

Investigation of condensed matter via resonant neutron scattering. Correlation-function formalism with application to the study of the interatomic force density

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Resonant epithermal neutron scattering provides a new regime for the study of the properties of condensed matter. The differential scattering cross section is developed in a resonant-correlation-function formalism involving the positions of two scattering centers at four different times. The resonant correlation functions contain information which cannot be obtained from a study of the Van Hove correlation functions which are related to the thermal neutron scattering law, and these resonant correlation functions enable one to observe phenomena which are beyond the scope of thermal neutron scattering. The extraction of the time-dependent interatomic force density is taken as an example.

I. INTRODUCTION

Thermal neutron scattering studies constitute a powerful and well-understood means for probing the microscopic properties of condensed matter.¹ It was first shown by Van Hove² that the differential cross section for the scattering of thermal neutrons may be expressed in terms of microscopic two-time correlation functions of dynamical variables for the target system. Thermal neutron scattering experiments enable one to measure quantities of interest to the theory of condensed matter.

Resonant neutron scattering provides a new regime for probing the properties of condensed matter. In contrast with the nonresonant thermal regime, the amplitude for resonant neutron scattering is strongly dependent upon the energy of the incident neutron. Consequently, as we shall show, the differential cross section for the resonant scattering of neutrons is related to a four-point correlation function of target-system dynamical variables.

The theory of neutron-nucleus resonance reactions was fully developed in the period of time from the 1930's to the 1950's, beginning with the pioneering work of Bohr³ and Breit and Wigner.⁴ In the case of a single epithermal neutron resonance, only *s*-wave scattering is appreciable. In the vicinity of such a resonance the scattering amplitude is given by

$$f = f_0 + \kappa \frac{\Gamma_n/2}{E - E_R + i\Gamma/2}, \quad (1.1)$$

where E is the energy of the (free) neutron-nucleus system in the barycentric coordinate system, $2\pi\lambda$ is the wavelength of the incident neutron, and f_0 is the potential scattering amplitude, which is typically of the order of the nuclear radius. E_R is the center of the resonance. Γ_n is the partial width for decay with the emission of a neutron, and Γ is the total width of the resonance.

We shall be concerned with the scattering of epithermal neutrons with energies less than a few electron volts. A few heavy isotopes have resonances in this energy range⁵ and their widths are in the range of several tens to several hundreds of millivolts (see Table I). For example, ²⁴⁰Pu has a resonance in the vicinity of $E_R = 1$ eV, for which the widths are $\Gamma = 0.03$ and $\Gamma_n = 0.002$ eV. These widths are of the order of typical thermal vibrational energies of these nuclei in condensed matter or molecules and we shall see that they effect a profound change in the neutron cross section from that obtained in the potential scattering regime as given, for example, by the Van Hove formalism.

The differences which arise in the resonant regime stem from two causes: (a) At resonance the scattering amplitude is quite large so that even for rather small samples multiple scattering effects may become important. (b) The resonant scattering amplitude exhibits a Breit-Wigner line shape as a function of incident neutron energy. As an example of the former, we consider the resonant scattering of neutrons which are well collimated with an incident energy of $E = 1$ eV upon a single crystal of ²⁴⁰Pu. The planar

TABLE I. Partial list of low-energy neutron resonances. E_R is the resonant energy, Γ is the total width, and Γ_n is the neutron partial width.

	E_R (eV)	Γ (meV)	Γ_n (meV)
^{157}Gd	0.03	100	0.6
^{240}Pu	1	32	2.4
^{238}U	6.7	25	1.5
^{177}Hf	1.1	67	2
^{115}In	1.5	72	3
^{113}Cd	0.18	113	0.65

scattering amplitude is

$$F = \frac{n_0 \lambda d f_N f_D(\theta)}{\sin \theta}, \quad (1.2)$$

where n_0 is the atomic density, d is the lattice spacing, θ is the angle of incidence, and f_D is the Debye-Waller factor. The atomic density is of the order $n_0 = 4 \times 10^{-2}/\text{\AA}^3$; the wavelength of the 1-eV neutron

$$(4 \times 10^{-2}/\text{\AA}^3)(3 \times 10^{-1} \text{\AA})(3 \text{\AA})(3 \times 10^{-3} \text{\AA})(0.16)/0.707 = 2 \times 10^{-5}$$

If the crystal consists of a slab M layers thick and the incident neutron satisfies the Bragg condition, then in the Born approximation the scattering amplitude is MF . Multiple scattering can only be neglected if $MF \ll 1$ or $M \ll 10^5$ layers at a thickness $Md \ll 10^{-2}$ cm. For larger crystals, one must in considering the Bragg scattering use the dynamical theory,⁷ which for the resonant scattering of γ rays has been fully developed; this theory has been applied to resonant neutron diffraction by Kagan and Afaneslev *et al.*⁸

We shall not go into the multiple-scattering regime to any appreciable extent but we shall concentrate on the scattering from small samples. In this case it is the strong dependence of f_N (or the long "delay time," \hbar/Γ , between the entrance and the emergence of the neutron from a nucleus) which gives the interesting new effects.

The resonant absorption of neutrons by nuclei in a crystal was investigated by Lamb,⁹ who showed how target system relaxation gives rise to a Doppler broadening of the resonance width. The elastic scattering of neutrons at resonance from bound nuclei was investigated by Trammell,⁶ who demonstrated that information on target-system dynamics can be obtained from the elastic cross section about resonance. This result is remarkable in that the same information can be obtained from nonresonant neutron scattering experiments only by looking at the inelastic component. Trammell showed that the cross section for the elastic scattering of neutrons at resonance from nuclei bound in a crystal may be expressed in terms of the same two-time correlation functions which are related to the inelastic component of the

is $\lambda = 3 \times 10^{-1} \text{\AA}$. We may use the value $d = 3 \text{\AA}$ as the order of magnitude estimate for the lattice parameter. The single-site scattering amplitude is given by Eq. (1.1) to be $f_N = 3 \times 10^{-3} \text{\AA}$. The Debye-Waller factor at 1 eV is of the order⁶ $f_D = 0.16$. Taking, for example $\theta = 45^\circ$, the planar scattering amplitude is of the order

nonresonant case.

For many years, sources of epithermal neutrons (such as conventional reactors) were of insufficiently high flux to make resonant neutron scattering studies of condensed matter a real possibility. More recently, the arrival of spallation sources on the scene has promised to give much higher neutron fluxes in the epithermal region¹⁰; this arrival points to new vistas in the field of experimental resonant neutron scattering.

Our purpose in this series of papers is to elucidate the nature and properties of the correlation functions which, in a manner analogous to Van Hove's result, may be used to express the resonant scattering law; we shall investigate precisely what information is contained in them, in comparison with the information which may be obtained from a study of Van Hove's two-time correlation functions. Our principle interest is to obtain phenomena which may be observed by the use of resonant neutron scattering but which are beyond the scope of nonresonant scattering.

II. RESONANT CORRELATION FUNCTION FORMALISM; THE SHORT- AND LONG-COLLISION-TIME LIMITS; THE DYNAMICAL DUAL ASYMPTOTIC EXPANSION

In order to describe resonant epithermal neutron scattering from condensed matter target systems in terms of correlation functions for the target system, we begin with Lamb's formula^{6,9} for the amplitude for the resonant scattering of a neutron from an incident state of wave vector \vec{k}_0 to a final state of wave vector \vec{k}_f

$$f_R(\vec{k}_0, \vec{k}_f) = \left(\frac{\Gamma_n}{2k_0} \right) \sum_{ni} \frac{\langle \chi_{n_f} | e^{-i\vec{k}_f \cdot \vec{r}_i} | \chi_n \rangle \langle \chi_n | (A_R + B_R \vec{S}_i \cdot \vec{s}) e^{i\vec{k}_0 \cdot \vec{r}_i} | \chi_{n_i} \rangle}{(E_{k_f} - E_R) - (\epsilon_n - \epsilon_{n_f}) + i\Gamma/2}, \quad (2.1)$$

where the spin dependence is included. The symbol \vec{r}_i denotes the position operator for the i th scattering nucleus. E_{k_f} is the energy of the scattered neutron, ϵ_n and ϵ_{n_f} are the energies of the intermediate and final target collective states $|\chi_n\rangle$ and $|\chi_{n_f}\rangle$, respectively ($|\chi_{n_i}\rangle$ is the initial target collective state), the summation in n is over a basis of target-system states in which the target-system Hamiltonian is diagonal. \vec{S}_i and \vec{s} are, respectively, the spin of the target nucleus in its ground state and the spin of the neutron; thus, matrix elements between incident and final neutron spin states must still be taken. Provided that $S \neq 0$, the spin-independent part of the projection operator is

$$A_R = \frac{S(S+1) + s(s+1) - J'(J'+1)}{J(J+1) - J'(J'+1)}, \quad (2.2)$$

while the coefficient B_R is given by

$$B_R = \frac{2}{J(J+1) - J'(J'+1)}; \quad (2.3)$$

J is the spin corresponding to the resonant part of the interaction, J' is the spin corresponding to the non-resonant part of the interaction; the latter is expressed by the relation

$$J' = 2S - J. \quad (2.4)$$

In the case that $S=0$, the amplitudes A_R and B_R are, respectively, unity and zero.

For the purposes of the present development, we consider only the coherent part of Eq. (2.1), which is obtained in a well-known manner.²¹ Taking the incident beam to be unpolarized, and the nuclear spins to be random, the coherent part of the amplitude (2.1) becomes

$$f_R = w \left(\frac{\Gamma_n}{2k_0} \right) \sum_{ni} \frac{\langle \chi_{n_f} | e^{i\vec{k}_f \cdot \vec{r}_i} | \chi_n \rangle \langle \chi_n | e^{i\vec{k}_0 \cdot \vec{r}_i} | \chi_{n_i} \rangle}{(E_{k_f} - E_R) - (\epsilon_n - \epsilon_{n_f}) + i\Gamma/2}, \quad (2.5)$$

where w is a weighting factor for the spin multiplicity given roughly by

$$w = \left(\frac{(2J+1)}{(2S+1)(2s+1)} \right)^{1/2}. \quad (2.6)$$

The energy dependence of the resonance denominator in Eq. (2.5) prevents the summation over the intermediate states by means of closure. This obstacle may be removed by representing the denominator in the integral form

$$\frac{1}{(E_{k_f} - E_R) - (\epsilon_n - \epsilon_{n_f}) + i\Gamma/2} = \frac{i}{\hbar} \int_0^\infty dt \exp \left[\frac{i}{\hbar} [(E_{k_f} - E_R) - (\epsilon_n - \epsilon_{n_f}) + i\Gamma/2] t \right], \quad (2.7)$$

so that the scattering amplitude becomes

$$\begin{aligned} f_R &= w \left(\frac{i\Gamma_n}{2\hbar k_0} \right) \sum_{ni} \int_0^\infty dt \exp \left[\frac{i}{\hbar} [(E_{k_f} - E_R) + i\Gamma/2] t \right] \\ &\quad \times \langle \chi_{n_f} | \exp \left[\frac{i}{\hbar} \epsilon_{n_f} t \right] e^{-i\vec{k}_f \cdot \vec{r}_i} \exp \left[\frac{-i}{\hbar} \epsilon_n t \right] | \chi_n \rangle \langle \chi_n | e^{i\vec{k}_0 \cdot \vec{r}_i} | \chi_{n_i} \rangle \\ &= w \left(\frac{i\Gamma_n}{2\hbar k_0} \right) \sum_{ni} \int_0^\infty dt \exp \left[\frac{i}{\hbar} [(E_{k_f} - E_R) + i\Gamma/2] t \right] \\ &\quad \times \langle \chi_{n_f} | \exp \left[\frac{i}{\hbar} H t \right] e^{-i\vec{k}_f \cdot \vec{r}_i} \exp \left[\frac{-i}{\hbar} H t \right] | \chi_n \rangle \langle \chi_n | e^{i\vec{k}_0 \cdot \vec{r}_i} | \chi_{n_i} \rangle, \end{aligned} \quad (2.8)$$

where H is the Hamiltonian for the target system. Writing the Heisenberg operator

$$\vec{r}_i(t) = \exp \left[\frac{i}{\hbar} H t \right] \vec{r}_i \exp \left[-\frac{i}{\hbar} H t \right], \quad (2.9)$$

the summation over the intermediate states may now be performed by closure to give

$$f_R = w \left(\frac{i\Gamma_n}{2\hbar k_0} \right) \sum_i \int_0^\infty dt \exp \left(\frac{i}{\hbar} [(E_{k_f} - E_R) + i\Gamma/2] t \right) \langle \chi_{n_f} | e^{-i\vec{k}_f \cdot \vec{r}_i(t)} e^{i\vec{k}_0 \cdot \vec{r}_i(0)} | \chi_{n_i} \rangle . \quad (2.10)$$

The scattering cross section, which is the quantity directly measured in the experiment, contains interference terms associated with the scattering from different sites; this gives rise to higher orders of correlation of nuclear motion. The scattering cross section is given by the absolute square of the scattering amplitude¹

$$\frac{d\sigma}{d\Omega} = \frac{k_f}{k_0} |f_R|^2 . \quad (2.11)$$

The differential scattering cross section for inelastic

scattering is the scattering cross section per unit interval of energy transfer

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_f}{k_0} |f_R|^2 \delta(E + \Delta\epsilon) , \quad (2.12)$$

where the Dirac δ factor is required in order to express conservation of energy, E is the quantity of energy transferred to the neutron upon scattering, and $\Delta\epsilon$ is the difference in energy between initial and final target system states.

Substituting the result (2.10) for resonant scattering, we obtain

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} \Big|_{\chi_0, \chi_{n_f}} &= \frac{k_f}{k_0} w^2 \left(\frac{\Gamma_n}{2\hbar k_0} \right)^2 \sum_{i, i'} \int_0^\infty dt \int_0^\infty dt' \exp \left(\frac{i}{\hbar} [(E_{k_f} - E_R) + i\Gamma/2] t \right) \\ &\quad \times \exp \left(\frac{-i}{\hbar} [(E_{k_f} - E_R) + i\Gamma/2] t' \right) \langle \chi_{n_f} | e^{-i\vec{k}_f \cdot \vec{r}_i(t)} e^{i\vec{k}_0 \cdot \vec{r}_i(0)} | \chi_0 \rangle \\ &\quad \times \langle \chi_0 | \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(0)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(t')] | \chi_{n_f} \rangle \delta(\epsilon_{n_f} - \epsilon_0 + E) . \end{aligned} \quad (2.13)$$

The total scattering cross section is the sum of Eq. (2.13) over all possible initial and final target system states weighted by the statistical probabilities for the initial states. Writing the Dirac δ function in terms of its Fourier transform

$$\delta(\epsilon_{n_f} - \epsilon_0 + E) = \frac{1}{2\pi\hbar} \int_{-\infty}^\infty dT \exp \left(\frac{-i}{\hbar} (\epsilon_{n_f} - \epsilon_0 + E) T \right) , \quad (2.14)$$

the differential scattering cross section takes the form

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} \Big|_{\chi_0, \chi_{n_f}} &= \frac{k_f}{k_0} w^2 \left(\frac{\Gamma_n}{2\hbar k_0} \right)^2 \sum_{i, i'} \int_{-\infty}^\infty dT \exp \left(\frac{-i}{\hbar} ET \right) \int_0^\infty dt \exp \left(\frac{i}{\hbar} \Delta E t \right) \int_0^\infty dt' \exp \left(\frac{-i}{\hbar} \Delta E^* t' \right) \\ &\quad \times \langle \chi_{n_f} | \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] | \chi_0 \rangle \\ &\quad \times \left\langle \chi_0 \left| \exp \left(\frac{i}{\hbar} \epsilon_0 T \right) \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(0)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(t')] \exp \left(\frac{-i}{\hbar} \epsilon_{n_f} T \right) \right| \chi_{n_f} \right\rangle , \end{aligned} \quad (2.15)$$

where $\Delta E = E_{k_f} - E_R + i\Gamma/2$. Once again substituting the Heisenberg representation for the operators, the summation over the final target system states may be performed by closure, while the summation over the initial states yields a statistical mechanical expectation of the operators in question

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} &= \frac{1}{2\pi\hbar} \frac{k_f}{k_0} w^2 \left(\frac{\Gamma_n}{2\hbar k_0} \right)^2 \sum_{i, i'} \int_{-\infty}^\infty dT \exp \left(\frac{-i}{\hbar} ET \right) \int_0^\infty dt \exp \left(\frac{i}{\hbar} \Delta E t \right) \int_0^\infty dt' \exp \left(\frac{-i}{\hbar} \Delta E^* t' \right) \\ &\quad \times \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T+t')] \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle . \end{aligned} \quad (2.16)$$

Equation (2.16) is the basic result for resonant epithermal neutron scattering; it shows that the requisite correlation functions are four-time correlation functions involving the correlated motion of two different position operators indexed by i and i' .

The cross section for elastic scattering is obtained by setting $E = 0$

$$\begin{aligned} \left. \frac{d^2\sigma}{d\Omega dE} \right|_{E=0} &= \lim_{E \rightarrow 0} \int_{t, t' > 0} dT dt dt' \exp\left[\frac{-i}{\hbar} ET\right] \exp\left[\frac{i}{\hbar}(\Delta Et - \Delta E^* t')\right] \\ &\times \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T+t')] \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle . \end{aligned} \quad (2.17)$$

The integrals in t and t' are effectively restricted above by the presence of the decay width; the integral in T suffers no such restriction. Hence, the only significant contribution to the integral in T arises from values of T which are so large that the operators at this time have become uncorrelated with the operators on the right

$$\begin{aligned} &\langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T+t')] \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle \\ &= \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T+t')] \rangle \langle \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle . \end{aligned} \quad (2.18)$$

But the two-time correlation function depends only upon the difference in the respective times, so that T can be removed from the correlation function to the left

$$\langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T+t')] \rangle = \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(0)] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(t')] \rangle . \quad (2.19)$$

Thus, the total elastic cross section becomes

$$\frac{d\sigma}{d\Omega} = \left| w \frac{\Gamma_n}{2\hbar k_0} N \int_0^\infty dt \exp\left[\frac{i}{\hbar} \left(E_{k_f} - E_R + i\frac{\Gamma}{2} \right) t \right] \langle e^{-i\vec{k}_f \cdot \vec{r}_i(t)} e^{i\vec{k}_0 \cdot \vec{r}_i(0)} \rangle \right|^2 , \quad (2.20)$$

where N is the total number of scattering centers.

The presence of nonresonant contributions to the scattering interaction, such as nuclear potential scattering, will give rise to interference contributions to the scattering cross section. For sufficiently small concentrations of the resonant isotope, the interference terms will be the largest resonant contribution; their form depends upon the correlation of resonant and nonresonant atoms, and since a lower order of correlation is involved, their interpretation is of a lower order of complexity.

The amplitude for nuclear potential scattering is given by

$$f_f = \sum_l \langle \chi_{n_f} | e^{-i\Delta\vec{k} \cdot \vec{R}_l} \hat{b}_l | \chi_{n_i} \rangle , \quad (2.21)$$

where $\Delta\vec{k}$ is the difference between the respective

$$\begin{aligned} \left. \frac{d^2\sigma}{d\Omega dE} \right|_{Rf} &= 2 \operatorname{Re} \left[\frac{k_f}{k_0} b w \frac{i\Gamma_n}{2\hbar k_0} \sum_{l, l'} \int_{-\infty}^{\infty} dT \exp\left[\frac{-i}{\hbar} ET\right] \right. \\ &\times \left. \int_0^\infty dt \exp\left[\frac{i}{\hbar} \Delta Et\right] \langle \exp[i\Delta\vec{k} \cdot \vec{R}_l(T)] \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle \right] . \end{aligned} \quad (2.24)$$

Interference between resonant nuclear and magnetic scattering may be developed in a similar fashion. Ignoring

wave vectors of the final state and the incident state of the neutron, \vec{R}_l is the position operator for the nonresonant scattering site indexed by l , and \hat{b}_l is the scattering length operator

$$\hat{b} = b + b' \hat{S}_l \cdot \hat{s} . \quad (2.22)$$

The interference term arising from the presence of the nonresonant scattering amplitude (2.22) is given by

$$2 \operatorname{Re} \left[\frac{k_f}{k_0} (f_R f_f^*) \right] . \quad (2.23)$$

Making the previous substitutions, we may express the interference contribution in terms of a three-time correlation function depending upon correlation in space and time between the motions of the resonant and nonresonant scattering centers

relativistic and other higher order effects, the amplitude for scattering which is due to the interaction between the neutron and the atomic spin may be written

$$f_m = -2F(\Delta\vec{k})\gamma_{\text{net}} \left[\frac{e^2}{m_e c^2} \right] \sum_i \langle \chi_{n_f} | e^{-i\Delta\vec{k} \cdot \vec{R}_i} I_{\vec{S}_i} \cdot [\Delta\vec{k} \times (\hat{S}_i \times \Delta\vec{k})] | \chi_{n_i} \rangle , \quad (2.25)$$

where $F(\Delta\vec{k})$ is the usual form factor for magnetic scattering, γ_{net} is the neutron's gyromagnetic ratio, and m_e is the mass of the electron; the vector $\Delta\vec{k}$ is a unit vector with the same direction as $\Delta\vec{k}$. Performing polarization analysis (summing over the spin coordinates of the neutron), the magnetic interference contribution to the scattering cross section is obtained to be, provided $\vec{p} = 0$:

$$\left. \frac{d^2\sigma}{d\Omega dE} \right|_{R_m} = -\text{Re} \left[\frac{k_f}{k_0} F(\Delta k) \gamma_{\text{net}} \frac{e^2}{m_e c^2} \frac{i\Gamma_n}{2\hbar k_0} \int_{-\infty}^{\infty} dT \exp\left\{ \frac{-i}{\hbar} ET \right\} \int_0^{\infty} dt \exp\left\{ \frac{i}{\hbar} \Delta Et \right\} \right. \\ \left. \times \langle \exp[-i\Delta\vec{k} \cdot \vec{R}_i(T)] \vec{p} \cdot [\Delta\vec{k} \times [S_i(T) \times \Delta\vec{k}]] \exp[-i\vec{k}_f \cdot \vec{r}_i(t)] \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle \right] , \quad (2.26)$$

where \vec{P} is the polarization of the incident state of the neutron.

More generally, the formula (2.16) may be extended to resonances of arbitrary energy dependence in the single collision approximation.¹¹ Representing the energy dependence of the rigidly bound scattering amplitude in terms of its Fourier components

$$\zeta(E) = \int_{-\infty}^{\infty} dt \exp\left\{ \frac{-i}{\hbar} Et \right\} \zeta(t) \quad (2.27)$$

the differential scattering cross section becomes¹²

$$\frac{d^2\sigma}{d\Omega dE} = \frac{m}{2\pi\mu} \frac{k_f}{k_0} \sum_{ii'} \int_{-\infty}^{\infty} dT \exp\left\{ \frac{-i}{\hbar} ET \right\} \int_0^{\infty} dt \exp\left\{ \frac{-i}{\hbar} E_0 t \right\} \zeta(t) \int_0^{\infty} dt' \exp\left\{ \frac{i}{\hbar} E_0 t' \right\} \zeta(t')^* \\ \times \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T+t')] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T)] \exp[-i\vec{k}_f \cdot \vec{r}_i(0)] \exp[i\vec{k}_0 \cdot \vec{r}_i(t)] \rangle , \quad (2.28)$$

where E_0 is the energy of the incident neutron, and μ is the reduced mass of the neutron and the target nucleus.

If the duration of the scattering interaction is very short compared with the target system relaxation time for the condensed matter process in question (the short collision time limit), then the spectral component $\zeta(t)$ may be replaced with a Dirac δ function in Eq. (2.28) to yield

$$\frac{d^2\sigma}{d\Omega dE} = \frac{m}{2\pi\mu} \frac{k_f}{k_0} \sum_{ii'} \int_{-\infty}^{\infty} dT \exp\left\{ \frac{-i}{\hbar} ET \right\} \langle \exp[i\Delta\vec{k} \cdot \vec{r}_{i'}(T)] \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle , \quad (2.29)$$

which reproduces Van Hove's result. Similarly, if the duration of the scattering interaction is very long compared with the target-system relaxation time (the long collision time limit), $\zeta(t)$ becomes flat; then the only contributions arise from large values of t , so that we may set

$$\langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(T+t')] \exp[i\vec{k}_f \cdot \vec{r}_{i'}(T)] \exp[-i\vec{k}_f \cdot \vec{r}_i(0)] \exp[i\vec{k}_0 \cdot \vec{r}_i(t)] \rangle \\ = \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(0)] \rangle \langle \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle \langle \exp[i\vec{k}_f \cdot \vec{r}_i(T)] \exp[-i\vec{k}_f \cdot \vec{r}_{i'}(0)] \rangle . \quad (2.30)$$

Hence, the cross section may then be written

$$\frac{d^2\sigma}{d\Omega dE} = \frac{m}{2\pi\mu} \frac{k_f}{k_0} |\zeta(E_0)|^2 \sum_{ii'} \langle \exp[-i\vec{k}_0 \cdot \vec{r}_{i'}(0)] \rangle \langle \exp[i\vec{k}_0 \cdot \vec{r}_i(0)] \rangle \\ \times \int_{-\infty}^{\infty} dT \exp\left\{ \frac{-i}{\hbar} ET \right\} \langle \exp[i\vec{k}_f \cdot \vec{r}_i(T)] \exp[-i\vec{k}_f \cdot \vec{r}_{i'}(0)] \rangle . \quad (2.31)$$

Formula (2.31) is the appropriate time-correlation function representation describing the Mossbauer effect.¹³ Resonant epithermal neutron scattering typically lies in a region intermediate between the two limiting cases of Eqs. (2.29) and (2.31). The intermediate status of resonant epithermal neutron scattering between the short- and long-collision-time limits is one of the unique features of this regime, the various facets of which will be illuminated in subsequent papers of this series.

In the present paper, we concentrate on an analog to the Placzek development,¹⁴ which may be most conveniently obtained in the case of an isotropic target by considering an asymptotic expansion for the scattering law in inverse powers of $\Delta E = E_{k_f} - E_R + i\Gamma/2$; since the scattering law develops a resonance only over a limited and well-defined region of incident state energies, it is more useful to work with the leading order moments of the scattering law (and the associated asymptotic expansion) in the case of resonant neutron scattering than the corresponding development in thermal neutron scattering (which is made in the parameter E rather than ΔE). Owing to the motions of the target-system nuclei, the resonant line shape is Doppler broadened in a fashion which is not independent of the energy and momentum transfer to the neutron upon scattering; the precise nature of the functional dependence of the broadening parameters (which can be measured experimentally) contains useful information about target-system dynamics, as we will show.

The resonant scattering law (i.e., the resonant cross section with the omission of some unimportant factors) varies as a function of six independent, externally adjustable parameters, which we choose to exhibit explicitly in the form $W(E, \Delta\vec{k}, E_{k_f}, \phi_k)$, where ϕ_k is the angle of the $k_0 k_f$ plane about the axis $\Delta\vec{k}$; alternatively, we employ $z = E_{k_f} - E_R$ in place of E_{k_f} as one of the six independent variables. The expression

$$W(z) \sim \sum_{n=1}^{\infty} a_n \left(\frac{i}{z + i\Gamma/2} \right)^n + b_n \left(\frac{-i}{z - i\Gamma/2} \right)^n \quad (2.32)$$

is defined to be a dual asymptotic development of the analytic function $W(z)$ provided that the generalized Poincare-Watson convergence criterion¹⁵⁻¹⁷ is satisfied:

$$\forall n \lim_{z \rightarrow \infty} z^n \left[\left(\frac{i}{2\pi} \right) \int_{-\infty}^{\infty} dz' \frac{W(z')}{(z - z') + i\Gamma/2} - \sum_{n'=1}^n \frac{a_n i^{n'}}{z^{n'}} \right] = 0, \quad (2.33a)$$

$$\forall n \lim_{z \rightarrow \infty} z^n \left[\left(\frac{-i}{2\pi} \right) \int_{-\infty}^{\infty} dz' \frac{W(z')}{(z - z') - i\Gamma/2} - \sum_{n'=1}^n \frac{b_n (-i)^{n'}}{z^{n'}} \right] = 0. \quad (2.33b)$$

It is readily shown that a function $W(z)$ has at most one dual asymptotic development for a fixed value of the width parameter Γ ; thus, the coefficients (a_n, b_n) are uniquely determined by the variation of $W(z)$. It is also seen that the dual asymptotic development of a function $W(z)$ must necessarily satisfy the simple Poincare-Watson convergence criterion

$$\forall n \lim_{z \rightarrow \infty} z^n \left\{ W(z) - \left[\sum_{n'=1}^n a_n \left(\frac{i}{z + i\Gamma/2} \right)^{n'} + b_n \left(\frac{-i}{z - i\Gamma/2} \right)^{n'} \right] \right\}. \quad (2.33c)$$

The simple Poincare-Watson convergence criterion (2.33c) alone does not suffice to determine the dual asymptotic expansion coefficients uniquely. However, the theorem of Stieltjes¹⁸ may be applied to the theory of dual asymptotic developments to show that the greatest error incurred in Eq. (2.33c) is in the last term. Moreover, by virtue of the imaginary part of the resonant denominators in Eq. (2.33c), there is an upper bound on the greatest error incurred for any value of z (which occurs at the center of the resonance). Thus, one of the local minima in a least-squares fit of the function with a dual asymptotic expansion chopped off at a suitable point provides a good estimate of the coefficients (a_n, b_n) provided that the effect of Doppler broadening is not too severe.

The asymptotic coefficients (a_n, b_n) may be obtained from the functional variation of $W(z)$ without recourse to approximation by employing a well-known Fourier technique¹⁹ for obtaining the asymptotic expansion of a function in terms of its width parameters. Thus, the term by term Fourier transform of Eq. (2.32) is an exact equation

$$\begin{aligned} \tilde{W}(\tau) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dz e^{-i\tau z} W(z) \\ &= \sum_{n=0}^{\infty} a_{n+1} \frac{1}{n!} \tau^n e^{-\tau\Gamma/2} \Theta(\tau) \\ &\quad + b_{n+1} \frac{1}{n!} (-\tau)^n e^{\tau\Gamma/2} \Theta(-\tau), \end{aligned} \quad (2.34)$$

Writing $\tilde{W}(\tau)$ for small $\tau \neq 0$ in terms of the power

series

$$\bar{W}(\tau) = \sum_{n=0}^{\infty} C_{>n} \tau^n \Theta(\tau) + C_{<n} \tau^n \Theta(-\tau) \quad , \quad (2.35)$$

Eq. (2.34) implies that the coefficients (a_n, b_n) satisfy the summation equation

$$(-1)^n n! \left(\frac{\Gamma}{2}\right)^{-n} C_{>n} = \sum_{n'=-0}^n a_{n'+1} \left(\frac{\Gamma}{2}\right)^{-n'} (-1)^{n'} \binom{n}{n'} \quad ,$$

$$n! \left(\frac{\Gamma}{2}\right)^n C_{<n} = \sum_{n'=-0}^n b_{n'+1} \left(\frac{\Gamma}{2}\right)^{-n'} (-1)^{n'} \binom{n}{n'} \quad , \quad (2.36)$$

the solution of which is given by

$$a_{n+1} = \sum_{n'=-0}^n \binom{n}{n'} n'! \left(\frac{\Gamma}{2}\right)^{n-n'} C_{>n'} \quad ,$$

$$b_{n+1} = \sum_{n'=-0}^n (-1)^{n'} \binom{n}{n'} n'! \left(\frac{\Gamma}{2}\right)^{n-n'} C_{<n'} \quad . \quad (2.37)$$

Equation (2.37) is an exact relation between the asymptotic coefficients (a_n, b_n) and the generalized

width parameters, which are given by

$$C_{>n} = \lim_{\alpha \rightarrow 0} \frac{1}{2\pi n!} \int_{-\infty}^{\infty} dz (-iz)^n e^{-i|z|} e^{-|\alpha z|} W(z) \quad ,$$

$$C_{<n} = \lim_{\alpha \rightarrow 0} \frac{1}{2\pi n!} \int_{-\infty}^{\infty} dz (-iz)^n e^{i|z|} e^{-|\alpha z|} W(z) \quad . \quad (2.38)$$

The dual asymptotic coefficients (a_n, b_n) bear an exact relation to experiment which is defined by the Eqs. (2.37) and (2.38); the approximation for the scattering law (2.32) is itself not wholly useless for the purpose of obtaining these quantities experimentally. The interpretation of (a_n, b_n) in terms of microscopic dynamical correlation functions of target system variables is obtained by writing the position operator $\bar{r}_i(t)$ in power series of t in Eq. (2.16), expanding the integrand in powers of t , and integrating term by term, which yields the requisite dual asymptotic expansion. The leading order terms in a $1/\Delta E$ expansion of the scattering law W_i corresponding to the interference between resonant and potential scattering [as it is obtained from Eq. (2.24)] are more compact, simple, and direct of interpretation than the corresponding expansion for the purely resonant scattering law corresponding to Eq. (2.16), and it is the former only which we exhibit explicitly here

$$W_i \sim 2 \operatorname{Re} \left\{ i \sum_{l,l'} \int_{-\infty}^{\infty} dT \exp\left[\frac{-i}{\hbar} ET\right] \left\{ \frac{\hbar}{i\Delta E'} \langle \exp[i\Delta\bar{k} \cdot \bar{R}_i(T)] \exp[-i\Delta\bar{k} \cdot \bar{r}_i(0)] \right\} \right. \\ \left. - \frac{\hbar^2}{\Delta E'^2} \langle \exp[i\Delta\bar{k} \cdot \bar{R}_i(T)] \left[i \frac{\bar{k}_f}{M} \cdot \bar{p}_i(0) \right] \exp[-i\Delta\bar{k} \cdot \bar{r}_i(0)] \right\} \\ \left. + \frac{i\hbar^3}{\Delta E'^3} \langle \exp[i\Delta\bar{k} \cdot \bar{R}_i(T)] \left[\frac{1}{4} \left(\frac{\bar{k}_f}{m} \cdot \bar{p}_i(0) \right)^2 + \frac{i}{4m} \bar{k}_f \cdot \bar{F}_i(0) \right] \exp[-i\Delta\bar{k} \cdot \bar{r}_i(0)] \right\} \right\} \quad . \quad (2.39)$$

The symbol \bar{p}_i denotes the momentum of the i th scattering center, while \bar{F}_i is the force acting on it. The nonvanishing of the commutator $[r_i, p_i]$ which occurs in the derivation of the asymptotic series has required the redefinition of the resonant parameter ΔE to

$$\Delta E' = \frac{\hbar^2 k_f^2}{2m} \left[1 - \frac{m}{M} \right] - E_R + i \frac{\Gamma}{2} \quad , \quad (2.40)$$

where M is the mass of the resonantly scattering target nucleus.

The various relations derived above raise the possibility that the several dynamical correlation functions occurring in Eq. (2.39) can be separated and measured by experiment. This possibility will be taken up and considered more carefully in Sec. IV below.

III. SPACE-SPACE COMPONENT OF THE RESONANT SCATTERING LAW: KINEMATICAL CONSIDERATIONS

The Fourier-like integral (2.16) obviously cannot be inverted in the usual way to obtain the full four-point dynamical correlation function, since the parameters \bar{k}_0 , \bar{k}_f , E , and ΔE are not all independent; if this is attempted, one obtains at best a "blurred" version of the full four-point dynamical correlation function. The question of how this blurriness can be precisely characterized is quite distinct from a consideration of the physical content of the four-point dynamical correlation functions, or from any attempt to compute them in a specific model; yet, it is an essential facet of the problem. We shall

consider the second two questions in Sec. IV, and more fully, in future papers in this series. For the present, we shall consider the nature of the blurriness inherent in the interpretation of Eq. (2.16) as the Fourier transform of a four-point dynamical correlation function, rather than probe its physical content.

The formula (2.29) shows that in the short-collision time limit, the information which is contained in the resonant scattering cross section becomes identical with the information which can be obtained in thermal neutron scattering experiments, and that the information is extracted in an identical fashion in both cases. In this limit, the differential scattering cross section exhibits four degrees of freedom: three degrees associated with the three components of the momentum transfer to the scattered neutron, and one degree of freedom associated with the corresponding energy transfer.

On the contrary, the general resonant scattering formula depends fully upon the variation in each of the components of \vec{k}_0 and \vec{k}_f ; the general differential

cross section for resonant scattering exhibits six degrees of freedom. The additional information which can be obtained from its study concerning microscopic correlations is bound up with the presence of two further degrees of freedom. The short-collision time limit yields information on microscopic correlations in a four-dimensional space-time parameter space; the resonant case contains information on microscopic correlations in a six-dimensional parameter space. But the four-point dynamical correlation function in Eq. (2.16) spans a 15-dimensional parameter space, so that the blurriness associated with Eq. (2.16) arises from the integration of 9 of the 15 degrees of freedom.

The latter point is clearly seen by writing the four-point dynamical correlation function in terms of particle densities

$$\hat{\rho}_i(\vec{r}) = \delta(\vec{r} - \vec{r}_i) , \quad (3.1)$$

so that the resonant scattering law takes the form

$$\begin{aligned} W(\vec{k}_0, \vec{k}_f) = \sum_{ii'} \int_{-\infty}^{\infty} dT \exp\left(\frac{-i}{\hbar} ET\right) \int_{-\infty}^{\infty} dt \exp\left(\frac{i}{\hbar} \Delta E t\right) \int_{-\infty}^{\infty} dt' \exp\left(\frac{-i}{\hbar} \Delta E^* t'\right) \int d^3 r_1 d^3 r_2 d^3 r_3 d^3 r_4 \\ \times \exp[i\vec{k}_0 \cdot (\vec{r}_4 - \vec{r}_1)] \exp[-i\vec{k}_f \cdot (\vec{r}_3 - \vec{r}_2)] \\ \times \langle \hat{\rho}_{i'}(\vec{r}_1, T) \hat{\rho}_i(\vec{r}_2, T + t') \hat{\rho}_i(\vec{r}_3, t) \rho_i(\vec{r}_4, 0) \rangle \Theta(t) \Theta(t') . \end{aligned} \quad (3.2)$$

The most straightforward transformation of Eq. (3.2) to microscopic target system variables is given by the space-space Fourier transform

$$\tilde{W}(\vec{r}, \vec{r}') = \int \int d^3 k_0 d^3 k_f W(\vec{k}_0, \vec{k}_f) e^{i\vec{k}_0 \cdot \vec{r}} e^{-i\vec{k}_f \cdot \vec{r}'} . \quad (3.3)$$

The variation of the parameters E and ΔE in Eq. (3.2) is given by their dependence on \vec{k}_f and \vec{k}_0 :

$$E = \frac{\hbar^2}{2m} (k_f^2 - k_0^2), \quad \Delta E = \frac{\hbar^2}{2m} k_f^2 - E_R + i\frac{\Gamma}{2} . \quad (3.4)$$

Substituting Eq. (3.2) into Eq. (3.3) and using the relations (3.4), the integrations are easily performed to yield

$$\begin{aligned} \tilde{W}(\vec{r}, \vec{r}') = \sum_{ii'} \int dT dt dt' d^3 r_1 d^3 r_2 d^3 r_3 d^3 r_4 \exp[it(i\Gamma/2 - E_R)] \exp[it'(E_R + i\Gamma/2)] \\ \times G_0(\vec{r} - \vec{r}_1, -T) G_0(\vec{r}' - \vec{r}_2, t' + T - t) \\ \times \langle \hat{\rho}_{i'}(\vec{r}_1 + \vec{r}_4, T) \hat{\rho}_i(\vec{r}_2 + \vec{r}_3, T + t') \hat{\rho}_i(\vec{r}_3, t) \hat{\rho}_i(\vec{r}_4, 0) \rangle \Theta(t) \Theta(t') , \end{aligned} \quad (3.5)$$

where G_0 is the free propagator for the neutron

$$G_0(\bar{r} - \bar{r}', t) = \left(\frac{m}{2\pi i\hbar t} \right)^{3/2} \exp\left(\frac{-|\bar{r} - \bar{r}'|^2 m}{2i\hbar t} \right). \quad (3.6)$$

Equation (3.5) is the requisite formulation which shows that the "blurriness" associated with the Fourier-like integral (2.16) is given explicitly by an integration of the coordinates of the four-point dynamical correlation function with the neutron pro-

pagator function involved as an integral kernel.

Another suggestive form is obtained by absorbing the oscillatory part of the exponentials in Eq. (3.5), defining the neutron propagator for motion in a constant potential

$$R(\bar{r}, t) = e^{iE_R t} G_0(\bar{r}, t) \quad (3.7)$$

bringing the propagators inside the expectation brackets, and performing the spatial integrals over the density operators

$$\begin{aligned} \tilde{W}(\bar{r}, \bar{r}') &= \sum_{i, i'} \int dT dt dt' d^3 r_3 d^3 r_4 \exp[-i\Gamma/2(t+t')] \\ &\times \langle R(\bar{r} + \bar{r}_4 - \bar{r}_i, T), -T \rangle R(\bar{r}' + \bar{r}_3 - \bar{r}_i, T+t'), T+t'-t) \\ &\times \hat{\rho}_i(\bar{r}_3, t) \hat{\rho}_i(\bar{r}_4, 0) \Theta(t) \Theta(t'). \end{aligned} \quad (3.8)$$

The formulation (3.8) may be brought into a symmetric expression by introducing the propagator function for a particle of twice the mass of a neutron moving in a constant potential equal to half the energy of the excited nuclear state

$$R_{1/2}(\bar{r}, t) = e^{iE_R t/2} \left(\frac{m}{4\pi i\hbar t} \right)^{3/2} \exp\left(\frac{-|\bar{r}|^2 m}{4i\hbar t} \right). \quad (3.9)$$

Then it is seen by performing the requisite integrations that

$$\begin{aligned} \tilde{W}(\bar{r}, \bar{r}') &= \sum_{i, i'} \int dT dt dt' d^3 r_3 d^3 r_4 \exp[-i\Gamma/2(t+t')] \\ &\times \langle R_{1/2}(\bar{r} + \bar{r}_4 - \bar{r}_i, T), -T \rangle R_{1/2}(\bar{r}' + \bar{r}_3 - \bar{r}_i, T+t'), T+t'-t) \\ &\times R_{1/2}(\bar{r}_3 - \bar{r}_i, t), T+t'-t) \bar{R}_{1/2}(\bar{r}_4 - \bar{r}_i, 0), -T) \Theta(t) \Theta(t'). \end{aligned} \quad (3.10)$$

Equations (3.8) and (3.10) show that the blurriness is characterized by replacing propagator function densities (integrated over all times) for sharp Dirac δ function densities.

The connection between the space-space Fourier transform (3.3) and the more familiar space-time Fourier transform in thermal neutron scattering is found by letting Eq. (3.3) develop a time dependence.¹² Let the spherical harmonic component of

Eq. (3.3) be given by

$$\begin{aligned} R^m(\bar{r}, k_f) &= \int d^3 \Delta k e^{-i\Delta \bar{k} \cdot \bar{r}} \\ &\times \int d\Omega_k W(\bar{k}_0, \bar{k}_f) Y_l^m(\theta_k, \phi_k), \end{aligned} \quad (3.11)$$

where θ_k and ϕ_k are the angular coordinates of \bar{k}_f . Then Eq. (3.3) develops the time dependence

$$W(\bar{r}, \bar{r}', t) = \sum_{lm} \int dk_f 4\pi (-i)^l j_l(k_f |\bar{r}' - \bar{r}|) Y_l^m(\theta_{\bar{r}' - \bar{r}}, \phi_{\bar{r}' - \bar{r}}) \Pi_l^m(\bar{r}, t, k_f, \phi_k) \quad (3.12)$$

in such a way that in the short-collision-time limit,

$$W(\bar{r}, \bar{r}', t) = (2\pi)^3 \delta^3(\bar{r}' - \bar{r}) \int dE d^3 \Delta k e^{-i\Delta \bar{k} \cdot \bar{r}} \exp\left(\frac{iEt}{\hbar} \right) W(\bar{k}_0, \bar{k}_f). \quad (3.13)$$

The solution (3.12) is unique, and it involves a spherical harmonic analysis of the scattering law, rather than the scattering amplitude, which is more usual in scattering theory; the propagated spherical harmonic components in Eq. (3.12) are defined by

$$\Pi^m(\bar{r}, t, k_f, \phi_k) = \int d^3 r'' R^m(\bar{r}'', k_f) Q^m(\bar{r} - \bar{r}'', t, k_f, \phi_k) \quad (3.14)$$

where the propagator, Q^m is given by the convolution with the neutron propagator

$$Q^m(\bar{r}, t, k_f, \phi_k) = \int d^3 r'' \tilde{Z}_l^m(\bar{r}'', t, k_f, \phi_k) G_0(\bar{r} - \bar{r}'', t) \quad (3.15)$$

and the convolution kernel \tilde{Z} is given in terms of the Fourier transform of the Legendre function of the second kind

$$Z_l^m(t) = (-1)^m \frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!} \int_{-\infty}^{\infty} dE P_l^m(E) e^{iEt} \quad (3.16)$$

by

$$\tilde{Z}_l^m(\bar{r}, t, k_f, \phi_k) = \int d^3 \Delta k e^{-i\Delta \bar{k} \cdot \bar{r}} Z_l^m \left(\frac{\hbar k_f \Delta k}{m} t \right) \times \frac{\hbar^2}{m} (k_f \Delta k) e^{im\phi_k} \quad (3.17)$$

The above discussion shows how a certain blurriness enters the measurement of the four-point dynamical correlation functions, which is an important consideration quite apart from the physical interpretation and information content of the resonant correlation functions. The connection between the microscopic resonant space-space correlation functions (3.10) and the space-time correlation functions introduced by Van Hove is exhibited in Eq. (3.13); that the former span a six-dimensional parameter space implicitly suggests that they contain additional information about target-system dynamics; the physical content of the four-point dynamical correlation

functions will be examined in the next section, and more fully, in succeeding papers in this series.

IV. INFORMATION CONTENT OF THE RESONANT WIDTH PARAMETERS; THE DETERMINATION OF THE INTERATOMIC FORCE DENSITY LINE SHAPE VIA RESONANT NEUTRON SCATTERING

As we have shown in Sec. II, the resonant scattering law may be developed in a $1/\Delta E$ asymptotic expansion (i.e., a dual asymptotic expansion), the coefficients of which are related exactly to the resonant width parameters (2.38). The interpretation of the asymptotic coefficients is given by the theory in terms of microscopic dynamical correlation functions of target-system variables. It is most convenient to consider the dual asymptotic development of the scattering law W_i corresponding to the interference between resonant and potential scattering; the purely resonant asymptotic coefficients have more complicated time correlation function expressions which still involve higher orders of correlation. We may consider, for example, the determination of the interatomic force density time correlation function via the analysis of the interference term.

The deviation of the associated scattering law $W_i(\bar{k}_0, \bar{k}_f)$ from a strict Breit-Wigner line shape of width $\Gamma/2$ owing to Doppler broadening arising from the motions of the target nuclei can be expressed by writing the scattering law in a power series

$$W_i(E, \Delta \bar{k}, \Delta E', \phi_k) \sim 2 \operatorname{Re} \left[\sum_{n=1}^{\infty} a_n(E, \Delta \bar{k}, \phi_k) \left(\frac{i}{\Delta E'} \right)^n \right] \quad (4.1)$$

Thus, the coefficients a_n vary independently of the resonant parameter $\Delta E'$, so that they are analogous to the ordinary time correlation functions useful in thermal neutron scattering. For example, using the relations (2.37), (2.38), and (2.39), one finds that

$$\int_{-\infty}^{\infty} dz' W_i(E, \Delta \bar{k}, \Delta E', \phi_k) = 2\pi\hbar \operatorname{Re} \left[\sum_{li} \int_{-\infty}^{\infty} dT \exp \left(\frac{-i}{\hbar} ET \right) \langle \exp[i\Delta \bar{k} \cdot \bar{R}_l(T)] \exp[-i\Delta \bar{k} \cdot \bar{r}_l(0)] \rangle \right] \quad (4.2)$$

(where $z' = \Delta E' - i\Gamma/2$); thus, the total area under the resonance as a function of E and $\Delta \bar{k}$ (for the interference term) simply reproduces the nonresonant (interference) scattering law.

However, owing to kinematical considerations of the kind considered in Sec. III, the coefficients a_n in Eq. (4.1) are not correctly obtained by superficially

equating them with the corresponding coefficients of powers of $1/\Delta E'$ in Eq. (2.39); indeed, the study of anisotropic samples requires some generalization of the asymptotic development (4.1) to account for odd powers of k_f in Eq. (2.39), which we do not consider here. The variable θ_k (the angle between $\Delta \bar{k}$ and \bar{k}_f) is not independent of E , $\Delta \bar{k}$, or k_f ; it satisfies

the relation

$$\cos\theta_k = \frac{2mE/\hbar^2 + |\Delta k|^2}{2|k_f||\Delta k|} \quad (4.3)$$

The variation of θ_k must be extracted from the coefficients in Eq. (2.39) in order to obtain their correct placement in Eq. (4.1); this extraction may be accomplished by introducing the spherical harmonic components of the various dynamical correlation functions.

Consider, for example, the term in Eq. (2.39) involving the force, which may be written in the form

$$\begin{aligned} & \langle \exp[i\Delta\vec{k} \cdot \vec{R}_i(T)] [\vec{k}_f \cdot \vec{F}_i(0)] \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle \\ &= \int \int d^3r_1 d^3r_2 \exp[i\Delta\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)] \\ & \quad \times \langle \hat{\rho}_i(\vec{r}_1, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(\vec{r}_2, 0) \rangle, \quad (4.4) \end{aligned}$$

which is the Fourier transform of the dynamical force density correlation function. By virtue of the assumption of spatial isotropy, the latter quantity must

satisfy the symmetry conditions

$$\begin{aligned} & \langle \hat{\rho}_i(\vec{r}_1, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(\vec{r}_2, 0) \rangle \\ &= \langle \hat{\rho}_i(\vec{r}_1 - \vec{r}_2, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(0, 0) \rangle, \quad (4.5a) \end{aligned}$$

$$\begin{aligned} & \langle \hat{\rho}_i(\vec{r}_1, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(0, 0) \rangle \\ &= -\langle \hat{\rho}_i(-\vec{r}_1, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(0, 0) \rangle. \quad (4.5b) \end{aligned}$$

The symmetry condition (4.5b) requires that the Fourier transform (4.4) must be purely imaginary [so that its contribution to Eq. (2.39) is purely real]; clearly it is in general nonzero. The isotropy of the sample requires that Eq. (4.5) must transform as an $l=1$ spherical harmonic with $m=0$ along the \vec{k}_f axis; i.e., it may be written in the form

$$\langle \hat{\rho}_i(\vec{r}, T) [\vec{k}_f \cdot \vec{F}_i(0)] \hat{\rho}_i(0, 0) \rangle = Z(r, T) \cos\theta_r, \quad (4.6)$$

where θ_r is the angle between \vec{r} and \vec{k}_f . Expanding plane waves in terms of spherical harmonics and spherical Bessel functions, the Fourier transform of Eq. (5.4) becomes

$$\sqrt{4\pi/3} \int d^3r Z(r, T) \sum_{l=0}^{\infty} 4\pi i^l j_l(r\Delta k) \sum_{m=-l} Y_l^{m*}(\theta_k, \phi_k) Y_l^m(\theta_r, \phi_r) Y_l^0(\theta_r, \phi_r) = 4\pi i \cos\theta_k \int_0^{\infty} dr Z(r, T) j_1(r\Delta k). \quad (4.7)$$

Hence, it is seen that Eq. (4.4) may be rewritten in the form

$$\begin{aligned} & \langle \exp[i\Delta\vec{k} \cdot \vec{R}_i(T)] [\vec{k}_f \cdot \vec{F}_i(0)] \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle = \int \int d^3r_1 d^3r_2 \exp[i\Delta\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)] \\ & \quad \times \frac{2mE/\hbar^2 + |\Delta k|^2}{2|\Delta k|^2} \langle \hat{\rho}_i(\vec{r}_1, T) [\Delta\vec{k} \cdot \vec{F}_i(0)] \hat{\rho}_i(\vec{r}_2, 0) \rangle. \quad (4.8) \end{aligned}$$

Thus, it is seen that the dynamical force density correlation function is indeed given its correct placement in a_3 , by virtue of the relations (4.7) and (4.8), in which the variation of θ_k has been extracted. An identical argument may be applied to the second term in Eq. (2.39) (which is a dynamical momentum density term). But the square momentum density correlation function must be handled somewhat differently, since it may contain Y_0^0 and Y_2^0 components. Although the more general formulation may be easily written out, for the sake of simplicity, we will assume that equipartition among the various components of momentum is perfect, so that only the Y_0^0 component occurs; (by virtue of the equipartition theorem, this should be an excellent approximation). Then the dynamical square momentum density correlation function can be written

$$\begin{aligned} & -\frac{1}{4} i\hbar^3 \langle \exp[i\Delta\vec{k} \cdot \vec{R}_i(T)] [\vec{k}_f/M \cdot \vec{p}_i(0)]^2 \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle \\ &= -\frac{1}{2} i\hbar \Delta E' m \langle \exp[i\Delta\vec{k} \cdot \vec{R}_i(T)] [p_{i\alpha}(0)/M]^2 \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle \\ & \quad -\frac{1}{2} (E_R + i\Gamma/2) i\hbar m \langle \exp[i\Delta\vec{k} \cdot \vec{R}_i(T)] [\vec{p}_i(0)/M]^2 \exp[-i\Delta\vec{k} \cdot \vec{r}_i(0)] \rangle, \quad (4.9) \end{aligned}$$

where $\vec{p}_{i\alpha}$ is any component of the momentum \vec{p}_i . The equation (4.9) shows that the dynamical square momentum density correlation function contributes to both a_2 and a_3 . Hence, the three leading-order coefficients of Eq.

(4.1) may be written in the form

$$\begin{aligned}
 a_1 &= \frac{\hbar}{i} \sum_{li} \int_{-\infty}^{\infty} dT \exp\left[\frac{-i}{\hbar} ET\right] \int \int d^3r_1 d^3r_2 \exp[i\Delta\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)] \langle \hat{\rho}_l(\vec{r}_1, T) \hat{\rho}_l(\vec{r}_2, 0) \rangle, \\
 a_2 &= \sum_{li} \int_{-\infty}^{\infty} dT \exp\left[\frac{-i}{\hbar} ET\right] \int \int d^3r_1 d^3r_2 \exp[i\Delta\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)] \\
 &\quad \times \left[i \frac{2mE + \hbar^2 |\Delta\vec{k}|^2}{2|\Delta\vec{k}|^2} \langle \hat{\rho}_l(\vec{r}_1, T) \left[i \frac{\Delta\vec{k}}{M} \cdot \vec{p}_l(0) \right] \hat{\rho}_l(\vec{r}_2, 0) \rangle \right. \\
 &\quad \left. - \frac{1}{2} \hbar m \langle \hat{\rho}_l(\vec{r}_1, T) \left[\frac{\vec{p}_{l\alpha}(0)}{M} \right]^2 \hat{\rho}_l(\vec{r}_2, 0) \rangle \right], \\
 a_3 &= \sum_{li} \int_{-\infty}^{\infty} dT \exp\left[\frac{-i}{\hbar} ET\right] \int \int d^3r_1 d^3r_2 \exp[i\Delta\vec{k} \cdot (\vec{r}_1 - \vec{r}_2)] \\
 &\quad \times \left[-\frac{\hbar^3}{4M} \langle \hat{\rho}_l(\vec{r}_1, T) [i\vec{k}_f \cdot \vec{F}_l(0)] \hat{\rho}_l(\vec{r}_2, 0) \rangle \right. \\
 &\quad \left. - \frac{1}{2} \hbar m \left[E_R + i\frac{\Gamma}{2} \right] \langle \hat{\rho}_l(\vec{r}_1, T) \left[\frac{\vec{p}_{l\alpha}}{M} \right]^2 \hat{\rho}_l(\vec{r}_2, 0) \rangle \right]. \tag{4.10}
 \end{aligned}$$

The assumption of spatial isotropy requires that the coefficient a_1 in the above expression must be purely imaginary; the information in it is fully extracted from the scattering law by the use of the relation (4.2); i.e., the area under the resonance as a function of E and $\Delta\vec{k}$ is proportional to the Fourier transform of the usual two time correlation functions. More generally, for anisotropic samples, a_1 must have both a real and an imaginary part, owing to quantum-mechanical effects; the imaginary part is then exactly given once again by the relation (4.2), but the real part of a_1 is given exactly by the limit of $zW_l(z)$ as z goes to infinity. Alternatively, it is obtained by retaining only the leading order term in the asymptotic approximation to the scattering law (4.1); the latter point of view may be visualized by noting that the phase of the Breit-Wigner scattering amplitude varies rapidly from 0 to π through the resonance, so that the interference term gives the phase of the two time correlation function (4.2). Thus, for example, the phase problem in neutron crystallography may be solved by chemically attaching resonant scatterers, and measuring the intensity of Bragg reflections as a function of z ; however, this simple picture is not ex-

act [since the first term in Eq. (4.1) is only an approximation to the scattering law]. An exact measurement of the phase of the static structure factor by this method requires more careful consideration, which we will take up elsewhere. Again, this approach promises to yield phase information about phonon eigenmodes, and we will treat this problem carefully in the next paper in this series. For the present, we consider isotropic samples only.

The quantities a_2 and a_3 have both real and imaginary parts [which are obtained experimentally from the generalized width parameters (2.38) by virtue of the relation (2.37), or by using an asymptotic approximation (4.1)]. The real part of a_2 and the imaginary part of a_3 are both simply proportional to the dynamical square momentum density correlation function; thus, its determination may be doubly checked. The subtraction of the real contribution of the dynamical square momentum density correlation function to a_3 then yields the dynamical force density correlation function. The Fourier transform [which by virtue of the extraction (4.8) may be performed in the usual way] of the latter quantity to microscopic target system variables is given by

$$\begin{aligned}
 F_d(\vec{r}, T) &= \left[\frac{1}{2\pi} \right]^4 \int_{-\infty}^{\infty} d\omega e^{i\omega T} \int d^3\Delta k e^{-i\Delta\vec{k} \cdot \vec{r}} \\
 &\quad \times \left(\sum_{li} \int_{-\infty}^{\infty} dT' e^{-i\omega T'} \int d^3r' e^{i\Delta\vec{k} \cdot \vec{r}'} \langle \hat{\rho}_l(\vec{r}', T') [i\Delta\vec{k} \cdot \vec{F}_l(0)] \hat{\rho}_l(0, 0) \rangle \right) \\
 &= \vec{\nabla} \cdot \sum_{li} \langle \hat{\rho}_l(\vec{r}, T) \vec{F}_l(0) \hat{\rho}_l(0, 0) \rangle, \tag{4.11}
 \end{aligned}$$

where ω is E/\hbar . The formula (4.11) is analogous to a result obtained by de Gennes^{20,21} for thermal neutron scattering, who showed that the fourth moment (in the parameter E) in a Placzek expansion of the scattering law contains a term proportional to the second derivative of the interatomic interaction potential. De Gennes made the approximation of interpreting the quantum-mechanical operators as classical random variables; if the same approximation is applied to Eq. (4.11), it becomes identical at $T=0$ to the quantity found by de Gennes; but since we consider the interference scattering law, it is found in the second moment of the resonant line shape [as given by Eqs. (2.37) and (2.38)]. Epithermal resonances typically have widths of the order 0.1 eV, hence the determination of the quantity (4.11) is not plagued by the difficulties associated with the resolution of the quasielastic line shape which is required for the corresponding measurement in thermal neutron scattering. Moreover, Eq. (4.11) is a more general quantity, since it has a T dependence: the associated correlation may be followed in time; this is an interesting result, since the interatomic motion is in large measure due to the pair interaction potential. Since the wave vector of the epithermal neutron is of the order 10 \AA^{-1} , Eq. (4.11) shows that resonant neutron scattering studies hold the promise of probing the nature of the chemical bond in its correlations with interatomic motion. We note in passing that the real part of a_3 (with the subtraction of the square momentum part) is convoluted as shown in Eq. (4.8):

$$a_3'(\vec{r}, T) = \frac{-Vh^3}{4M} \left[\frac{1}{2} F_d(\vec{r}, T) - \frac{im}{2\pi^2\hbar} \frac{d}{dT} \times \int d^3r' \frac{F_d(\vec{r}', T)}{|\vec{r} - \vec{r}'|} \right], \quad (4.12)$$

where V is the volume of the sample. Thus, the second moment of $W_i(z)$ also has a contribution proportional to the second term in Eq. (4.12); but the deconvolution is easily performed by extracting the factor $\cos(\theta_k)$ from $a_3'(\Delta\vec{k}, E)$, which upon transformation gives directly the force density (4.11).

The dynamical momentum density correlation function may be measured in experiment by taking the real part of a_2 , as given in the formula (4.10). The Fourier properties of this quantity are exactly the same as those for the force density, which are shown in Eqs. (4.11) and (4.12). The coefficient $\text{Re}(a_2)$ is seen to be a quantity of interest in transport theory, but we shall not dwell further on it here.

Next, we shall consider the practical feasibility of measuring the force density correlation function in an experiment by computing its contribution to the scattering law relative to a_1 in a simple model. Let us take, for example, the case of PuO_2 , in which the chief contribution to the interatomic force density

arises from the chemical bond between the plutonium and oxygen atoms.

The ratio between the interference term and the coherent potential scattering term in the differential scattering cross section is given by

$$r = \frac{\Gamma_n}{\Delta E'} \frac{b}{2k_0} \frac{N_i}{N_l},$$

with neglect of the difference in variation of the respective correlation functions, where N_i and N_l are, respectively, the molar concentrations of the resonant and nonresonant scattering centers. If we use for the value of the coherent scattering length of oxygen $b = 0.58 \times 10^{-12} \text{ cm}$, we find that with a 1 at.% concentration of the resonantly scattering isotope of plutonium that the interference and purely resonant terms contribute, respectively, about 10% and 1% of the scattering cross section at the center of the resonance. The variation of the cross section with molar concentration of the respective isotopes is given by

$$\Delta_{\text{cs}} \sim N_l^2 f_a^{\alpha\alpha} + N_l f_b^{\alpha\alpha} + N_l N_i f_a^{\alpha\beta} + N_l f_b^{\beta\beta} + N_i^2 f_a^{\beta\beta}, \quad (4.13)$$

where α and β refer to resonant and nonresonant scattering, respectively, and a and b refer to coherent and incoherent scattering, respectively; the N 's are molar concentrations, and the f 's refer to the respective scattering laws for which separation is desired. Thus, concentration analysis easily suffices to separate the terms of interest; hereafter, we shall refer only to the nonresonant (potential scattering) and resonant plutonium interference terms.

We consider molten PuO_2 so that the dynamical structure factor is characterized by diffusive motions of the PuO_2 molecule. (PuO_2 melts at about 2390°C .²²) From the experimental point of view, this material is a poor choice to consider in view of the difficulty of maintaining the sample in the liquid state; but it is useful for the purpose of a theoretical feasibility estimate, since the force density is typical of that of any chemically bonded compound, while the square momentum density, which tends to spoil the feasibility of measuring the force density, is taken in a worst case example.

We compute the correlation functions in the convolution approximation first introduced by Vineyard.²³ It is difficult to know the error in this approximation without recourse to experiment, but it should suffice for the purpose of our feasibility estimate. Of course, the requisite correlation functions can be computed (for some assumed interaction potential) via computer-generated molecular-dynamics simulations,²⁴ but such an effort is not required for our purpose here. In the convolution approximation, the time correlation functions are propagated forward in time via the self diffusive propagator $w(\vec{r}, T)$ for the PuO_2 molecule

$$\langle \hat{\rho}_l(\vec{r}, T) \hat{\rho}_i(0, 0) \rangle = \int d^3 r' w(\vec{r} - \vec{r}', T) \langle \hat{\rho}_l(\vec{r}', 0) \hat{\rho}_i(0, 0) \rangle, \quad (4.14)$$

$$\langle \hat{\rho}_l(\vec{r}, T) \vec{F}_i(0) \hat{\rho}_i(0, 0) \rangle = \int d^3 r' W(\vec{r} - \vec{r}', T) \langle \hat{\rho}_l(\vec{r}', 0) \vec{F}_i(0) \hat{\rho}_i(0, 0) \rangle. \quad (4.15)$$

By the consideration of time reversal invariance, the momentum density correlation function is necessarily zero at $T=0$, and in the convolution approximation, it can develop no subsequent correlation; thus, it is set equal to zero in our model. Next we assume that the square momentum is decoupled in its correlation function, and that it takes on the canonical value M/β associated with the kinetic energy of the plutonium nucleus, so that

$$\begin{aligned} \langle \hat{\rho}_l(\vec{r}, T) \left(\frac{\vec{p}_{l\alpha}}{M} \right)^2 \hat{\rho}_i(0, 0) \rangle \\ = \frac{1}{M\beta} \langle \hat{\rho}_l(\vec{r}, T) \hat{\rho}_i(0, 0) \rangle. \end{aligned} \quad (4.16)$$

The approximation (4.16) is equivalent to treating the momentum as a classical random variable, and assigning the square momentum its equipartition value; thus, it should be an excellent approximation for the system under consideration.

The static pair distribution function in the convolution integral on the right-hand side of Eq. (4.14) [which we will denote without exhibiting the functional arguments explicitly by the notation $g(l, i)$] may be expressed in terms of the direct correlation $c(l, i)$ between the two atoms, where $c(l, i)$ is the interatomic correlation in the absence of the remaining atoms²⁵

$$g(l, i) = c(l, i) + \sum_{j \neq i} \frac{1}{n} \int d^3 r_j g(i, j) c(l, j), \quad (4.17)$$

where the summation in j is over the remaining plu-

tonium atoms in the sample, and n is the atomic density of plutonium. If l and i denote a chemically bonded pair, then all the direct correlations $c(l, j)$ on the right-hand side of Eq. (4.17) are between unbonded pairs, and hence they are negligible. Therefore, for a bonded pair, the static density correlation function is given to an excellent approximation by

$$g(l, i) = c(l, i). \quad (4.18)$$

Thus, the static density-density correlation function is given to an excellent approximation by the lowest-order term in a cluster expansion (corresponding to the direct correlation):

$$\sum_{l, i} \langle \hat{\rho}_l(\vec{r}, 0) \rho_i(0, 0) \rangle \sim e^{-\beta U(r)}, \quad (4.19)$$

where U is the interatomic potential between the plutonium and oxygen atoms.

The classical interpretation of the static force density correlation function is given by

$$\begin{aligned} \langle \hat{\rho}_l(\vec{r}, 0) \vec{F}_i \hat{\rho}_i(0, 0) \rangle \\ = \vec{F}_i \langle \hat{\rho}_l(\vec{r}, 0) \hat{\rho}_i(0, 0) \rangle, \end{aligned} \quad (4.20)$$

where \vec{F}_i is an effective screened force arising from the remaining interactions in the fluid. Here l and i refer once again to a bonded pair, and in accordance with the above discussion, we substitute the direct interaction for the screened force.

Utilizing the convolution theorem, the interference term (4.1) is given to leading orders of $1/\Delta E'$ by

$$\begin{aligned} W_i \sim 2 \operatorname{Re} \left\{ \frac{2|\Delta k|^2 D C_l C_i}{(E/\hbar)^2 + (|\Delta k|^2 D)^2} \right\} & \left(\frac{\hbar}{i\Delta E'} \rho(\Delta \vec{k}) - \frac{1}{2} i\hbar \frac{m}{M\beta} \frac{1}{\Delta E'^2} \rho(\Delta \vec{k}) - \frac{1}{2} i\hbar \frac{m}{M\beta} \frac{E_R + i\Gamma/2}{\Delta E'^3} \rho(\Delta \vec{k}) \right. \\ & \left. - \frac{i\hbar^3}{4M} \frac{2mE/\hbar^2 + |\Delta k|^2}{2|\Delta k|} \frac{1}{\Delta E'^3} \rho_F(\Delta \vec{k}) \right), \end{aligned} \quad (4.21)$$

where D is the diffusion constant for the PuO_2 molecule, C_l and C_i are the atomic concentrations of O and Pu^{240} ,

respectively, and the Fourier transforms are given by

$$\rho(\Delta\vec{k}) = \sum_{ii} \int d^3r \langle \bar{\rho}_i(\vec{r}, 0) \hat{\rho}_i(0, 0) \rangle e^{i\Delta\vec{k} \cdot \vec{r}} , \quad (4.22)$$

$$\rho_F(\Delta\vec{k}) = \sum_{ii} \int d^3r \langle \hat{\rho}_i(\vec{r}, 0) \bar{F}_i(0) \cdot \frac{\Delta\vec{k}}{|\Delta\vec{k}|} \hat{\rho}_i(0, 0) \rangle e^{i\Delta\vec{k} \cdot \vec{r}} .$$

In accordance with the theorem of Stieltjes, the error in Eq. (4.21) is in the last term, so that it is a poor approximation just when the force density effect for which extraction is sought is large; but in spite of this, it is clearly useful for the purpose of estimating the relative order of magnitude of the contributions of the respective effects. [When the force density term is much larger than the leading order terms in Eq. (4.21), it is necessary to include succeeding terms in the asymptotic expansion in a least-squares fit against experimental data; or, if this fails, one must generate the width parameters of the resonant line shape, which bear an exact relation to the force density contribution, as previously indicated.] We note also that the quasielastic peak is considerably broadened for the large momentum transfers Δk required to probe the interatomic variation. Thus, assuming the same degree of absolute resolution in the epithermal region as in the thermal region, it is easier to obtain information on the T variation in the resonant epithermal regime than in the case of the thermal regime. (But the resolution of the energy of the epithermal neutron is a nontrivial problem on which progress is still being made²⁶; it is to be hoped that high resolutions in the epithermal region will ultimately be obtainable.)

We fit the oxygen-plutonium interaction with a Morse potential

$$U(r) = \bar{D}(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) . \quad (4.23)$$

The force constant for PuO_2 has been measured to be about 675×10^3 dynes/cm.²⁷ Using the empirical chemical relation²⁸

$$|\chi_{\text{O}} - \chi_{\text{Pu}}|^2 = \Delta/96, \quad \chi_{\text{O}} = 3.50, \quad \chi_{\text{Pu}} = 1.22 , \quad (4.24)$$

where χ_{O} and χ_{Pu} are the electronegativities of the oxygen and plutonium atoms, respectively, and Δ is the dissociation energy in kJ per mole of bond, we may estimate the value $\bar{D} = 2.6$ eV, which requires $a = 3.04 \text{ \AA}^{-1}$ in order to fit Eq. (4.23) to the value of the force constant. We may estimate r_0 by the sum of the respective ionic radii of plutonium and oxygen to be 2.21 \AA . In our model, the ratio of the density contributions to W_i in a_2 and a_3 to that of the leading-order term depends only upon $\Delta E'$; hence we do not plot these quantities but we caption them as

the parameters $d_2(\Delta E')$ and $d_3(\Delta E')$, respectively.

Figure 1 is a plot of the density-density and force-density correlation functions in our model. Figures 2(a) and 2(b) are plots of the Fourier transforms of these quantities. Figure 3 contains a number of constant $E, \Delta E'$ plots of the respective contributions to the double differential scattering cross section of the two terms as a function of Δk . Figure 4 is a constant $E, \Delta k$ plot as a function of E' ; it shows the variation in the magnitudes of the density-density and force-density contributions which must be used to separate the two kinds of terms.

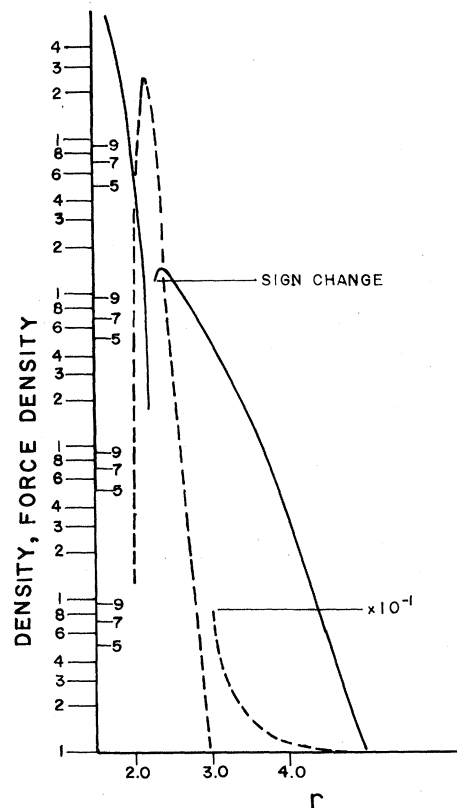


FIG. 1. Plot of oxygen-plutonium density-density (broken) and force-density (solid) line shapes in PuO_2 as a function of r measured in angstroms. The computation was performed for a temperature of 2400°C .

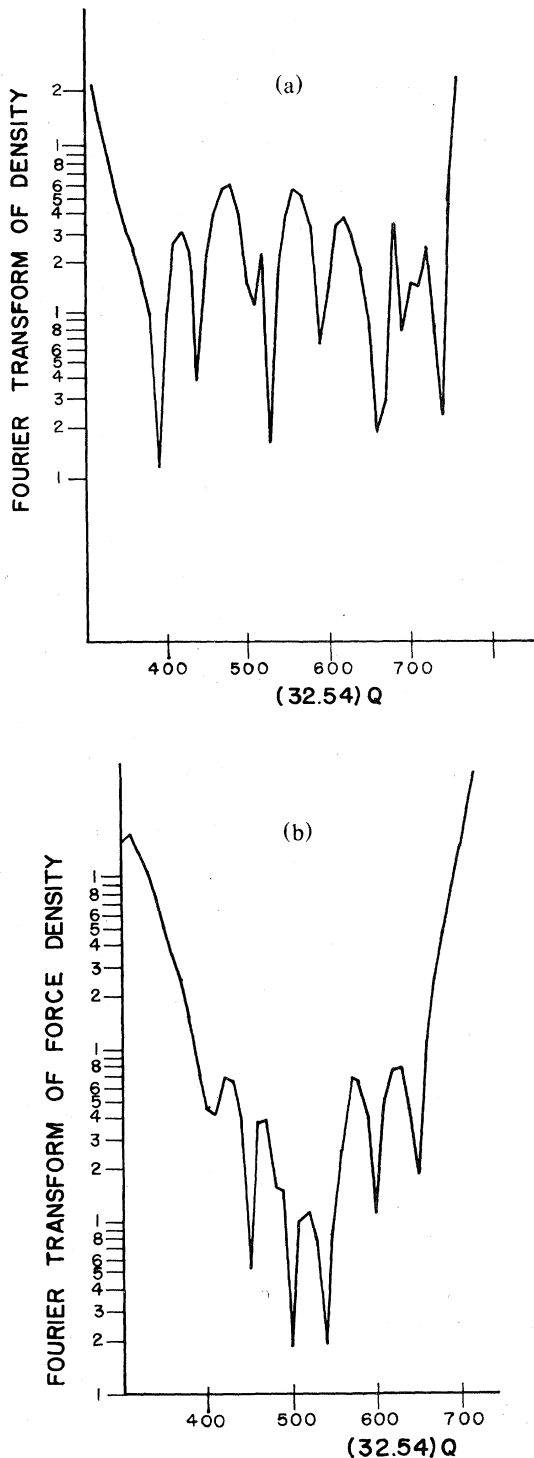


FIG. 2. Plots of the Fourier transforms of the correlation functions as a function of Q^{-1} measured in units of $(1/32.54)$ inverse angstroms. (a) Fourier transform of the density-density correlation function. (b) Fourier transform of the force-density correlation function.

Our computations show that the ratio of the contribution of the force density term to that of the density-density term in Eq. (4.1) varies between 10^3 and 10^{-3} depending upon the values of the parameters E , Δk , and $\Delta E'$. This is a large effect, and it should be worthwhile to investigate it experimentally; the square momentum contribution to Eq. (4.1) is never larger than 10% of the leading order term in this worst case example, so that its presence clearly does not interfere with the measurement of the force-density correlation function.

Experiments of this type require good high-flux sources of epithermal neutrons, such as will be provided by the pulsed neutron sources in planning.²⁹ The IPNS-II and the WNR+PSR-II are designed to produce a flux of 10^{17} $n/cm^2 sec eV$, so that in spite of the additional resolution of the independent parameter ΔE required for resonant epithermal neutron scattering experiments, the availability of the pulsed sources should make possible the rapid performance of the resonant experiments.

V. CONCLUSION

Resonant neutron scattering represents a new regime for the study of the properties of condensed matter. The arrival of spallation sources on the scene opens up the real possibility of doing experiments along these lines.

The resonant neutron scattering cross section involves orders of correlation for target-system variables which are of higher order than the two-time correlation functions which are related to the thermal neutron scattering law. These resonant correlation functions span a six-dimensional parameter space, in distinction from the two-time correlation functions, which span a four-dimensional parameter space. A certain blurriness enters the transformation of the resonant scattering law to microscopic target-system variables, which is characterized by the substitution of propagator densities for sharp Dirac δ densities in the requisite four-point dynamical correlation function. But the higher dimensionality of the resonant correlation functions suggests that they contain information beyond that which is contained in the familiar two-time correlation functions.

Resonant neutron scattering is a process in which the target nucleus executes dynamical motions under the influence of its environment for the finite duration of the scattering interaction. In the limit of infinitely short lifetime of the excited nuclear state, the resonant result goes over to the Van Hove formula; an asymptotic expansion for the resonant scattering law (the coefficients of which are related exactly to the resonant width parameters which characterize Doppler broadening) about the short-collision-time limit shows that the resonant correlation functions in-

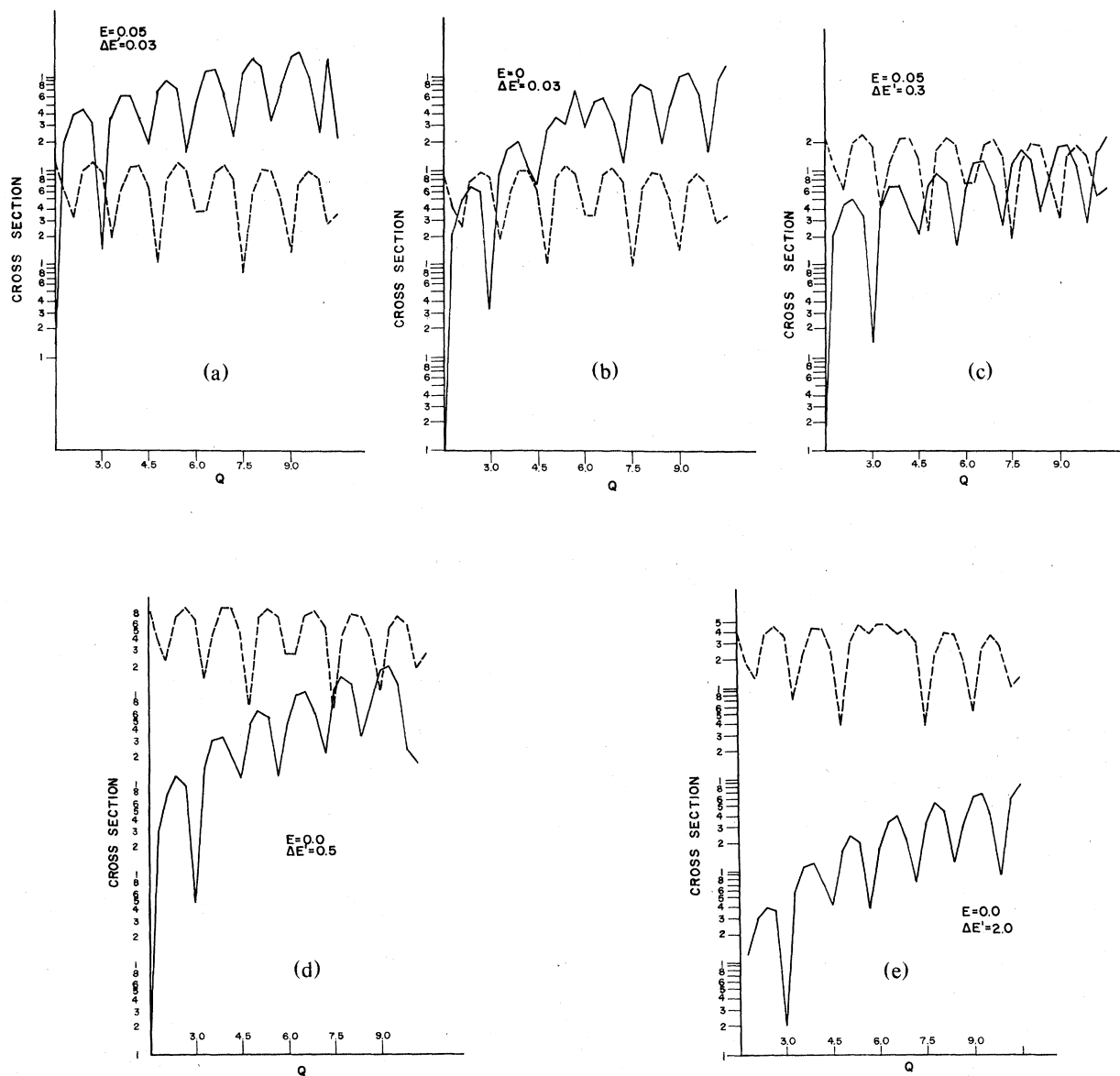


FIG. 3. Plots of constant E , $\Delta E'$ scans of the contributions of the density-density (broken) and the force-density (solid) contributions to the cross section in arbitrary units as a function of $|\Delta k| = Q$ measured in units of inverse angstroms. The energies are given in eV; the real part of $\Delta E'$ is tabulated. (a) $E = 0.05$, $\Delta E' = 0.03$, $d_2 = 1.78\%$, $d_3 = 5.48\%$. (b) $E = 0.0$, $\Delta E' = 0.03$, $d_2 = 1.78\%$, $d_3 = 5.48\%$. (c) $E = 0.05$, $\Delta E' = 0.30$, $d_2 = 3.18\%$, $d_3 = 0.526\%$. (d) $E = 0.0$, $\Delta E' = 0.50$, $d_2 = 0.191\%$, $d_3 = 0.191\%$. (e) $E = 0.0$, $\Delta E' = 2.0$, $d_2 = 0.048\%$, $d_3 = 0.012\%$.

involve additional dynamical variables. In particular, the second moment of the scattering law corresponding to interference between resonant and potential scattering involves a time-dependent force density correlation function (which is analogous to a result obtained by de Gennes in thermal neutron scatter-

ing). The typical resonant neutron interaction time is an interval over which many typical microscopic condensed matter processes occur; thus, the resonant modifications of the Van Hove result give rise to large effects which enable one to probe more deeply into condensed matter. For example, in PuO_2 , the

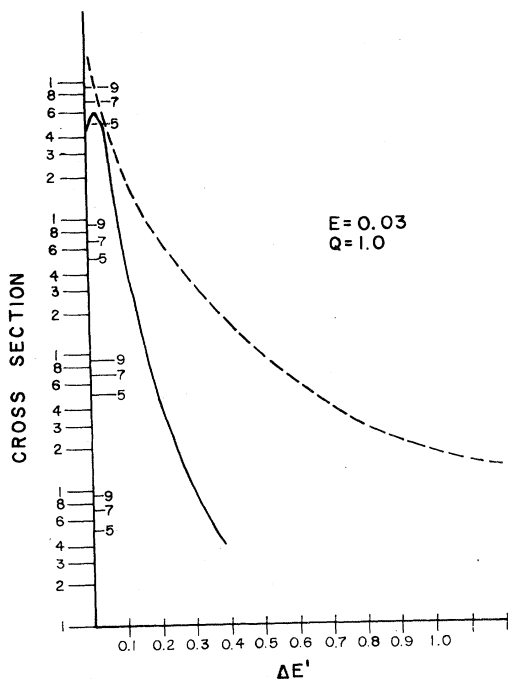


FIG. 4. Constant E , $|\Delta k|$ scan of the respective contributions to the scattering cross section as a function of $\Delta E'$ in eV; $E = 0.03$ eV, $Q = 1 \text{ \AA}^{-1}$.

force density contribution to the scattering cross section varies between 10^3 and 10^{-3} of the magnitude of the leading-order density-density contribution with adjustment of external parameters; the time-dependent force density correlation function may be easily separated from the remaining contributions to the scattering law. This is a large effect, and it should be worthwhile to investigate it experimentally.

In future papers in this series, we shall show that it is possible to obtain the amplitudes of specific phonon anharmonic processes of cubic order via resonant neutron studies.³⁰ In the case of diffusion, we shall show that it is possible to obtain information on higher order diffusive propagators associated with the conditional diffusion of a particle over distinct intervals of space and time. In the case of molecular diffusion, the novel result which we shall show is that one may obtain information on the diffusion of those molecules which are selected to be in some definite state of vibrational excitation.

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- ¹W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, Oxford, 1971).
- ²L. Van Hove, *Phys. Rev.* **95**, 249 (1954).
- ³N. Bohr, *Nature* **137**, 344 (1936).
- ⁴G. Breit and E. Wigner, *Phys. Rev.* **49**, 519 (1936).
- ⁵D. J. Hughs and R. Schwartz, *Neutron Cross Sections* (Brookhaven National Laboratory Report No. BNL-325, U.S. Government Printing Office, Washington, D.C., 1958).
- ⁶G. T. Trammell, *Phys. Rev.* **126**, 1046 (1962).
- ⁷J. P. Hannon and G. T. Trammell, *Phys. Rev.* **186**, 306 (1969).
- ⁸Y. Kagan and A. M. Afanes'ev, *Sov. Phys. JETP* **22**, 1032 (1966).
- ⁹W. E. Lamb, *Phys. Rev.* **55**, 190 (1939).
- ¹⁰S. A. Werner, *Proceedings of the 1977 Particle Accelerator Conference* (IEEE, Chicago, Illinois, 1977).
- ¹¹G. T. Trammell and J. D. Chalk, *Phys. Rev.* **141**, 815 (1966).
- ¹²R. E. Word, *The Fourier-like Properties of the Resonant (n, n) Scattering Law $W(k_0, k_f)$ in the Single Collision Approximation* (in press).
- ¹³A. J. F. Boyle and H. E. Hall, *Rep. Prog. Phys.* **25**, 441, (1962).
- ¹⁴G. Placzek, *Phys. Rev.* **86**, 377 (1952).
- ¹⁵H. Poincare, *Acta Math.* **8**, 295 (1886).

- ¹⁶R. B. Dingle, *Asymptotic Expansions: Their Derivation and Interpretation* (Academic, London, 1973).
- ¹⁷W. B. Ford, *Studies on Divergent Series and Summability* (Macmillan, New York, 1916).
- ¹⁸T. J. Stieltjes, *Ann. Sci. Ecole Norm. Suppl.* **3**, 201 (1886).
- ¹⁹M. J. Lighthill, *Fourier Analysis and Generalized Functions* (Cambridge University Press, Cambridge, 1960).
- ²⁰P. G. de Gennes, *Physica (Utrecht)* **25**, 825 (1959).
- ²¹S. W. Lovesey and T. Springer, *Dynamics of Solids and Liquids by Neutron Scattering* (Springer-Verlag, New York, 1977).
- ²²W. L. Lyon and W. E. Bailey, *J. Nucl. Mater.* **22**, 332 (1967).
- ²³H. Vineyard, *Phys. Rev.* **110**, 999 (1958).
- ²⁴P. Lykos, *Computer Modeling of Matter* (American Chemical Society, Washington, D.C., 1978).
- ²⁵Clive Croxton, *Progress in Liquid Physics* (Wiley, New York, 1978).
- ²⁶W. Brugger (private communication).
- ²⁷K. Ohwada, *Spectrochim. Acta* **24A**, 97, (1968).
- ²⁸J. E. Huheey, *Inorganic Chemistry* (Harper and Row, New York, 1978).
- ²⁹J. M. Carpenter, T. H. Blewitt, D. L. Price, and S. A. Werner, *Phys. Today* **32** No. 12, 42 (1979).
- ³⁰R. E. Word, Ph.D. thesis (Rice University, 1979) (unpublished).