

Chapter 1

## Introduction to Scattering Experiments

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### 1. Introduction

Fig. 1a shows the top view of a typical scattering experiment. Radiation is incident on a sample (or scattering medium), say a suspension of colloidal particles or a solution of polymers or surfactants. Some of the radiation passes through the sample unaffected, some is scattered. A detector is set up at scattering angle  $\theta$ , and the intensity  $I(\theta, t)$  of the scattered radiation is measured. (Since, in general, the intensity fluctuates in time, or undergoes a shift in frequency, we indicate its time dependence explicitly.) Typically, the incident and scattered beams are shaped by apertures, slits, the walls of the sample's container, or by optics such as lenses. The region of sample which is both illuminated by the incident beam and 'seen' by the detector is called the 'scattering volume'  $V$ .

As we will see shortly, a (hypothetical) totally homogeneous medium does not scatter radiation away from the incident direction. Scattering is caused by *fluctuations* in the medium. Usually these fluctuations are associated with variations in the 'density of scattering material' within the medium. Thus, for example, a colloidal particle scatters light when it has a different index of refraction from the liquid in which it is dispersed.

Basically, three types of scattering experiment, each giving different information, can be performed. First, measuring the dependence on angle of the average scattered intensity – frequently called 'static' scattering – yields structural information. Thus, in a dilute system, we learn about the shapes of the individual particles and the arrangement of material within them. In a concentrated system, we gain information about positional correlations, the average spatial arrangement of the particles in the sample. Second, analysis of the time dependence of fluctuations in the scattered radiation (or analysis of frequency or energy changes) – 'dynamic', 'quasielastic', or 'inelastic' scattering – yields dynamic information. It tells us, for example, how the particles are moving in Brownian motion and how their shapes, or configurations, fluctuate in time. Third, if the equipment is fully calibrated, the absolute magnitude of the scattered intensity (averaged over time or frequency) gives information on the mass or molecular weight of the scattering objects.

The aim of this chapter is to introduce scattering experiments as applied to the study of soft condensed matter, emphasising the physical principles of simple situations rather than going into great detail. The emphasis is further restricted to static scattering. References listed at the end of this article, and later chapters in this book, can be consulted for more detail as well as for discussions of dynamic and inelastic scattering. Light (Berne and Pecora, 1976; Brown,

1996; D'Aguzzo and Klein, 1996), X-rays (Guinier and Fournet, 1955; Glatter and Kratky, 1982) and neutrons (Higgins and Benoit, 1994) are the radiations most commonly used to study soft matter. While light scattering is associated with variations in dielectric properties (or refractive index), X-rays are scattered by electrons and neutrons are scattered by nuclei. For these and other reasons, each type of radiation has its own advantages and disadvantages as a probe of soft matter. We return to these briefly in Section 7. For simplicity we first outline the theory of light scattering, noting that similar principles apply to X-rays and neutrons.

### 2. Basic theory of light scattering

In Fig. 1b, a beam of plane-wave, monochromatic light,

$$E_i(r, t) \equiv E_0 \exp[i(k_1 \cdot r - \omega t)] \quad (1)$$

with electric vector  $E_0$  polarised perpendicular to the scattering plane (the plane of the paper), is incident on a region of scattering medium;  $k_1$  is the propagation vector of the incident light, having magnitude  $k_1 \equiv |k_1| = k = 2\pi/\lambda$  where  $\lambda$  is the wavelength of light in the medium;  $\omega$  is its angular frequency. Light of the same polarisation is scattered at angle  $\theta$  to a detector in the far field. (Thus we consider only polarised scattering, and assume that the dielectric behaviour (below) of the medium is scalar rather than tensorial. For a discussion of depolarised scattering and optically anisotropic media, see Berne and Pecora, (1976).)

We assume that the scattering is weak so that: (i) most photons pass through the sample undeviated, a few are scattered once, and the probability of double and higher-order scattering is negligible; (ii) the incident beam is not distorted significantly by the medium. (This corresponds to the first Born approximation or, in the specific context of light scattering, the so-called Rayleigh-Gans-Debye approximation.) We also assume that the scattering process is 'quasielastic', implying only a very small change in frequency. Thus the magnitude  $k_s$  of the propagation vector  $k_s$  of the scattered light is also  $2\pi/\lambda$ .

We apply Maxwell's equations to the problem of a plane electromagnetic propagating through a medium described by a local dielectric constant  $\epsilon(r, t)$ ;  $\epsilon(r, t)$  is the dielectric constant of the medium at position  $r$ , relative to an arbitrary origin  $O$  (Fig. 1b), and at time  $t$ . Details of this calculation are given, for example, by Berne and Pecora (1976) and D'Aguzzo and Klein (1996); here we simply quote the result. The amplitude  $E_s(R, t)$  of the electric field of the radiation scattered to a point detector at position  $R$  in the far field is given by:

$$E_s(R, t) = -\frac{k^2 E_0}{4\pi R} \int_V \frac{\exp[i(kR - \omega t)]}{\epsilon_0} \exp(-iq \cdot r) d^3r. \quad (2)$$

Here  $\epsilon_0$  is the average dielectric constant of the medium,  $V$  is the scattering volume, and the 'scattering vector'  $q$  is defined as the difference between the propagation vectors of the scattered and incident light (Fig. 1b)

$$q \equiv k_s - k_1; \quad q \equiv |q| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. \quad (3)$$

Insight into the physics underlying Eq. (2) can be obtained by rewriting it as the sum of the

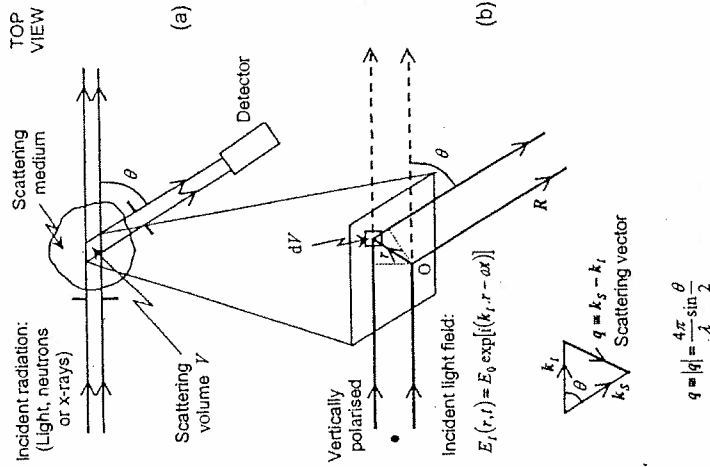


Fig. 1. (a) Top view of a typical scattering experiment. (b) Expanded view of the scattering volume, showing rays scattered at the origin  $O$  and by a volume element  $dV$  at position  $r$ .

amplitudes of the fields  $dE_s(R, t)$  scattered by volume elements ( $dV \equiv d^3r$ ) at positions ( $r$ ):

$$E_s(R, t) = \int_V dE_s(R, t), \quad (4)$$

where

$$dE_s(R, t) = -\frac{k^2 E_0}{4\pi R} \exp[i(kR - \omega t)] \left[ \frac{\epsilon(r, t) - \epsilon_0}{\epsilon_0} \right] dV \exp(-iq \cdot r). \quad (5)$$

Eq. (5) can be recognised as the formula describing the radiation due to an oscillating point dipole. The incident electric field, of strength  $E_0$  and propagation vector  $k$ , induces in the volume element  $dV$  at position  $r$  a dipole moment of strength proportional to  $E_0[\epsilon(r, t) - \epsilon_0]dV$  which oscillates at angular frequency  $\omega$ . This elementary dipole radiates, or scatters, light in all directions. The second factor in Eq. (5) describes a spherical wave of scattered radiation emanating from the origin  $O$ . The final term,  $\exp(-iq \cdot r)$ , allows

for the fact that the radiation scattered by the volume element at position  $r$  is shifted in phase relative to that scattered by an element at the origin  $O$ . Referring to Fig. 1b, simple geometry shows that the extra distance travelled by the light scattered at  $r$ , compared to that scattered at  $O$ , is  $(k_1 \cdot r - k_s \cdot r)/k$  which, with use of Eq. (3), gives a phase shift of  $-q \cdot r$  radians.

It is immediately apparent from Eq. (2) that, as noted in Section 1, if the medium is totally homogeneous, so that  $\epsilon(r, t) = \epsilon_0$ , there is no scattering. In other words, scattering of radiation (for  $q \neq 0$ ) is caused by *fluctuations* in the dielectric properties of the medium.

Eq. (2) embodies the fundamental physics of light scattering. The scattered light field consists of a spherical wave emanating from the scattering volume with an angle- or  $q$ -dependent amplitude which is the spatial Fourier transform of instantaneous variations in the dielectric constant of the sample. As we will see, the intensity of the scattering, averaged over time, provides information on the sample's structure, essentially spatial correlations of the particles. Clearly any variation in time of the local dielectric constant is directly reflected in temporal variations of the amplitude of the scattered field (and its intensity). Light scattering therefore probes directly the *structure and dynamics of a sample in reciprocal space (or  $q$ -space)*.

### 3. Discrete scatterers

We now specialise to the case of a sample containing discrete scattering objects suspended in a liquid. For simplicity we will call these objects 'particles', a term which could refer to a polymer molecule, a micelle, and so on, as well as to a colloidal particle. Although Eq. (6), below, is physically plausible, the development of Eq. (2) to give this result is rather subtle and is therefore relegated to the Appendix.

We consider  $N$  particles in the scattering volume  $V$  whose centres of mass at time  $t$  are described by position vectors  $\{R_j(t)\}$  (see Fig. 2). If  $r_j(t)$  is the position of volume element

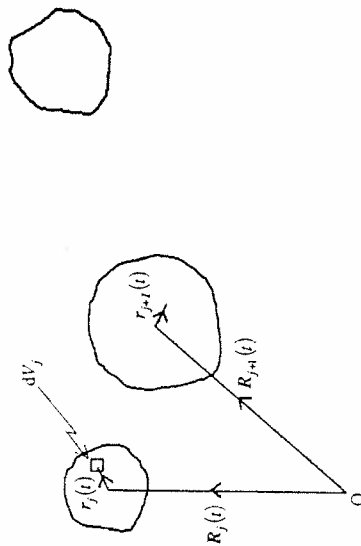


Fig. 2. Co-ordinates for discrete scatterers. Relative to an arbitrary origin  $O$ ,  $R_j(t)$  is the position of the centre of mass of particle  $j$  at time  $t$  and  $r_j(t)$  is the position of volume element  $dV_j$  in particle  $j$ , relative to its centre of mass.

$dV_j (= d^3r_j)$  in particle  $j$  relative to its centre of mass (Fig. 2), Eq. (2) becomes (see Appendix)

$$E_S(R, t) = -\frac{k^2 E_0 \exp[i(kR - \omega t)]}{4\pi R} \times \sum_j \left\{ \int_{V_j} \left[ \frac{\epsilon_p(r_j, t) - \epsilon_L}{\epsilon_0} \right] \exp(-iq \cdot r_j) d^3r_j \right\} \exp[-iq \cdot R_j(t)] \quad (6a)$$

or

$$E_S(R, t) = -E_0 \frac{\exp[i(kR - \omega t)]}{R} \times \sum_j \left\{ \int_{V_j} \Delta\rho(r_j, t) \exp(-iq \cdot r_j) d^3r_j \right\} \exp[-iq \cdot R_j(t)]. \quad (6b)$$

Here  $V_j$  is the volume of particle  $j$  and  $\Delta\rho(r_j, t)$  is defined by

$$\Delta\rho(r_j, t) = \frac{k^2}{4\pi} \left[ \frac{\epsilon_p(r_j, t) - \epsilon_L}{\epsilon_0} \right], \quad (7)$$

where  $\epsilon_p(r_j, t)$  is the local dielectric constant at position  $r_j$  in particle  $j$ ,  $\epsilon_L$  is the average dielectric constant of the liquid, and  $\epsilon_0$  is, as before, the average dielectric constant of the whole suspension. We see that the strength of the scattering depends on the difference between the dielectric properties of the particles and the liquid. As described in the Appendix, we assume that the 'background' scattering due to spontaneous fluctuations in the liquid itself is negligible. The quantity  $\Delta\rho(r_j, t)$  can be regarded as a measure of the local 'density of scattering material'. With the appropriate identification of  $\Delta\rho(r_j, t)$ , the results to be discussed henceforth apply to X-ray and neutron scattering as well as to light scattering (see Section 7). Eq. (6) can be rewritten as

$$E_S(R, t) = -E_0 \frac{\exp[i(kR - \omega t)]}{R} \sum_{j=1}^N b_j(q, t) \exp[-iq \cdot R_j(t)] \quad (8)$$

where the 'scattering length' of particle  $j$  (see Section 6) is defined by

$$b_j(q, t) = \int_{V_j} \Delta\rho(r_j, t) \exp(-iq \cdot r_j) d^3r_j. \quad (9)$$

From Eq. (8) we see that the total scattered electric field is the sum of the fields scattered by the individual particles. Each of these is the product of a scattering length, determined by the instantaneous distribution of material within the particle, and a phase factor determined by the instantaneous position of the particle in the sample.

Usually it is the scattered intensity that is measured directly, rather than the electric field. Intensities and fields are related by  $I(q, t) = |E(q, t)|^2$ . (Henceforth we regard the scattered fields and intensities as functions of the scattering vector  $q$  rather than of the position of the detector  $R$ . The two are equivalent since  $R$  is in the direction of the propagation vector  $k_s$  of

the scattered light, Fig. 1, and  $k_s$  and  $q$  are related by Eq. (3). Thus from Eq. (8) we get an expression for the instantaneous scattered intensity:

$$I_S(q, t) = \frac{E_0^2}{R^2} \sum_{j=1}^N \sum_{k=1}^N b_j(q) b_k^*(q, t) \exp\{-iq \cdot [R_j(t) - R_k(t)]\}. \quad (10)$$

For structural information we require the ensemble average, indicated by  $\langle \dots \rangle$ , of this intensity (equivalent to a time average if the scattering medium is ergodic):

$$\langle I_S(q) \rangle = \frac{E_0^2}{R^2} \left\langle \sum_{j=1}^N \sum_{k=1}^N b_j(q) b_k^*(q) \exp[-iq \cdot (R_j - R_k)] \right\rangle. \quad (11)$$

By writing the average scattered intensity as a function of the modulus  $q$  of the scattering vector, we have assumed the sample to be spatially isotropic on average, as expected for a 'liquid-like' dispersion or solution.

Eq. (11) is the general result for the average intensity scattered by an assembly of discrete particles. We now consider some simple special cases.

### 3.1. Dilute systems

In a dilute system the individual particles are, on average, widely separated spatially so that their behaviours are uncorrelated. Omitting for simplicity the prefactors, Eq. (11) can then be written

$$\begin{aligned} \langle I_S(q) \rangle &= \sum_{j=1}^N \langle |b_j(q)|^2 \rangle + \sum_{j \neq k=1}^N \langle b_j(q) \exp(-iq \cdot R_j) \rangle \langle b_k^*(q) \exp(iq \cdot R_k) \rangle \\ &= \sum_{j=1}^N \langle |b_j(q)|^2 \rangle, \end{aligned} \quad (12)$$

where, in discarding the second term, we have exploited the fact that, over time, particle  $j$  can take up any position in the sample, unaffected by the positions of others. Thus, in the average, the exponential factors are randomly distributed about zero and  $\langle b_j(q) \exp(-iq \cdot R_j) \rangle = 0$ . Eq. (12) shows that, in the dilute limit, the average scattered intensity is just the sum of the average intensities scattered by the individual particles. Thus a measurement of  $\langle I_S(q) \rangle$  as a function of  $q$  gives information on the size, structure and shape of the particles, averaged over orientation and over any distribution of size and shape.

The average intensities scattered by identical particles are the same, so that

$$\langle I_S(q) \rangle = N \langle |b(q)|^2 \rangle, \quad (\text{identical particles}) \quad (13)$$

which can be written

$$\langle I_S(q) \rangle = N \langle |b(0)|^2 \rangle P(q) \quad \text{with } P(q) = \frac{\langle |b(q)|^2 \rangle}{\langle |b(0)|^2 \rangle}. \quad (14)$$

$P(q)$  is called the 'form factor' of the particle. It is defined so that  $P(q) \rightarrow 1$  as  $q \rightarrow 0$  and provides information on the structure of the individual particles.

### 3.2. The form factor of a homogeneous sphere

For a homogeneous spherical particle, the distribution of scattering material is uniform throughout the sphere so that the scattering length [Eq. (9)] becomes

$$b(q) = \Delta \rho \int_{\text{sphere}} \exp(-iq \cdot r) d^3r. \quad (15)$$

The integral is easily evaluated on conversion to spherical polar co-ordinates, giving

$$\begin{aligned} b(q) &= \Delta \rho \frac{4}{3} \pi R^3 \frac{3}{(qR)^3} (\sin qR - qR \cos qR) \\ &= \left[ \Delta \rho \frac{4}{3} \pi R^3 \frac{3}{qR} j_1(qR) \right] \end{aligned} \quad (16)$$

where  $R$  is the sphere's radius (and  $j_1$  is a spherical Bessel function of the first kind). Since  $(3/x)j_1(x) \rightarrow 1$  as  $x \rightarrow 0$ , the form factor for a sphere is

$$P(q) = \left[ \frac{3}{(qR)^3} (\sin qR - qR \cos qR) \right]^2; \quad (17)$$

this function has zeros at  $\tan qR = qR$ , or  $qR = 4.49, 7.73, \dots$  (see Fig. 3).

### 3.3. The form factor of a random-coil polymer molecule

The simplest model of a polymer molecule is the 'freely-jointed chain' in which the molecule is represented by  $N_p$  links each of length  $b_0$ , and the angle between adjacent links can take any value with equal probability (Fig. 4). For a flexible enough polymer,  $b_0$  (roughly speaking the molecule's persistence length) is much smaller than the wavelength of light  $\lambda$ . Then, from the point of view of scattering, one can regard the links as point scatterers at positions  $\{R_m\}$ . Thus, omitting pre-factors, the instantaneous amplitude of the field scattered by the molecule can be written

$$b_P(q) = \sum_{m=1}^{N_p} \exp[-iq \cdot R_m(t)]. \quad (18)$$

giving for the corresponding intensity averaged over all configurations of the molecule

$$\langle |b_P(q)|^2 \rangle = \sum_m \sum_n \langle \exp[-iq \cdot (R_m - R_n)] \rangle. \quad (19)$$

For a large molecule,  $N_p \gg 1$ , the quantity  $m - n$  is also much greater than 1 for most values of  $m$  and  $n$ , so that  $R_m - R_n$  describes the end-to-end vector of a three-dimensional random walk of many steps. Thus, by the central limit theorem,  $R_m - R_n$  is a Gaussian-distributed random variable and, on performing the average, Eq. (19) becomes

$$\langle |b_P(q)|^2 \rangle = \sum_{m=1}^{N_p} \sum_{n=1}^{N_p} \exp \left[ -\frac{q^2}{6} \langle |R_m - R_n|^2 \rangle \right]. \quad (20)$$

from Eqs. (14) and (18) we can write its orientationally-averaged form factor as

$$P(q) = \frac{1}{N_p^2} \sum_{m=1}^{N_p} \sum_{n=1}^{N_p} \langle \exp[-iq \cdot (R_m - R_n)] \rangle_{\text{OR}} \quad (27)$$

For a vector  $S$  averaged over all orientations in three-dimensional space we have

$$\langle \exp(-iq \cdot S) \rangle_{\text{OR}} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \exp(-iqS \cos\theta) = \frac{\sin qS}{qS}, \quad (28)$$

giving

$$P(q) = \frac{1}{N_p^2} \sum_{m=1}^{N_p} \sum_{n=1}^{N_p} \frac{\sin q |R_m - R_n|}{q |R_m - R_n|}, \quad (29)$$

another result due to Debye (1947). Expanding this expression in powers of  $q$  and using Eq. (26) gives

$$P(q) = 1 - \frac{1}{3} q^2 R_G^2 + O(q^4) = 1 - \frac{1}{3} q^2 \langle R_G^2 \rangle + O(q^4), \quad (30)$$

where the first expression applies to a rigid particle and the second allows for flexibility by averaging over configurations.

Eq. (30), known as Guinier's expression (Guinier and Fournet, 1955), is a very useful result since it shows that a well-defined measure of the size of any scattering object, its (mean-square) radius of gyration, can be obtained directly from its small- $q$  scattering. (In the case of a polydisperse sample, the radius of gyration obtained from small- $q$  scattering is further averaged over the distributions of size, shape etc.) It is straightforward to show that expanding the expressions, Eqs. (17) and (23), for the form factors of a sphere ( $R_{G,\text{sphere}} = \sqrt{3/5} R$ ) and a polymer molecule leads to Eq. (30), as it must (see Fig. 3b). Finally we note that the Guinier expression is sometimes written

$$P(q) = \exp[-(q^2 \langle R_G^2 \rangle)/3]. \quad (31)$$

As can be seen by comparison with the exact result, Eq. (30), this expression is not, in general, valid beyond the  $O(q^2)$  term.

#### 4. Data analysis

We now consider briefly the analysis of experimental scattering data,  $I_S(q)$  versus  $q$ , a subject which will be treated in detail later in this book by Glatter. For simplicity we limit the discussion to dilute suspensions of identical particles so that [Eqs. (13) and (14)]

$$\langle I_S(q) \rangle = N \langle |b(q)|^2 \rangle = N \langle |b(0)|^2 \rangle P(q). \quad (32)$$

Various approaches to data analysis can be taken. First, as noted above, provided that the experimental data extend to sufficiently low values of  $q$ , one can derive the particles' radius of gyration from Eq. (30). This gives a measure of the size of the particles, but no direct information on their shape or the distribution of material within them. Second, one can try

comparing data spanning a wider range of  $q$  with specific models for the form factor  $P(q)$  e.g. those for a sphere, a random coil, a rod, etc. However, if a good fit of the data cannot be obtained in this way, one is forced to a more general 'inversion' approach. From the expression [Eq.(9)]

$$b(q) = \int_V d^3r \Delta\rho(r) \exp(-iq \cdot r) \quad (33)$$

we get, for the intensity from a single particle,

$$|b(q)|^2 = \int_V d^3r \int_V d^3r' \Delta\rho(r) \Delta\rho(r') \exp[-iq \cdot (r - r')]. \quad (34)$$

A change of variables,  $r \rightarrow r' - R$  so that  $r' \rightarrow r - R$ , gives

$$\begin{aligned} |b(q)|^2 &= \int d^3R \int d^3r \Delta\rho(r) \Delta\rho(r - R) \exp(-iq \cdot R) \\ &= \int d^3R \overline{\Delta\rho^2(R)} \exp(-iq \cdot R), \end{aligned} \quad (35)$$

where

$$\overline{\Delta\rho^2(R)} = \int d^3r \Delta\rho(r) \Delta\rho(r - R). \quad (36)$$

Following a procedure similar to that used in Section 3.4, we average Eq. (35) over all orientations of  $R$ , to give

$$\langle |b(q)|^2 \rangle = 4\pi \int dR p(R) \frac{\sin qR}{qR} \quad (37)$$

where

$$p(R) = R^2 \overline{\Delta\rho^2(R)} \quad (38)$$

is known as the 'pair-distance distribution function'. Finally, Fourier inversion of Eq. (37) gives

$$p(R) = \frac{1}{2\pi^2} \int_0^\infty \langle |b(q)|^2 \rangle q R \sin qR dq. \quad (39)$$

Thus the pair-distance distribution function  $p(R)$  for the particles can be obtained by numerical Fourier transformation of scattering data using Eqs. (32) and (39). It can be seen from Eqs. (36) and (38), that  $p(R)$  essentially describes the number of ways in which one can choose a vector of length  $|R|$  which connects scattering material within the particle. As will be discussed in detail by Glatter, it contains valuable information on the particle's structure.

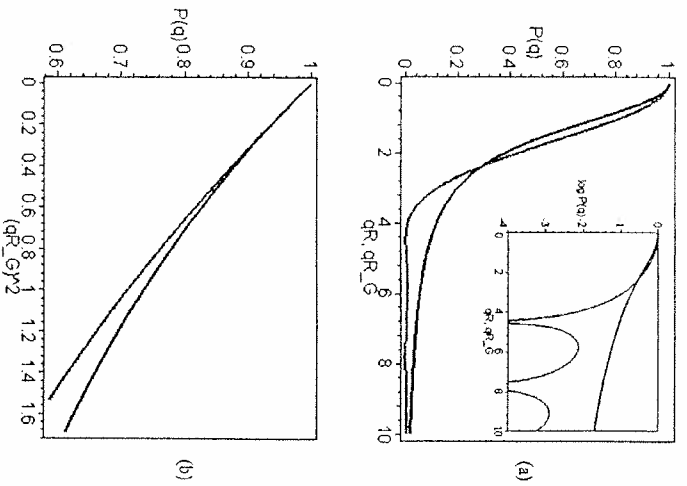


Fig. 3. (a) Form factors of a sphere (grey line, Eq. (17)), plotted against  $qR$ , where  $R$  is the radius and a Gaussian polymer coil (black line, Eq. (23)), plotted against  $qR_0$ , where  $R_0$  is the coil's root-mean-square radius of gyration). The inset shows the same functions with a logarithmic vertical scale, the 'diffraction lobes' of the sphere's form factor, with zeros at  $\tan qR = qR$ , are clearly evident. (b) The same form factors plotted against  $(qR_0)^2$ , showing the validity of Guinier's expression, Eq. (30), for  $(qR_0)^2$  less than about 0.25 or  $qR_0$  less than about 0.5. (For a homogeneous sphere,  $R_0 = \sqrt{3/5} R$ .)

For a random walk with step length  $b_0$ ,

$$|\mathbf{R}_n - \mathbf{R}_n|^2 = (n-m)b_0^2 \quad (21)$$

Evaluation of Eqs. (20) and (21) in the limit  $N_p \gg 1$  then gives

$$\langle |b_p(q)|^2 \rangle = N_p^2 P(q) \quad (22)$$

with

$$P(q) = \frac{2}{[q^2 \langle R_G^2 \rangle]^2} [\exp(-q^2 \langle R_G^2 \rangle) + q^2 \langle R_G^2 \rangle - 1] \quad (23)$$

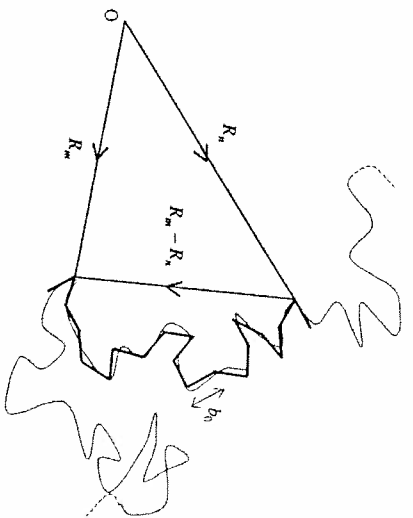


Fig. 4. A random-coil polymer molecule modelled by a freely-jointed chain. The chain contains  $N_p$  links of length  $b_0$ , at positions  $\{\mathbf{R}_m\}$ . The angles between adjacent links can take on any value. (In reality, of course, the chain occupies three dimensions.)

a result first obtained by Debye in 1947 (see Fig. 3). Here  $\langle R_G^2 \rangle$  is the mean-square radius of gyration of the freely-jointed chain, given by

$$\langle R_G^2 \rangle = \frac{N_p b_0^2}{6} \quad (24)$$

We note that, in general, the radius of gyration of  $N_p$  point masses located at positions  $\{\mathbf{R}_m\}$  is defined by

$$R_G^2 \equiv \frac{1}{N_p} \sum_{m=1}^{N_p} |\mathbf{R}_m - \mathbf{R}_{CM}|^2 \quad (25)$$

where  $\mathbf{R}_{CM} \equiv N_p^{-1} \sum_{m=1}^{N_p} \mathbf{R}_m$  is the position of the centre-of-mass of the molecule. Eq. (25) can be rewritten as (e.g. Doi and Edwards, 1986)

$$R_G^2 = \frac{1}{2N_p^2} \sum_{m=1}^{N_p} \sum_{n=1}^{N_p} |\mathbf{R}_m - \mathbf{R}_n|^2 \quad (26)$$

The result of Eq. (24) follows from averaging Eq. (26) over configurations of the random-coil molecule and using Eq. (21).

3.4. The form factor for an arbitrary particle – Guinier's expression

Any homogeneous particle can be regarded as being made up from  $N_p$  equal-sized 'beads' or volume elements at positions  $\{\mathbf{R}_m\}$ . First we assume the particle to be rigid (so that the relative positions  $\mathbf{R}_m - \mathbf{R}_n$  of the beads do not vary) but allow it to take any orientation. Thus,

### 5. Concentrated systems

The general expression for the average intensity scattered by an assembly of discrete particles is (Eq. (11), omitting pre-factors)

$$\langle I_S(q) \rangle = \sum_{j=1}^N \sum_{k=1}^N [b_j(q)b_k^*(q) \exp[-iq \cdot (R_j - R_k)]] \quad (40)$$

For simplicity we first assume the particles to be identical homogeneous spheres, so that all  $b_j(q) = b(q)$ . Then use of Eq. (14) gives

$$\langle I_S(q) \rangle = b^2(q) \sum_{j=1}^N \sum_{k=1}^N [\exp[-iq \cdot (R_j - R_k)]] = Nb^2(0)P(q)S(q), \quad (41)$$

where  $S(q)$  is the 'static structure factor', defined by

$$S(q) \equiv \frac{1}{N} \sum_{j=1}^N \sum_{k=1}^N [\exp[-iq \cdot (R_j - R_k)]]. \quad (42)$$

In Eq. (41) the product  $Nb^2(0)P(q)$  describes the scattering by  $N$  uncorrelated particles [compare Eq. (14)] and the structure factor represents the modification of the intensity due to the spatial correlation of the particles. Clearly, in a dilute system where particle positions are uncorrelated, cross terms,  $i \neq j$ , in Eq. (42) vanish and  $S(q) = 1$ .

The spatial correlations, or structure, in a concentrated system are usefully described in terms of the 'radial distribution function',  $g(R)$ , related to the probability of finding the centre of any particle at a distance  $R$  from the centre of a given particle. Specifically, for  $N$  particles in a volume  $V$ ,  $(N/V)g(R)dV$  is the number of particles in volume element  $dV$  at a distance  $R$  from a given particle. It is not difficult to show that the structure factor is related to the radial distribution function by

$$S(q) = 1 + 4\pi \frac{N}{V} \int_0^\infty [g(R) - 1] R^2 \frac{\sin qR}{qR} dR. \quad (43)$$

Fourier inversion of Eq. (43) gives the radial distribution function in terms of the structure factor:

$$g(R) = 1 + \frac{1}{2\pi^2} \frac{V}{N} \int_0^\infty [S(q) - 1] q^2 \frac{\sin qR}{qR} dq. \quad (44)$$

The strategy for measuring the structure factor is obtained from Eq. (41). First one measures the intensity scattered by a sample dilute enough that  $S(q) = 1$ :

$$\langle I_S(q) \rangle_{\text{dil}} = Nb^2(0)P(q). \quad (45)$$

Then one measures the intensity scattered by the concentrated sample of interest:

$$\langle I_S(q) \rangle_{\text{conc}} = Nb^2(0)P(q)S(q). \quad (46)$$

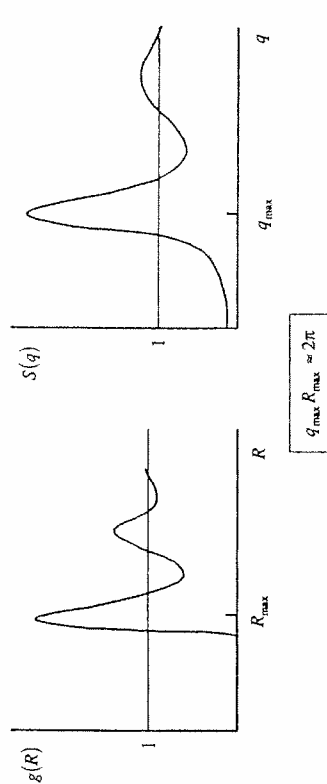


Fig. 5. Typical radial distribution function  $g(R)$  and structure factor  $S(q)$  for a suspension of strongly interacting colloidal particles.

The structure factor is then obtained from the ratio of these two measurements:

$$S(q) = \frac{\langle I_S(q) \rangle_{\text{conc}} N_{\text{dil}}}{\langle I_S(q) \rangle_{\text{dil}} N_{\text{conc}}}. \quad (47)$$

Even if the sample is polydisperse, data can be analysed in the same way. Then one obtains the so-called 'measured structure factor'  $S^M(q)$ . Use of Eqs. (40), (12) and (47) shows that

$$S^M(q) = \left[ \sum_{j=1}^N (b_j(q))^2 \right]^{-1} \sum_{j=1}^N \sum_{k=1}^N [b_j(q)b_k^*(q) \exp[-iq \cdot (R_j - R_k)]], \quad (48)$$

which clearly reduces to Eq. (42) for identical particles where all  $b_j(q) = b(q)$ . As will be discussed later in this book by Klein,  $S^M(q)$  can be written as a generalisation of Eq. (43) in terms of 'partial' radial distribution functions which describe the spatial correlations between different species.

Fig. 5 shows sketches of a typical radial distribution function, for example for a concentrated suspension of hard-sphere colloids or a suspension of strongly interacting charged colloids, and the corresponding structure factor. Since two particles cannot occupy the same space,  $g(R)$  is zero for centre-to-centre interparticle separations smaller than the particle diameter. The main peak in  $g(R)$  describes the nearest-neighbour shell or 'cage' of particles around any given particle. At large interparticle separations  $g(R) \rightarrow 1$  implying that spatial correlations are usually short-ranged (a crystal is an exception). The peak in  $S(q)$  can be considered, approximately, to be a 'Bragg reflection' from planes of particles separated by distances equal to the mean nearest-neighbour separation. Thus one finds that the positions  $R_{\text{max}}$  and  $q_{\text{max}}$  of the main peaks in  $g(R)$  and  $S(q)$  are related by an approximate 'Bragg condition'  $q_{\text{max}} R_{\text{max}} \approx 2\pi$ . For this reason it is often said that a scattering experiment, operating at scattering vector  $q$ , 'measures structure' on a spatial scale  $2\pi/q$ . While this is a useful 'rule of thumb' it should not be taken too literally: it is clear from Eq. (43) that the value of  $S(q)$  at a particular scattering vector  $q$  is determined by the values of  $g(R)$  at all  $R$ .

## 6. Absolute intensities

So far we have calculated the intensity scattered to a point in the far field, and have considered only normalised  $q$ -dependent quantities such as the form and structure factors. Valuable information is also contained in the absolute magnitude of the scattered intensity. In an experiment one uses a detector of area  $A_d$ , say, and measures the flux of scattered energy by counting photons (or neutrons). Thus Eq. (11), for example, can be written as

$$\frac{\langle I_s(q) \rangle A_d}{E_0^2(A_d/R^2)} = \left\langle \sum_{j=1}^N \sum_{k=1}^N b_j(q) b_k^*(q) \exp[-iq \cdot (R_j - R_k)] \right\rangle. \quad (49)$$

On the left-hand side of Eq. (49), the numerator describes the detected scattered energy per unit time and the denominator is the product of the incident flux (energy per unit area per unit time) and the detection solid angle. Thus Eq. (49) has the units of (length)<sup>2</sup> and can be regarded as describing the sample's 'scattering cross-sectional area ( $\sigma$ ) per unit solid angle ( $\Omega$ )'. As noted in Section 3, the quantity  $b_j(q)$ , having the units of length, is called the 'scattering length'. Eq. (49) is frequently written in the form

$$\frac{d\sigma(q)}{d\Omega} = \left\langle \sum_{j=1}^N \sum_{k=1}^N b_j(q) b_k^*(q) \exp[-iq \cdot (R_j - R_k)] \right\rangle. \quad (50)$$

This result applies to X-ray and neutron scattering, as well as to light scattering, provided the appropriate scattering lengths (which include the coupling between the radiation and the scattering medium) are used.

For light scattering, using Eq. (7) and the relationship  $\varepsilon = n^2$  between dielectric constant and refractive index, we get

$$\Delta\rho(r, t) = \frac{k^2}{4\pi} \left[ \frac{n^2(r, t) - n_L^2}{n_0^2} \right], \quad (51)$$

where  $n_L$  and  $n_0$  are respectively the average refractive indices of the liquid and the suspension. If, as is frequently the case, the difference between the refractive indices of the particles and the liquid is not too large, this becomes

$$\Delta\rho(r, t) \approx \frac{k^2}{2\pi n_0} [n(r, t) - n_L]. \quad (52)$$

Thus from Eqs. (52) and (9) we get

$$b_j(q, t) = \frac{k^2}{2\pi n_0} \int_V [n(r_j, t) - n_L] \exp(-iq \cdot r_j) d^3r_j. \quad (53)$$

For identical homogeneous particles of refractive index  $n_p$  and volume  $V_p$ , the  $q \rightarrow 0$  limit of this expression becomes

$$b(q \rightarrow 0) = \frac{k^2}{2\pi n_0} (n_p - n_L) V_p. \quad (54)$$

If the refractive index of the particles is not known, the dependence of suspension refractive index on concentration  $c$  (mass of particles per unit volume of suspension) can be measured,

providing  $dn_0/dc$ , the so-called 'refractive index increment'. Then, if we assume additivity by volume of refractive indices,

$$n_0 = \phi n_p + (1 - \phi) n_L, \quad (55)$$

where  $\phi$  is the volume fraction of particles, we get

$$\frac{dn_0}{dc} = \frac{dn_p}{d\phi} \frac{d\phi}{dc} = (n_p - n_L) \frac{V_p}{m_p}, \quad (56)$$

where  $m_p$  is the particles' mass and the identities  $\phi = NV_p/V$  and  $c = Nm_p/V$  have been used. Thus Eq. (54) becomes

$$b(q \rightarrow 0) = \frac{k^2}{2\pi n_0} m_p \left( \frac{dn_0}{dc} \right). \quad (57)$$

Then, in the limit of a dilute suspension at  $q \rightarrow 0$ , Eq. (50) becomes

$$\frac{1}{V} \frac{d\sigma(q)}{d\Omega} = \frac{N}{V} b^2(0) = \frac{N}{V} \left( \frac{k^2}{2\pi n_0} \right)^2 m_p^2 \left( \frac{dn_0}{dc} \right)^2. \quad (58)$$

Finally, with the further identification  $m_p = M/N_A$ , where  $M$  is the particle's molecular mass and  $N_A$  is Avogadro's number, we get

$$\frac{1}{V} \frac{d\sigma(q)}{d\Omega} = \left( \frac{k^2}{2\pi n_0} \right)^2 \left( \frac{dn_0}{dc} \right)^2 \frac{M}{N_A} c. \quad (59)$$

We recall that the propagation vector of the light is given by  $k = 2\pi/\lambda$ , where  $\lambda = \lambda_0/n_0$  is the wavelength of light in the medium and  $\lambda_0$  is its wavelength in vacuum. Thus Eq. (59) can be written in the frequently quoted form:

$$\frac{1}{V} \frac{d\sigma(q)}{d\Omega} = KMc, \quad (60)$$

where the 'optical constant'  $K$  is

$$K = \frac{1}{N_A} \frac{4\pi^2 n_0^2}{\lambda_0^4} \left( \frac{dn_0}{dc} \right)^2. \quad (61)$$

This result is the basis of a method to determine molecular weights from measurements of the intensity of scattered radiation, relative to the incident intensity, extrapolated to zero scattering angle and zero concentration – all the quantities in Eqs. (60) and (61) (except  $M$ ) are known or can be measured.

Finally, we note that, for a concentrated system studied away from the small scattering angle limit, Eq. (60) becomes

$$\frac{1}{V} \frac{d\sigma(q)}{d\Omega} = KMcP(q)S(q) \quad (62)$$

A small- $q$  expansion of Eq. (43) gives

$$S(q) = 1 - 2\frac{N}{V} B_2 + \frac{2}{3}\pi\frac{N}{V} q^2 C + \dots \quad (63)$$



where

$$B_2 = -2\pi \int [g(R) - 1] R^2 dR \quad (64)$$

and

$$C = - \int [g(R) - 1] R^4 dR. \quad (65)$$

Note that, at low concentrations, where  $g(R) \approx \exp[-V(R)/K_B T]$ ,  $V(R)$  being the potential energy of interaction of two particles,  $B_2$  reduces to the second virial coefficient. Eq. (62), along with (63)–(65) and Guinier's expansion of  $P(q)$  [Eq. (30)], form the basis of 'Zimm plots' which allow extrapolation to zero concentration and zero scattering angle of measurements made away from these limits (Zimm, 1948).

### 7. X-rays and neutrons

X-rays are scattered by the electrons of atoms. Except for frequencies near to an electronic transition, the scattering occurs as if the electrons were free. The scattering by a single electron (Thomson scattering) is described by a scattering length  $b_0^X = 2.8 \times 10^{-15}$  m. The X-ray scattering length  $b_j^X$  of an atom or molecule containing  $z$  electrons is then  $b_j^X = zb_0^X$ . As with light scattering (Appendix), we must consider the contrast between the particle and the liquid in which it is dispersed. Thus we define a contrast scattering length density  $\Delta\rho(r, t)$  in a small volume  $\Delta V$  of the particle at position  $r$  by

$$\Delta\rho(r, t) = \frac{1}{\Delta V} \sum_j \left[ b_j^{X,P} - \frac{v_P}{v_L} b_j^{X,L} \right], \quad (66)$$

where  $b_j^{X,P}$  and  $b_j^{X,L}$  are respectively the scattering lengths of the molecules comprising the particles and the liquid,  $v_P$  and  $v_L$  are the volumes of the molecules, and the sum runs over all atoms in  $\Delta V$ . With this identification of  $\Delta\rho(r, t)$ , the formulae described above for light scattering can be used also for X-ray scattering.

Neutrons are scattered by the nuclei of atoms. Knowing the scattering lengths of various nuclei (these are tabulated), one can proceed, as for X-rays, to a contrast scattering length density.

Aside from the different mechanisms by which the radiation is scattered, a major difference between light and X-rays and neutrons is their wavelengths:  $\sim 400$  nm (in the sample) for light,  $\sim 0.1$  nm for X-rays and neutrons. For various scattering angles, Table 1 shows approximate values of the scattering vector  $q$ , and the spatial scale  $2\pi/q$  probed by scattering. We see that, at scattering angles of  $5-10^\circ$ , X-rays and neutrons probe structure on a scale almost as small as that of molecules. To reach the scales of interest,  $> 10$  nm, in much of soft matter, scattering angles smaller than  $1^\circ$  must be used. The minimum scale,  $\sim 300$  nm, probed by light scattering at large angles overlaps the maximum scale of very small-angle X-ray and neutron scattering.

While the X-ray scattering lengths of atoms are simply proportional to the atomic number, neutron scattering lengths vary irregularly with the type of nucleus and can be negative (corresponding to a phase shift of  $\pi$  radians in the scattering) as well as positive. Furthermore, different isotopes of the same atom (or nucleus) can have very different scattering lengths. In

Table 1

Approximate magnitudes of the scattering vector and its reciprocal for X-rays, neutrons and light at various scattering angles

X-rays, neutrons ( $\lambda = 0.1$ nm)			Light ( $\lambda = 400$ nm)		
$\theta$ (degrees)	$q$ (nm $^{-1}$ )	$2\pi/q$ (nm)	$\theta$ (degrees)	$q$ (nm $^{-1}$ )	$2\pi/q$ (nm)
0.01	0.01	600	1	$3 \times 10^{-4}$	$2 \times 10^4$ (20 $\mu$ m)
0.1	0.1	60	10	$3 \times 10^{-3}$	2000
1	1	6	100	$2.4 \times 10^{-2}$	300
10	10	0.6			

particular, the scattering length of hydrogen's nucleus (a proton) is  $-3.74 \times 10^{-15}$  m whereas that of deuterium is  $6.67 \times 10^{-15}$  m. Thus partial deuteration of the components of a sample leads to marked changes in its neutron scattering properties, frequently without seriously affecting its chemical and physical properties. It is possible by this means to 'highlight' different parts of a particle and to obtain thereby detailed structural information.

The ability to vary contrast by isotopic substitution constitutes a major advantage of neutron scattering, particularly in the study of soft matter where many materials of interest contain hydrogen (see the article later in this book by Schurtenberger for more details). Limited contrast variation is possible in light scattering by using materials with different refractive indices, but this is done at the risk of changing the sample's other properties in a way which can be hard to quantify. With tunable X-rays from synchrotron sources, some contrast variation can be achieved by exploiting the fact that, close to an allowed electronic transition, an atom's scattering length varies with the frequency of the radiation.

An advantage of X-rays over neutrons, which has recently been exploited, is the ability to perform X-ray photon correlation spectroscopy, the X-ray analogue of dynamic light scattering (see, for example, Lurio et al., 2000, and Riese et al., 2000, for recent applications of this technique). Dynamic scattering of this kind requires that the incident radiation be coherent over the scattering volume of the sample. Laser light is intrinsically coherent; X-rays from intense modern synchrotron sources can be made coherent by suitable spatial and frequency filtering. (While neutron beams can also, in principle, be filtered in the same way, the resulting flux of coherent neutrons from current neutron sources is much too small to be of practical use in scattering experiments.) The advantages of X-ray dynamic scattering over dynamic light scattering are that samples opaque to light can be studied and that larger scattering vectors, and therefore smaller spatial scales, can be reached.

### Appendix

It is clear from Eq. (2) that there is scattering both from the particles, dielectric constant  $\epsilon_P(r, t)$ , and the liquid, dielectric constant  $\epsilon_L(r, t)$ . Thus we can write

$$\begin{aligned} \epsilon(r, t) - \epsilon_0 &= \epsilon_P(r, t) - \epsilon_0 & (\text{r inside any particle}) \\ &+ \epsilon_L(r, t) - \epsilon_0 & (\text{r outside all particles}) \end{aligned} \quad (A1)$$

where  $\varepsilon_0$  is, as before, the average dielectric constant of the medium. If we define  $\varepsilon_L$  to be the average dielectric constant of the liquid, Eq. (A1) can be written in the more useful form

$$\varepsilon(\mathbf{r}, t) - \varepsilon_0 = [\varepsilon_P(\mathbf{r}, t) - \varepsilon_L] + (\varepsilon_L - \varepsilon_0) \quad (\text{r inside any particle}) \\ + [\varepsilon_L(\mathbf{r}, t) - \varepsilon_L] + (\varepsilon_L - \varepsilon_0) \quad (\text{r outside all particles})$$

or

$$\varepsilon(\mathbf{r}, t) - \varepsilon_0 = \varepsilon_P(\mathbf{r}, t) - \varepsilon_L \quad (\text{r inside any particle}) \\ + \varepsilon_L(\mathbf{r}, t) - \varepsilon_L \quad (\text{r outside all particles}) \\ + \varepsilon_L - \varepsilon_0 \quad (\text{r anywhere in } V).$$

When substituted into Eq. (2), Eq. (A2) leads to three contributions to the scattering. The first is the contribution of interest, essentially the scattering by the particles due to the difference between their dielectric constant (or refractive index) and that of the liquid in which they are suspended. The second corresponds to the scattering from spontaneous density fluctuations in the liquid itself (or density + concentration fluctuations if the suspension medium is a mixture of liquids). In this article we will, for simplicity, assume the intensity of this 'background' scattering to be negligible (though in practice it can be measured and subtracted from the total scattering). The third contribution in Eq. (A2) does not depend on position  $\mathbf{r}$ , so leads to a term in Eq. (2) proportional to  $\int_V \exp[-i\mathbf{q} \cdot \mathbf{r}] d^3r$ . This integral describes diffraction by the whole scattering volume which, if the dimensions of  $V$  are much greater than the wavelength of the radiation, is strongly peaked around  $\mathbf{q} = 0$  and can also be neglected.

We consider  $N$  particles in the scattering volume  $V$  whose centres of mass at time  $t$  are described by position vectors  $\{\mathbf{R}_j(t)\}$  (see Fig. 2). If  $\mathbf{r}_j$  is the position of volume element  $dV_j$  ( $= d^3\mathbf{r}_j$ ) in particle  $j$  relative to its centre of mass (Fig. 2), we can write

$$\varepsilon_P(\mathbf{r}, t) d^3r = \sum_{j=1}^N \delta[\mathbf{r} - \mathbf{R}_j(t) - \mathbf{r}_j] \varepsilon_P(\mathbf{r}_j, t) d^3r_j \quad (\text{A3})$$

where  $\varepsilon_P(\mathbf{r}_j, t)$  is the local dielectric constant at position  $\mathbf{r}_j$  in particle  $j$ . Substitution of the first term of Eq. (A2), with (A3), into (2) gives

$$E_S(\mathbf{R}, t) = -\frac{k^2 E_0 \exp[i(kR - \omega t)]}{4\pi R} \\ \times \sum_j \int_{V_j} \left[ \frac{\varepsilon_P(\mathbf{r}_j, t) - \varepsilon_L}{\varepsilon_0} \right] \exp(-i\mathbf{q} \cdot \mathbf{r}_j) d^3r_j \exp[-i\mathbf{q} \cdot \mathbf{R}_j(t)], \quad (\text{A4})$$

where  $V_j$  is the volume of particle  $j$ .

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