The Mathematical Foundations of Neutron Scattering

In 1954 Van Hove derived a general expression for the intensity, $I(\mathbf{Q}, \epsilon)$, of neutrons scattered by any assembly of nuclei. His result makes use of Fermi observation that the actual interaction between a neutron and a nucleus may be replaced by an effective potential that is much weaker than the actual interaction. This pseudo-potential causes the same scattering as the actual interaction but is weak enough to be used in the perturbation expansion derived by Max Born. The Born approximation says that the probability of an incident plane wave of wave vector k being scattered by a weak potential V (r) to become an outgoing plane wave with wave vector **k’** is proportional to

$$\left\| \int e^{i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) e^{-i\mathbf{k}'\cdot\mathbf{r}} d^3r \right\|^2 = \left| \int e^{i\mathbf{Q}\cdot\mathbf{r}} V(\mathbf{r})\, d^3r \right|^2, \tag{1}$$

where the integration is over the volume of the scattering sample. (We should note that even though individual nuclei scatter spherically, $V(\mathbf{r})$ represents the potential due to the entire sample, and the resulting disturbance for the assembly of’ atoms is a plane wave.)

The potential to be used in Eq. 1 is Fermi’s pseudo-potential. which, for a single nucleus, is given by $b_j \delta(\mathbf{r} - \mathbf{r}_j)$, where b_j is the scattering length of a nucleus labeled j located at position $\mathbf{r}_j$ and δ is a Dirac delta function that is zero unless the position vector **r** coincides with r_j. Thus, for an assembly of nuclei, such as a crystal, the potential V **(r)** is the sum of individual neutron-nuclei interactions:

$$V(\mathbf{r}) = \sum_j b_j \delta(\mathbf{r} - \mathbf{r}_j), \tag{2}$$

where the summation is over all the nuclear sites in the crystal.

Using Eqs. 1 and 2, Van Hove was able to show that the scattering law—that is, the number of neutrons scattered per incident neutron-can be written as

$$I(\mathbf{Q}, \epsilon) = \frac{1}{h}\frac{k'}{k} \sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \langle e^{-i\mathbf{Q}\cdot\mathbf{r}_k(0)} e^{i\mathbf{Q}\cdot\mathbf{r}_j(t)} \rangle e^{-i\epsilon t}\, dt. \tag{3}$$

Note that the sum here is over *pairs* of nuclei *j* and *k* and that the nucleus labeled j is at position r;(f) at time *t*, whereas the nucleus labeled *k* is at position $\mathbf{r}_k(\mathbf{0})$ at time $t = 0$. The angular brackets (. .) denote an average over all possible starting times for observations of the system, which is equivalent to an average over all the possible thermodynamic states of the sample.

The position vectors $\mathbf{r}_j$ in Eq. 3 are quantum-mechanical operators that have to be manipulated carefully. Nevertheless, it is instructive to ignore this subtlety and treat the equation as if it described a system obeying classical mechanics because such an approach clarifies the physical meaning of the equation. The sum over atomic sites in Eq. 3 can then be rewritten as

$$\sum_{j,k} b_j b_k \langle e^{-i\mathbf{Q}\cdot[\mathbf{r}_k(0) - \mathbf{r}_j(t)]} \rangle = \sum_{j,k} b_j b_k \int_{-\infty}^{\infty} \delta\langle(\mathbf{r} - [\mathbf{r}_k(0) - \mathbf{r}_j(t)])\rangle e^{-i\mathbf{Q}\cdot\mathbf{r}} d^3r, \tag{4}$$

in which the Dirac delta function appears again, this time in terms of **r** and a difference vector between the position of nucleus *j* at time *t* and that of nucleus *k* at time zero.

Let us suppose for the moment that the scattering lengths of all the atoms in our sample are the same $(b_j = b_k = b)$. In this case, the scattering lengths in Eq. 4 can be removed from the summation, and the right side becomes

$$Nb^2 \int_{-\infty}^{\infty} G(\mathbf{r}, t) e^{-i\mathbf{Q}\cdot\mathbf{r}} d^3r, \tag{5a}$$

where

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{j,k} \langle \delta(\mathbf{r} - [\mathbf{r}_k(0) - \mathbf{r}_j(t)]) \rangle \tag{5b}$$

and *N* is the number of atoms in the sample. The delta function in the definition of *G(r, t)* is zero except when the position of an atom *k* at time zero and the position of atom *j* at time *t* are separated by the vector **r.** Because the delta functions are summed over all possible pairs of atoms to obtain *G* **(r, t),** this function is equal to the probability of an atom being at the origin of a coordinate system at time zero *and* an atom being at position **r** at time *t. G* **(r,** *t)* is generally referred to as the *time-dependent pair-correlation function* because it describes how the correlation between two particles evolves with time.

Van Hove's neutron-scattering law (Eq. 3) can now be written as

$$I(\mathbf{Q}, \epsilon) = \frac{Nb^2}{h} \frac{k'}{k} \int_{-\infty}^{\infty} G(\mathbf{r}, t) e^{-i\mathbf{Q}\cdot\mathbf{r}} e^{-i\epsilon t} d^3r\, dt, \tag{6}$$

which allows us see that $I(\mathbf{Q}, \epsilon)$ is proportional to the space and time Fourier transforms of the time-dependent pair-correlation function. This general result gave a unified description for all neutron-scattering experiments and thus provided the framework for defining neutron scattering as a field.

As discussed in the text of the main article, this fact—that $I(\mathbf{Q}, \epsilon)$ is simply the Fourier transform of a function that gives the probability of finding two atoms a certain distance apart-is responsible for the power of neutron scattering. By inverting Eq. 6, information about both structure and dynamics of condensed matter may be obtained from the scattering law.

Coherent and Incoherent Scattering

Even for a sample made up of a single isotope, all of the scattering lengths that appear in Eq. 3 will not be equal. This is because the scattering length of a nucleus depends on its spin state, and most isotopes have several spin states. Generally, however, there is no correlation between the spin of a nucleus and its position in a sample of matter. For this reason, the scattering lengths that appear in Eq. 3 can be averaged over the nuclear spin states without affecting the thermodynamic average (denoted by the angular brackets).

Two spin averages come into play: the average value of b $(\bar{b})$ and the average value of $b^2 (b^2)$. In terms of these quantities, the sum in Eq. 3 can be averaged over the nuclear spins to give

$$\sum_{j,k} \overline{b_j b_k} A_{jk} = \sum_{j,k} (\bar{b})^2 A_{jk} + \sum_{j} (\overline{b^2} - (\bar{b})^2) A_{jj}, \tag{7}$$

where A_{jk} is shorthand for the integral in Eq. 3. The first term on the right side of Eq. 7 represents the so-called *coherent scattering,* whereas the second represents the *incoherent scattering.* Thus, we can define the coherent and. incoherent scattering lengths as

$$b_{\text{coh}} = \bar{b} \text{ and}$$
$$b_{\text{inc}} = \sqrt{b^2 - (\bar{b})^2}. \tag{8}$$

The expression for the coherent scattering law is a sum over both *j* and *k* and thus involves correlations between the position of an atom j at time zero and the position of a second atom *k* at time *t.* Although j and *k* are occasionally the same atom, in general they are not the same because the number *N* of nuclei in the sample is large. We can thus say that coherent scattering essentially describes interference between waves produced by the scattering of a single neutron from all the nuclei in a sample. The intensity for this type of scattering varies strongly with the scattering angle.

Incoherent scattering, on the other hand, involves correlations between the position of an atom *j* at time zero and the position of the *same* atom at time *t.* Thus, in incoherent scattering, the scattered waves from different nuclei do not interfere with each other. For this reason, incoherent scattering provides a good method of examining processes in which atoms diffuse. In most situations, the incoherent scattering intensity is isotropic; that is, it is the same for any scattering angle. This effect often allows incoherent scattering to be ignored when observing coherent scattering because the incoherent effects just add intensity to a structureless background.

The values of the coherent and incoherent scattering lengths for different elements and isotopes do not vary in any obviously systematic way throughout the periodic table. For example, hydrogen has a large incoherent scattering length (25.18 fermis) and a small coherent scattering length (–3.74 fermis). Deuterium, on the other hand, has a small incoherent scattering length (3.99 fermis) and a relatively large coherent scattering length (6.67 fermis). As mentioned in the main article, the difference between the coherent scattering lengths of hydrogen and deuterium is the basis of an isotopic-labeling technique, called *contrast matching,* that is especially important in applications of neutron scattering to structural biology and polymer science.

Diffraction

One of the important applications of Van Hove's equation (Eq. 3) is the scattering law for diffraction, which we develop here for a crystal containing a single isoope. Even though diffraction is predominantly an elastic scattering process ($\epsilon = 0$), neutron diffractometers actually integrate over the energies of scattered neutrons. Thus, rather than setting $\epsilon = 0$ in Eq. 3 to calculate the diffracted intensity, we integrate the equation over ϵ. This procedure ensures that the effect of atomic vibrations s included in the diffraction cross section. The integral of Eq. 3 over ϵ gives another Dirac delta function, $\delta(t)$, that tells us that the pair correlation function, $G(\mathbf{r}, t)$, has to be evaluated at t = O for diffraction. The result, for a crystal containing a single isotope, is

$$(\mathbf{Q}) = b_{\text{coh}}^2 \sum_{j,k} \langle e^{i\mathbf{Q}\cdot(\mathbf{r}_j - \mathbf{r}_k)} \rangle, \tag{9}$$

where the atomic positions r_j and r_k are evaluated at the same instant.

If the atoms in a sample were truly stationary, the thermodynamic averaging brackets could be removed from Eq. 9 because r_j and r_k would be constant. In reality the atoms oscillate about their equilibrium positions and only spend a fraction of their time at these positions, When this is taken into account, the thermodynamic average introduces another factor, called the Debye-Wailer factor, and Eq. 9 then becomes

$$(\mathbf{Q}) = b_{\text{coh}}^2 \sum_{j,k} e^{i\mathbf{Q}\cdot(\mathbf{r}_j - \mathbf{r}_k)} e^{-\frac{1}{2}Q^2\langle u^2 \rangle} \equiv S(\mathbf{Q}), \tag{10}$$

where $\langle u^2 \rangle$ is the average of the square of the displacement of an atom from its equilibrium position and diffracted intensity is now also called S (Q), the structure factor. This equation is the basis of any crystallographic analysis of neutron-diffraction data.

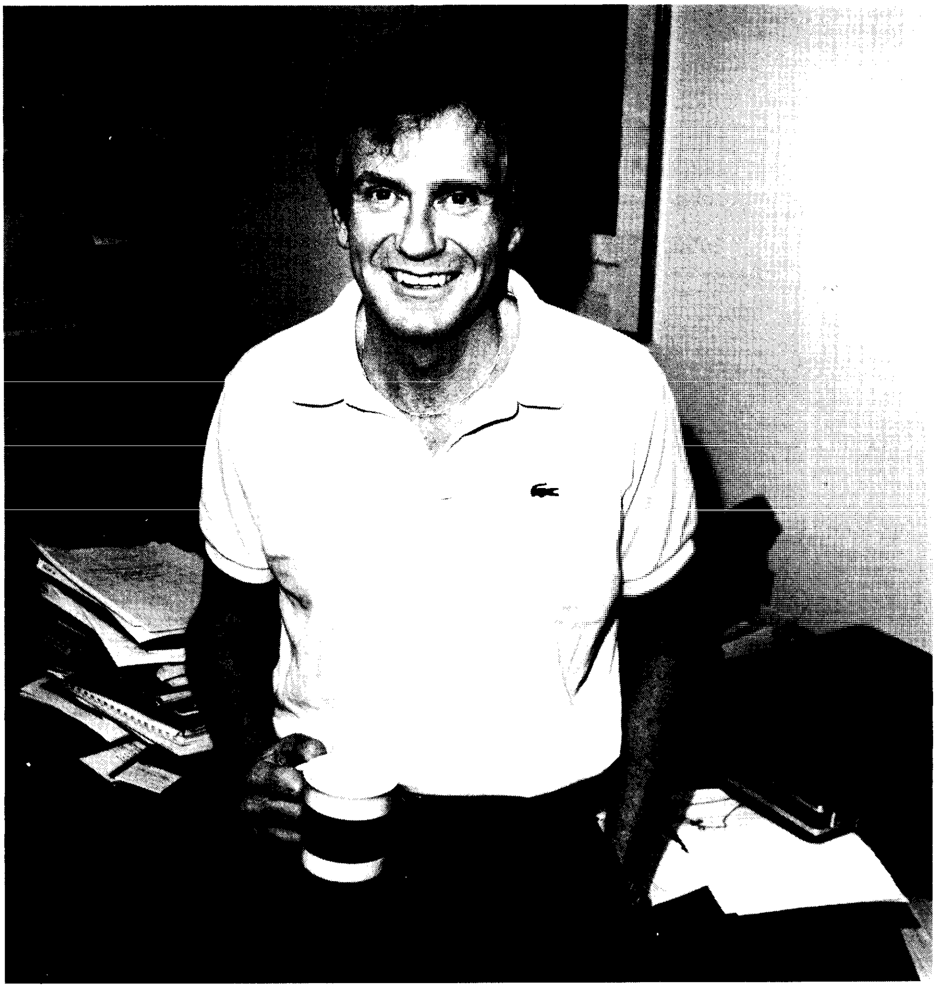
Small-Angle Scattering.

An important simplification of Eq. 3 occurs when the scattering angle is small. This approximation leads to the formula for one of the most popular neutron-scattering techniques—SANS, or small-angle neutron scattering.

Although Eq. 3 correctly describes neutron scattering at *any* scattering angle, when the magnitude of Q is very small compared to a typical interatomic distance, the exponential factors in Eq. 3 do not vary much from atom to atom, and the sum over the atomic sites may be replaced by an integral. As a result, the small-angle scattering law for coherent, elastic scattering from an assembly of "objects" (such as those depicted in Fig. 13 in the main text) can be written

$$I(\mathbf{Q}) = \left| \int b(\mathbf{r}) e^{-i\mathbf{Q}\cdot\mathbf{r}} d^3 r \right|^2 , \tag{1 }$$

where b **(r)** is the scattering-length density and the integral extends over the entire sample. To calculate b **(r)** for a large molecule, for example, we simply add up the coherent scattering lengths of the atoms in the molecule and divide by the molecular volume. Equation 11 is essentially a coarse-grained version of the "truth" given by Eq. 3 and is valid only when Q is small. However, it is the basic analytic tool of small-angle scattering. ■



Roger Pynn was born and educated in England. He received his M.A. from the University of Cambridge in 1966 and his Ph.D. in neutron scattering, also from the University of Cambridge, in 1969. He was a Royal Society European Fellow to Sweden in 1970; he did two years of postdoctoral research in Norway; and then he was an associate physicist for two years at Brookhaven National Laboratory. After spending eleven years at the world's leading center for neutron scattering, the Institut Laue Langevin in Grenoble, France, he was appointed as the Director of the Manuel Lujan, Jr. Neutron Scattering Center at Los Alamos.

Acknowledgments

I would like to thank the staff of *Los Alamos Science* for encouraging me to write this article in a coherent fashion and for being patient throughout its many iterations.

Further Reading

G. L. Squires. 1978. *Introduction to Thermal Neutron Scattering.* Cambridge: Cambridge University Press.

C. G. Windsor. 1981. *Pulsed Neutron Scattering.* London: Taylor and Francis.

Physics Today, January 1985. A special issue on neutron Scattering.