
Local density To specify the positions of atoms in an arbitrary solid arrangement is an impossible task, unless the positions happen to follow some strict pattern. Happily, it often suffices to specify the statistical properties of the environment of each atom. To this end we define the *local density* $\langle\rho(r)\rangle_0$ as the average (number) density of atoms at a displacement $\vec{r}$ from an arbitrary given atom. If there are several species of atoms present, there are several kinds of local density. To demonstrate the usefulness of local density, though, it suffices to consider a single species.

Scattering The behavior of the local density $\langle\rho(r)\rangle_0$ is directly observable by scattering †. This is an important way in which scattering senses not only the overall size of a large body but also the internal distribution of matter within it. In a scattering experiment a plane wave or beam of scattering particles (photons, neutrons, etc.) impinges on an unknown object, such as a liquid containing polymers. For definiteness we will imagine that our beam particles are neutrons: the waves are then complex scalar Schrödinger waves. The beam wave has the form $A\exp(i\vec{k}\cdot\vec{r}-i\omega t)$. The constant A is the amplitude of the wave; its square is the number of neutrons per unit volume in the beam. The angular frequency ω is proportional to the kinetic energy of the neutrons. The wavevector $\vec{k}$ is proportional to their momentum. Evidently, one can change k and ω together by varying the speed of the neutron beam. But one cannot vary k and ω independently.

When this wave encounters an atomic nucleus, such as a carbon nucleus in our solvent liquid, the great majority of it continues unperturbed. But a tiny fraction radiates outward from the nucleus in a spherical wave of the form $B\exp(i\ |k|\ r)/r$. Of course doubling the number of neutrons in the beam doubles the number scattered in this spherical wave. Thus B is proportional to A; the proportionality factor is the (complex) scattering amplitude f. A detector receives the wave far away in some particular direction (Figure 1). The part of this spherical wave entering the detector is a plane wave with some wavevector $\vec{k}'$ of magnitude k. The detector measures the intensity of the wave as a function of the direction of $\vec{k}'$. The r^{-1} factor in the scattered wave is virtually the same distance for all the scatterers, since the detector is far away from the sample.

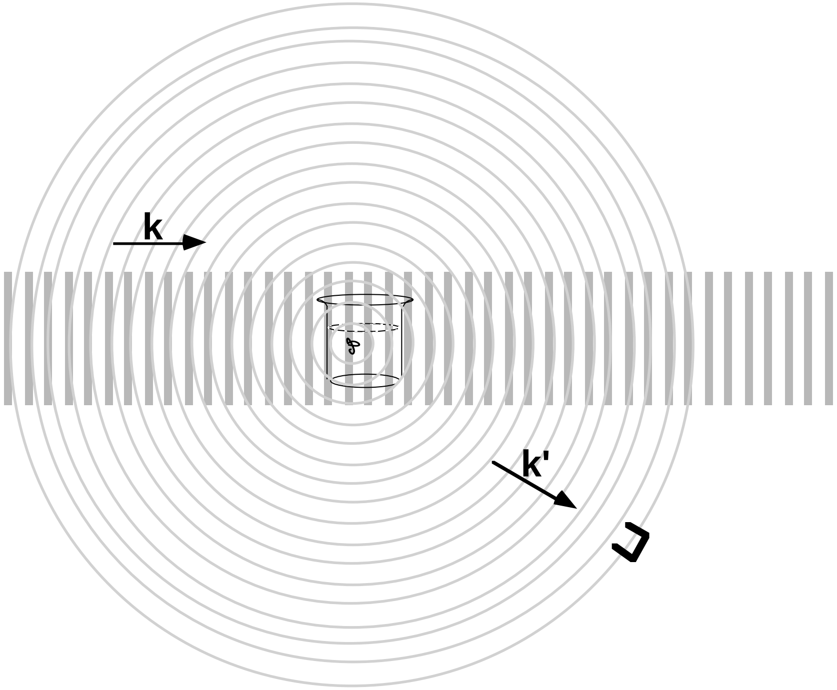

Figure 1. Schematic view of neutron scattering from a solution containing a globular polymer, an assembly of atoms in a particular spatial arrangement. The beam and the scattered waves are indicated by their wavefronts. The detector is shown and the wavevectors $\vec{k}$ and $\vec{k}'$ are indicated.

The detector senses the scattered waves from all the M scatterers j in a given volume. The amplitude from a particular scatterer at r_j is $\frac{B}{r}\exp(\vec{k}'\cdot(\vec{r}-\vec{r}_j))$. As we have noted, the prefactor B must be proportional to the wavefunction of the incident wave: $B = fA\exp(i\vec{k}\cdot\vec{r}_j - i\omega t)$. The wave entering the detector is the sum of these contributions. The *intensity* I is proportional to the absolute square of this wave. Since the scatterers in our liquid are generally

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† The subject of scattering from condensed matter is discussed in detail in *eg.* Stephen W. Lovesey *Theory of neutron scattering from condensed matter* (Oxford, Clarendon Press, 1984). Chaikin and Lubensky [*Principles of Condensed Matter Physics*, Cambridge, 1995] has an extended discussion about the scattering signature of many types of non-crystallline structure.

in motion, the intensity I fluctuates in time. To obtain a time-independent characterization of the system, we consider the average intensity. This intensity grows with the amount of sample; to remove this uninteresting size dependence, we consider the average intensity per scatterer $\langle I\rangle/M \propto \langle|\psi|^2\rangle/M$.

$$\frac{\langle I\rangle}{M} \propto |A\ f|^2 \frac{1}{M}\left\langle \left|\sum_j \exp(i(\vec{k}' - \vec{k})\cdot \vec{r}_j)\right|^2\right\rangle |\exp(i\vec{k}'\cdot\vec{r} - i\omega t)|^2/r^2. \tag{1}$$

The last factor, with the r and t dependence, is an unimportant constant, as is the prefactor giving the dependence on beam intensity and intrinsic scattering power of the nuclei. The rest gives information about the structure. Evidently it depends on $\vec{k}$ and $\vec{k}'$ only through the difference $\vec{k}' - \vec{k} \equiv \vec{q}$ †.

This remaining factor is called the *structure function* $S(q)$ ‡. We may simplify it by expressing the squared sum as an explicit product of two sums:

$$\begin{aligned} S(q) =& \frac{1}{M}\sum_{j,k}\langle\exp(i\vec{q}\cdot\vec{r}_j)\exp(-i\vec{q}\cdot\vec{r}_k)\rangle \\ =& \frac{1}{M}\sum_{j,k}\langle\exp(i\vec{q}\cdot(\vec{r}_j - \vec{r}_k))\rangle\,. \end{aligned} \tag{2}$$

One important property of the scattering intensity is immediately apparent from this expression. The spatial information in $S(q)$ is strongly blurred. The degree of blurring can be expressed in terms of the *scattering wavelength* λ defined as $2\pi/q$. To see this, we imagine that the scatterers i were moved by arbitrary small displacements u_j. The effect would be to add a new factor $\exp(i\vec{q}\cdot(\vec{u}_j - \vec{u}_k))$ in (2). But if all the u_j were much smaller than the scattering wavelength λ, these new factors would all be nearly unity, and $S(q)$ would hardly change. That is, $S(q)$ cannot detect anything about the positions of the scatterers to a precision of much less than a wavelength λ. We could for example gather all the scatterers lying within a tenth of a wavelength of one another into bunches and the effect on $S(q)$ would be minor. Conversely, it is immaterial whether the scattering occurs from discrete scatterers at specific points r_j or from a smeared distribution of scattering spread over a small regions around each r_j—provided the region is much smaller than $2\pi/q$.

We may use our density language to simplify the expression in (2). The density $\rho(r)$ is the probability per unit volume that one of the scatterers is at r. If the scatterers are at positions $\{r_j\}$ the density is given by $\rho(\vec{r}) = \sum_j \delta^3(\vec{r}-\vec{r}_j)$. Inserting $\int d^3r_1\delta^3(r_1 - r_j)$ $(= 1)$ and $\int d^3r_2\delta^3(r_2 - r_k)$, We may re-arrange (2) to read

$$S(q) = \frac{1}{M}\int d^3r_1 \int d^3r_2 \,\langle\rho(r_1)\rho(r_2)\rangle \exp[i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)]. \tag{3}$$

The absolute location of r is clearly immaterial in the $\langle\rho\rho\rangle$. Both points may be shifted by $\vec{r}_2$ so that $\langle\rho(\vec{r}_1)\rho(\vec{r}_2)\rangle = \langle\rho(\vec{r}_1 - \vec{r}_2)\rho(0)\rangle$. Now we note that the integrand depends only on $\vec{r}_1 - \vec{r}_2$, which we denote by $\vec{r}$:

$$S(q) = \frac{\int d^3r_1}{M}\int d^3r\,\langle\rho(\vec{r})\rho(0)\rangle\exp[i\vec{q}\cdot\vec{r}]. \tag{4}$$

Moreover, $\langle\rho\rho\rangle$ is simply related to the local density discussed above. We may think of it as the joint probability that a monomer is at the origin and that another is at $\vec{r}$. This is the overall probability that a monomer is at the origin times the *conditional* probability that a second monomer is at $\vec{r}$ given that one is at 0. The probability that a monomer is at the origin (or any other point in the sample) is $\langle\rho\rangle = M/(\int d^3r)$. The conditional probability is the same as the local density $\langle\rho(r)\rangle_0$. Thus $\langle\rho(\vec{r})\rho(0)\rangle = \langle\rho\rangle\langle\rho(r)\rangle_0$, and

$$S(q) = \int d^3r\,\langle\rho(r)\rangle_0\exp(i\vec{q}\cdot\vec{r}). \tag{5}$$

The reduced scattering intensity $S(q)$ is related to the local density by a simple integral transform—the Fourier transform. This means that if one expresses the scattering density $\rho(\vec{r})$ as a sum of plane waves of all different wavevectors, the scattering intensity and $S(q)$ arise from those waves that have wavevector $\vec{q}$. If the local density is *constant* the $S(q)$ is simply zero for $q > 0$.

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† Evidently q may be changed simply by varying the angle θ between the incident beam and the scattered rays that are detected. We are considering a case where the scattering particles lose no energy in the (elastic) scattering process, so that $|k'| = |k|$. Then some simple geometry shows that $|q| = 2|k|\sin(\theta/2)$.

‡ Sometimes it is necessary to consider the q dependence of the scattering amplitude f from each elementary scatterer. This q dependence reflects the distribution of matter within an elementary scatterer and is called the *form factor*. In some discussions of scattering, the elementary scatterers are taken to be an entire polyatomic structure such as a polymer. In that case, much of the information in the $S(q)$ above would appear in the form factor. The separation of the intensity of Eq. (1) into form and structure functions is evidently somewhat arbitrary. In our discussion we include all spatial information in the structure function.

In principle each nucleus in the fluid sample produces scattering. But in practice the scattering from a pure fluid is very weak for wavevectors q of interest here. We argued in the last chapter that structure at a given spatial scale R causes scattering at wavevectors q of order $1/R$. Thus we shall be interested in very small wavevectors relative to the size of an atom. We have seen above that the scattering from these atoms would not be appreciably changed if they were replaced by smeared-out densities several atoms in width (since such smearing is much less than $1/q$). The result in a uniform fluid is an essentially constant density. We have also seen that a perfectly constant density causes no scattering. It is thus not surprising that a simple fluid causes little scattering†.

Any departure from this uniform density of scatterers gives rise to scattering intensity. The polymers in the fluid do this: their atoms have scattering amplitudes f that differ from those of the solvent, so that there is a contrast between the scattering per unit volume from regions containing monomers and regions that do not. Thus, we may treat the scattering as though only the polymers were present. Whenever a liquid contains independent large objects of typical size R, the behavior of $S(q)$ depends on the size of q relative to the R. Evidently, the local density falls to zero for distances $r \gtrsim R$. When $qR \ll 1$ all then $\exp(iq \cdot r) \to 1$ for all $r < R$. Thus $S(q) \to \int^R d^3r \, \langle \rho(r) \rangle_0 \, 1 \to M$. That is, the internal structure is completely invisible to $S(q)$ and the scattering is about the same as though all the scatterers were concentrated at a point. Our polymers show this behavior like any other large object.

Note 1. Compressibility sum rule When scatterers are dispersed in a liquid, the small q limit of $S(q)$ has a general interpretation, even when the scatterers are interacting strongly. In this limit, the scattered wave sees only the large-scale modulation of the scatterer density. At such large scales the scatterers can be regarded as a uniform density with slight independent random variations from point to point. As we have noted, a uniform density cannot produce scattering, but the slight variations can. According to Eq. (4)

$$S(q \to 0) = \frac{\int d^3r}{M} \quad \lim_{q \to 0} \left[\int d^3r' \, \langle \rho(0)\rho(r') \rangle \exp(i\vec{q} \cdot \vec{r}') \right].$$

Here M is the number of scatterers in the sample. The limit as $q \to 0$ is not the same as $q = 0$. If $q = 0$ all the forward scattering along the original beam is mistakenly counted and $S(0)$ appears proportional to the sample size. To eliminate this spurious contribution we note that as long as $q \neq 0$, the scattering cannot be affected by adding a constant to $\rho(r)$ (since $\int (constant) e^{iq \cdot r} = 0$). Accordingly, we replace $\rho(r)$ by $\rho(r) - \bar{\rho}$, where $\bar{\rho} = M / \int d^3r$ is the average density of scatterers. With this choice, the limit $q \to 0$ can be taken:

$$S(q \to 0) = \frac{1}{\bar{\rho}} \left\langle (\rho(0) - \bar{\rho}) \int d^3r' (\rho(r') - \bar{\rho}) \right\rangle .$$

We consider the scattering from some large volume Ω within the sample. The number of scatterers N in this volume is evidently $\int_\Omega d^3r \rho(r)$; its average is $\bar{N} = \bar{\rho}\Omega$. In terms of N,

$$S(q \to 0) = \frac{1}{\bar{\rho}} \left\langle (\rho(r) - \bar{\rho})(N - \bar{N}) \right\rangle = \left\langle (N - \bar{N})^2 \right\rangle / \bar{N}.$$

The scattering at $q \to 0$ measures the mean-squared fluctuations of the average density. These fluctuations can be related to thermodynamic quantities. One can show that $S(q \to 0)$ $(= \left\langle (N - \bar{N})^2 \right\rangle / \bar{N}) = T(d\Pi/d\rho)^{-1}$, where Π is the pressure applied to the sample. This is shown in thermodynamics textbooks.

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† At these small wavevectors the scattering from the fluid is independent of q and can readily be subtracted. As discussed in Note 1 below, the amount of scattering can be shown to be proportional to the *compressibility* of the fluid relative to an ideal gas at the same density. All familiar liquids and solids are relatively incompressible; this leads to weak scattering.