kappa^2}{2mT}$$
$$\beta = \frac{\hbar\omega}{T} \qquad (61)$$

The standard form of this transform introduced by Egelstaff and Schofield is[5,6]

$$S(\underset{\sim}{\kappa},\omega) = \frac{\hbar}{T}\, e^{-\frac{1}{2}\beta}\, \tilde{S}(\alpha,\beta) \qquad (62)$$

where

$$\tilde{S}(\alpha,\beta) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\beta t}\, e^{-\alpha W(t)}\, dt \qquad (63)$$

is called the "scattering law." The width function in Equation (63) is obtained by the transformation

$$W(t) = \frac{mT}{\hbar^2}\,\Gamma\left(\frac{\hbar t}{T} - \frac{i\hbar}{2T}\right) \qquad (64)$$

and depends upon a dimensionless time parameter, t. From Equation (59) the integral representation of the width function is found

$$W(t) = \int_0^{\infty} \frac{\rho(\beta)}{\beta}\left[\coth \beta/2 - \frac{\cos \beta t}{\sinh \beta/2}\right] d\beta \qquad (65)$$

The dimensionless distribution function $\rho(\beta)$ in this expression is obtained from $f(\omega)$ and is the Lorentzian function

$$\rho(\beta) = \frac{2\lambda}{\pi} \frac{1}{(\beta^2 + \lambda^2)} \tag{66}$$

with half width

$$\lambda = \frac{\hbar\gamma}{T} = \frac{\hbar}{mD} \tag{67}$$

The dimensionless resistance parameter λ is the only experimentally determined quantity which enters into the present theory.

Egelstaff and Schofield[5,6] point out that the function $W(t)$ has three simple properties which can be related to properties of the scattering law. First, it is a real, even function of t. This implies that the scattering law is a real, even function of β, which, in turn, means that the cross section satisfies the principle of detailed balance. According to this principle, if a gas of neutrons is in thermal equilibrium with the liquid, then the number of neutrons scattered out of a given range of momentum states equals the number scattered into the same range. The other two properties are given by

$$W(i/2) = 0 \tag{68}$$

$$\frac{dW(i/2)}{dt} = i \tag{69}$$

These properties imply that the scattering law satisfies the two moment theorems

$$\int_{-\infty}^{+\infty} \tilde{S}(\alpha,\beta) \cosh \beta/2 \, d\beta = 1 \tag{70}$$

$$\int_{-\infty}^{+\infty} \tilde{S}(\alpha,\beta) \, \beta \sinh \beta/2 \, d\beta = \alpha \tag{71}$$

Equation (70) may be regarded as a normalization condition for the probability function $S(\kappa,\omega)$, whose interpretation is discussed in Appendix A. The first moment Equation (71) shows that the average energy exchange in a scattering process is the same as that which would occur if the system consisted of free, initially stationary particles.

EVALUATION OF THE SCATTERING LAW

To evaluate the scattering law, Equation (65) is integrated to give

$$W(t) = a + \frac{2}{\lambda} |t| + \frac{\csc \lambda/2}{\lambda} e^{-\lambda|t|} + \sum_{m=1}^{\infty} a_m e^{-2\pi m|t|} \qquad (72)$$

where the constant term a is

$$a = -\frac{2}{\lambda^2} + 2 \sum_{n=1}^{\infty} \frac{1}{(\pi n)(2\pi n + \lambda)} \qquad (73)$$

and the coefficients in the series term are

$$a_m = \frac{(-1)^m}{m\pi} \frac{2\lambda}{(4\pi^2 m^2 - \lambda^2)} \qquad (m = 1, 2, 3, \ldots) \qquad (74)$$

Expression (72) presupposes that λ does not equal $2\pi n$, n = 0, 1, 2, ... For these isolated values the integrand of Equation (65) has a double pole, and the width function assumes a different form. Figure 1 is a comparison of Equation (72) for λ equal to $\pi/2$ and for λ equal to zero the free gas width. The free gas width is

$$W_{fg}(t) = t^2 + \frac{1}{4} \qquad (\lambda = 0) \qquad (75)$$

whereas the long time behavior of the diffusive width is given by a linear function of t.

When Equation (72) is substituted into Equation (63), the result can be written as

$$\tilde{S}(\alpha,\beta) = \frac{e^{-v}}{\pi\lambda} \operatorname{Re}\left\{ \int_0^{\infty} \exp\left(-sz - ue^{-z} - \sum_{m=1}^{\infty} v_m e^{-m\eta z}\right) dz \right\} (76)$$

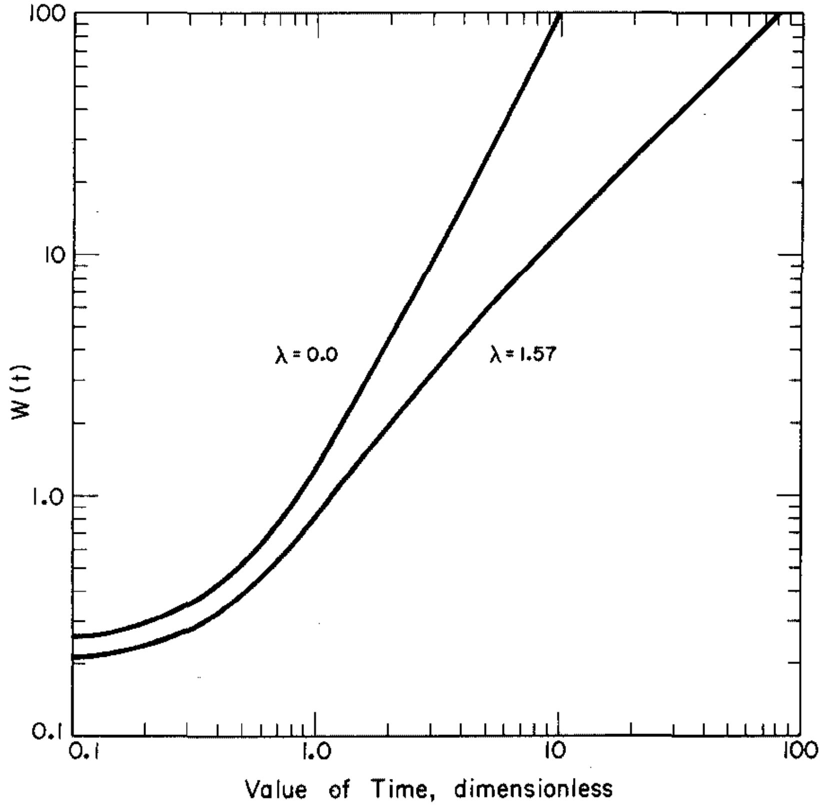

FIG. 1 WIDTH FUNCTION W(t) FOR λ = 0.0 (THE FREE GAS CASE) AND FOR λ = 1.57

where z is equal to λt, the real parameters are

$$u = \frac{\csc \lambda/2}{\lambda}\,\alpha \qquad v = a\alpha \tag{77}$$

$$v_m = a_m\alpha \qquad (m = 1, 2, 3, \ldots) \tag{78}$$

the complex parameter is

$$s = p + iq = \frac{2\alpha}{\lambda^2} + \frac{i\beta}{\lambda} \tag{79}$$

and the number is

$$\eta = \frac{2\pi}{\lambda} \tag{80}$$

The integration of Equation (76) can be written as the multiple series

$$\tilde{S}(\alpha,\beta) = \frac{1}{\pi\lambda} e^{-v} \sum_{N=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots\cdots \frac{(-1)^{N + n_1 + n_2 + \cdots}}{N!\ n_1!\ n_2!\ \cdots} \tag{81}$$

$$\times\ u^N v_1^{n_1} v_2^{n_2} \cdots \frac{[p + N + \eta(n_1 + 2n_2 + 3n_3 + \ldots)]}{[p + N + \eta(n_1 + 2n_2 + 3n_3 + \ldots)]^2 + q^2}$$

Equation (81) can be further arranged to take the form

$$\tilde{S}(\alpha,\beta) = \frac{1}{\pi\lambda} e^{-v} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{n_1} \sum_{n_3=0}^{n_2} \cdots \frac{(-1)^{n_1}}{(n_1 - n_2)!(n_2 - n_3)!\ \cdots} \tag{82}$$

$$\times\ v_1^{n_1} X_2^{n_2} X_3^{n_3} \cdots \sum_{N=0}^{\infty} \frac{(-1)^N u^N [p + N + \eta\ (n_1 + n_2 + \ldots)]}{N!\ ([p + N + \eta\ (n_1 + n_2 + \ldots)]^2 + q^2)}$$

where

$$X_m = v_m/v_{m-1} \qquad (m = 2, 3, \ldots) \tag{83}$$

and the ratios depend only on λ. To combine the terms of Equation (82) which satisfy

$$n_1 + n_2 + n_3 + \ldots = k \tag{84}$$

coefficients are defined as

$$C(k) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{n_1} \sum_{n_3=0}^{n_2} \cdots (-1)^{n_1} \tag{85}$$

$$\times\ \frac{v_1^{n_1} X_2^{n_2} X_3^{n_3} \cdots X_k^{n_k}}{(n_1 - n_2)!(n_2 - n_3)!\ \cdots\ n_k!}\ \delta k, n_1 + n_2 + \ldots + n_k$$

where the Kronecker delta symbol imposes the requirement of Equation (84). Note, the sum over N in Equation (82) can be written in closed form as

$$\sum_{N=o}^{\infty} \frac{(-1)^N u^N}{N!} \frac{[p + N + \eta k]}{[p + N + \eta k]^2 + q^2} = \mathrm{Re} \left\{ u^{-\sigma(k)} \gamma(\sigma(k),u) \right\} \quad (86)$$

where $\gamma\ (\sigma,u)$ is the incomplete gamma function with argument

$$\sigma(k) = s + \eta k \quad (87)$$

Figure 2 shows λ as a function of temperature for H_2O. This curve was obtained by assuming that the basic constituents of the liquid are single H_2O molecules so that m used in Equation (67) is the mass of a water molecule. The self-diffusion coefficients used are those given by Simpson and Carr.[14] The following discussion assumes that λ lies in the neighborhood of this range of values.

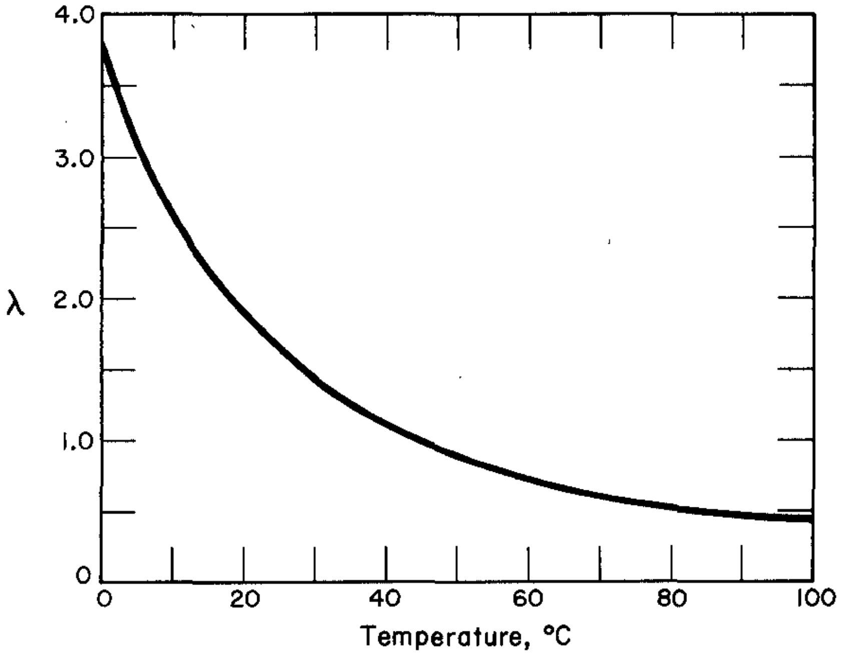

FIG. 2 VALUE OF $\lambda = \frac{\hbar}{mD}$ FOR H_2O

The numerical evaluation of the left side of Equation (86) was found to present an accuracy problem when u is large because in that case $u^N/N!$ increases initially as N increases and may become large even though the value of the total series is a relatively small number. This results in a loss of significant figures or a breakdown of the evaluation. A more satisfactory method of evaluation is to write the incomplete gamma function as

$$\gamma(\sigma,u) = u^{\sigma} e^{-u} \sum_{N=0}^{\infty} \frac{\Gamma(\sigma)}{\Gamma(\sigma + N + 1)} u^N \tag{88}$$

The scattering law then takes the final form

$$\tilde{S}(\alpha,\beta) = e^{-(u + v)} \sum_{k=0}^{\infty} C(k)\ G(k) \tag{89}$$

where

$$G(k) = \frac{1}{\pi\lambda} \operatorname{Re} \left\{ \sum_{N=0}^{\infty} \frac{\Gamma(\sigma\ (k))}{\Gamma(\sigma\ (k) + N + 1)} u^N \right\} \tag{90}$$

A FORTRAN code was written for the IBM 360 computer to evaluate the scattering law in this form for the values of λ shown in Figure 2. Figure 3 shows the diffusive scattering law evaluated for λ equal to $\pi/2$, which corresponds to a water temperature of 27°C. The dotted line in this figure shows the free gas law, which corresponds to λ equal to zero, for alpha equal to one. Figure 4 is a plot of the scattering law versus alpha for λ equal to $\pi/2$ and zero. The curve in general peaks in the neighborhood of alpha equal to beta when plotted for a fixed value of beta. For elastic scattering (beta equal to zero), the diffusive scattering law has a $1/\alpha$ singularity in contrast to the $1/\alpha^{\frac{1}{2}}$ singularity of the gas law. About 30 minutes was required to compute the scattering law for fifty values of alpha from 0 to 50 and twenty values of beta from 0 to 12. The magnitude of beta is limited by the time required to compute an increasing number of the coefficients C(K) as beta increases.

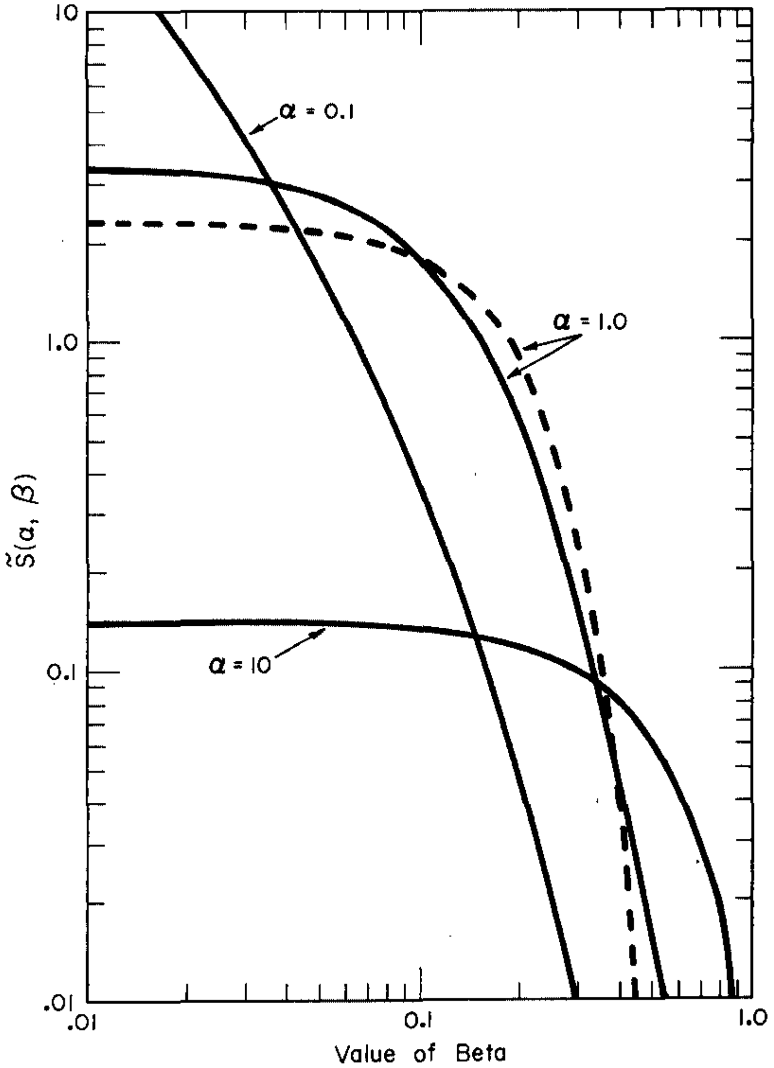

FIG. 3 DIFFUSIVE SCATTERING LAW FOR λ = 1.57
(Dotted Line is the Gas Law for α = 1.0)

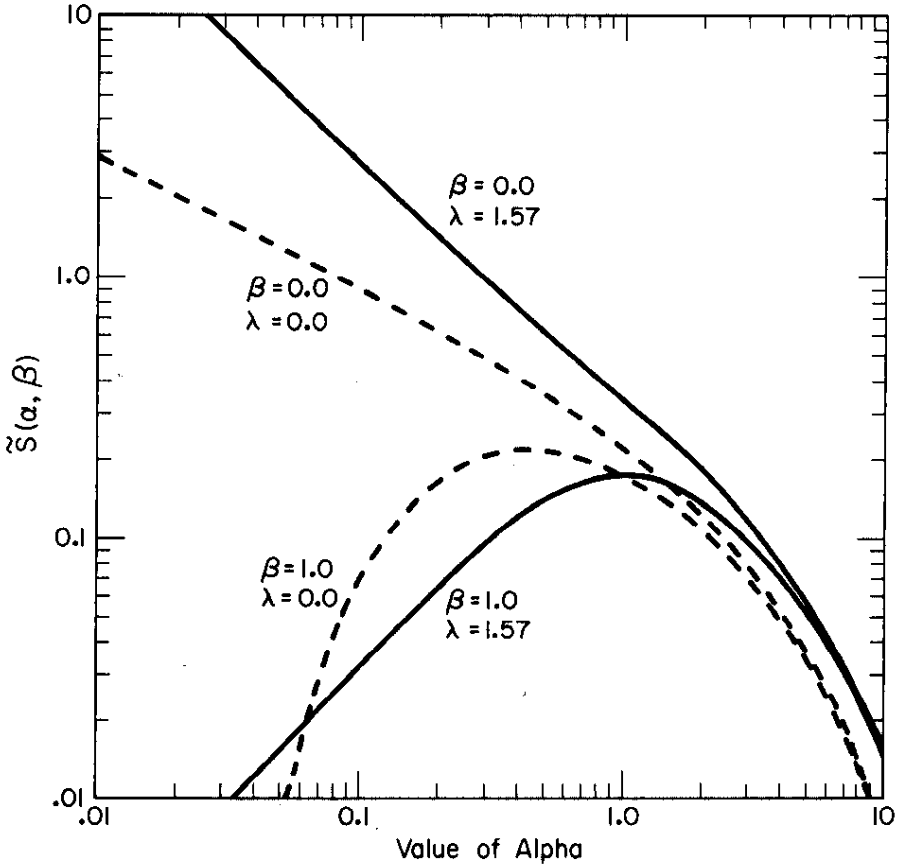

FIG. 4 TEMPERATURE DEPENDENCE OF $\tilde{S}(\alpha,\beta)$ FOR $\beta = 0.0$ AND $\beta = 1.0$

APPENDIX A

The function $S(\underset{\sim}{\kappa},\omega)$ is interpreted as being proportional to the probability that a neutron energy change $\hbar\omega$ will be in the range $(\omega, \omega + d\omega)$ if the neutron momentum change is $\hbar\kappa$. For a given neutron momentum change, the amplitude for the scattering system to make an energy transition from E_n to $E_{n'}$ is

$$\text{ampl.} = \sum_{\nu=1}^{N} a_\nu \left\langle n \middle| e^{i\underset{\sim}{\kappa} \cdot \underset{\sim}{r}_\nu} \middle| n' \right\rangle \tag{A1}$$

where N is the number of atoms in the scattering system (in our case the atoms of a single liquid particle), and a_ν and $\underset{\sim}{r}_\nu$ are the scattering length and position operator of the νth atom. The probability that the scattering system makes this energy change when the neutron is scattered is proportional to the quantity

$$P_n |\text{ampl.}|^2 \tag{A2}$$

where P_n is the probability that the system has the initial energy E_n. The sum of all such probabilities which are consistent with the energy conservation equation

$$\hbar\omega = E_n - E_{n'} \tag{A3}$$

gives the function $S(\underset{\sim}{\kappa},\omega)$, i.e.

$$\begin{aligned} \frac{1}{\hbar} S(\underset{\sim}{\kappa},\omega) &= \sum_{n,n'} P_n \sum_{\nu,\nu'} \left\langle a_\nu a_{\nu'} \right\rangle_{Av} \\ &\times \left\langle n \middle| e^{i\underset{\sim}{\kappa} \cdot \underset{\sim}{r}_\nu} \middle| n' \right\rangle \left\langle n' \middle| e^{-i\underset{\sim}{\kappa} \cdot \underset{\sim}{r}_{\nu'}} \middle| n \right\rangle \delta(\hbar\omega + E_{n'} - E_n) \end{aligned} \tag{A4}$$

Equation (4) is obtained from Equation (A4) by using the Fourier integral representation of the delta function.

APPENDIX B

The complete solution of differential Equation (28) for an arbitrary B(t) is

$$x_i(t) = x_i^o \frac{dg(t)}{dt} + \frac{1}{m} p_i^o \, g(t) - \frac{1}{m} \int_o^t g(t-t_1) \, E_i^{(o)}(t_1) \, dt_1 \quad \text{(B1)}$$

where the kernel g(t) is the solution of the corresponding homogeneous differential equation

$$m \frac{d^2 g}{dt^2} + \int_o^t B(t-t_1) \, g(t_1) \, dt_1 = 0 \quad \text{(B2)}$$

for the initial data

$$g(o) = 0; \qquad \frac{dg}{dt}(0) = 1 \quad \text{(B3)}$$

The commutators of position and momentum operators are therefore given by

$$\begin{aligned} \left[x_i(t), \, p_j(t)\right] &= \delta_{ij} \, i\hbar \left[\left(\frac{dg}{dt}\right)^2 - g \cdot \frac{d^2 g}{dt^2}\right] \\ &+ \frac{1}{m} \int_o^t \int_o^t \frac{dg}{dt}(t-t_1) \, g(t-t_2) \left[E_i^{(o)}(t_1), E_j^{(o)}(t_2)\right] dt_1 dt_2 \end{aligned} \quad \text{(B4)}$$

This expression already contains the effect of averaging the commutator of the fields which occurs in the equation of motion. If the commutator of fields which appears here is similarly averaged

$$\begin{aligned} \left\langle \left[x_i(t), \, p_j(t)\right] \right\rangle_T &= \delta_{ij} \, i\hbar \left[\left(\frac{dg}{dt}\right)^2 - g \, \frac{d^2 g}{dt^2}\right] \\ &+ \delta_{ij} \frac{i\hbar}{m} \int_o^t \int_o^t \frac{dg}{dt}(t_1) \, g(t_2) \, B(t_1 - t_2) \, dt_1 dt_2 \end{aligned} \quad \text{(B5)}$$

When the equation of motion for g(t) is substituted into Equation (B5), it reduces to the form

$$\left\langle \left[x_i(t),\ p_j(t) \right] \right\rangle_T = \delta_{ij}\ i\hbar \left(\frac{dg}{dt}(0) \right)^2 = \delta_{ij}\ i\hbar \qquad \text{(B6)}$$

Therefore, the particle coordinate and momentum operators satisfy the correct quantum mechanical commutation relations if the approximate treatment of the heat bath is carried out consistently.

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