

Time-Dependent Statistical Mechanics

16B. Light scattering

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Propagation of visible light in dielectric nonmagnetic nonabsorbing materials

Everything we discuss is for this special case.

However, we will not assume that the material is homogeneous or isotropic.

Maxwell's equations. There are four fundamental fields.

$\mathbf{E}(\mathbf{r}, t)$ electric field

$\mathbf{B}(\mathbf{r}, t)$ magnetic field

$\mathbf{D}(\mathbf{r}, t)$ electric displacement field

$\mathbf{H}(\mathbf{r}, t)$ magnetizing field (also called the magnetic field)

Maxwell's equations are partial differential equations - first order in space and time, plus some additional conditions involving the divergences of the fields. The fields are real.

Relationship between \mathbf{D} and \mathbf{E}

$$\mathbf{D}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}, t) + 4\pi\mathbf{P}(\mathbf{r}, t)$$

where $\mathbf{P}(\mathbf{r}, t)$ is the polarization density.

$\mathbf{P}(\mathbf{r}, t)$ is the dipole moment density in the material as a function of position and time in the system that is being subject to the electric field. It includes:

- permanent dipole moments
- induced dipole moments
 - induced by intermolecular interactions
 - induced by the electric field

The usual dielectric response theory assumes that the electric polarization responds linearly to the applied electric field at every point in space.

$$\mathbf{D}(\mathbf{r}, t) = \hat{\epsilon}(\omega) \mathbf{E}(\mathbf{r}, t)$$

It is, in effect, three equations, for the three components of the vectors.

$$\begin{aligned} D_x(\mathbf{r}, t) &= \epsilon(\omega) E_x(\mathbf{r}, t) \\ D_y(\mathbf{r}, t) &= \epsilon(\omega) E_y(\mathbf{r}, t) \\ D_z(\mathbf{r}, t) &= \epsilon(\omega) E_z(\mathbf{r}, t) \end{aligned}$$

We want to generalize this in two ways. (From here on, the frequency dependence of the dielectric constant is to be understood.)

Generalization to anisotropic materials. This is not the most general linear relationship between these two vectors. Why could we not have a relationship of the following form?

$$D_x(\mathbf{r}, t) = AE_x(\mathbf{r}, t) + BE_y(\mathbf{r}, t) + CE_z(\mathbf{r}, t)$$

Can an electric field in the y direction induce a polarization in the x direction?

In an isotropic material this can't happen. Symmetry arguments can be used to show this. The basic idea is that if the field is in the y direction, there is no reason for any induced polarization to be more likely to be in the $+x$ direction than in the $-x$ direction.

In a crystal or in an anisotropic material like a liquid crystal, there is no reason why we could not have this more general relationship. Also in a liquid with fluctuations, this could happen.

The more general relationship can be written as

$$\mathbf{D}(\mathbf{r}, t) = \epsilon(\omega) \cdot \mathbf{E}(\mathbf{r}, t)$$

where here $\hat{\epsilon}(\omega)$ is a second rank tensor. In effect, this is a matrix equation of the form

$$\begin{pmatrix} D_x \\ D_y \\ D_z \end{pmatrix} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

We have left out the position arguments and the ω dependence for simplicity.

Special case of an isotropic material. For an isotropic material, all the off-diagonal elements are zero, and all three diagonal elements are equal. The dielectric constant tensor or matrix is a multiple of the identity matrix.

$$\epsilon_{ij} = \epsilon \delta_{ij}$$

ϵ is an equilibrium thermodynamic quantity. It depends on the density, temperature, and composition of a material.

Generalization to inhomogeneous materials. In this case the matrix $\epsilon(\omega)$ depends on position (and perhaps time).

$$\mathbf{D}(\mathbf{r}, t) = \epsilon(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t)$$

$\epsilon(\mathbf{r}, t)$ is a property of the material that is doing the scattering. For weak electric fields, it is independent of the electric field.

Manipulation of Maxwell's equations. Reduce the equations to a single equation for $\mathbf{E}(\mathbf{r}, t)$ that contains $\epsilon(\mathbf{r}, t)$. Let's write

$$\epsilon(\mathbf{r}, t) = \epsilon \mathbf{I} + \delta\epsilon(\mathbf{r}, t)$$

$$\frac{\hat{\epsilon}_0(\omega)}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \nabla^2 \mathbf{E} - \nabla (\nabla \cdot \mathbf{E}) + \frac{\omega^2}{c^2} \delta\hat{\epsilon}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) + O(E^2)$$

In getting to the second of these, we used the fact that the electric field varies with time much more rapidly than the dielectric constant does.

Propagation of plane waves in a system with a dielectric constant independent of position and time. A plane wave solution of the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)$$

where

$$k = \frac{2\pi}{\lambda}$$

is a solution of Maxwell's equations if and only if

$$k = \frac{\omega}{c} n(\omega)$$

$$n(\omega) = \epsilon(\omega)^{1/2}$$

$n(\omega)$ is the index of refraction.

Scattering. The thing that scatters light is the dielectric constant fluctuations $\delta\epsilon(\mathbf{r}, t)$.

In an equilibrium material there are generally small fluctuations in the density. The net result is that there are fluctuations in the dielectric constant. It is these fluctuations that are responsible for light scattering.

The density fluctuations we are talking about are density fluctuations with a volume of the order of the wavelength of light. So the fluctuations are small. Secondly, their time dependence is in general very slow.

There are actually several types of fluctuations that could cause the dielectric constant to fluctuate - e.g. density fluctuations, energy fluctuations, composition fluctuations, orientational density fluctuations, conformational fluctuations (especially of large molecules). Some of them can cause the off-diagonal elements of the density matrix to deviate from the value of zero.

The frequency resolved intensity of the scattered light will be related to the space and time Fourier transform of a correlation function of something. The something turns out to be

$$\frac{\omega^2}{c^2} \hat{\mathbf{n}}_f \cdot \delta \hat{\epsilon}(\mathbf{r}, t) \cdot \hat{\mathbf{n}}_i$$

Here $\hat{\mathbf{n}}_i$ is the polarization vector of the incident light. It appears premultiplied by a factor of

$$\left(\frac{\omega^2}{c^2}\right)^2 = \frac{\omega^4}{c^4}$$

The relevant correlation function is

$$\langle (\mathbf{n}_f \cdot \delta \epsilon(\mathbf{r}, t) \cdot \mathbf{n}_i) (\mathbf{n}_f \cdot \delta \epsilon(\mathbf{0}, 0) \cdot \mathbf{n}_i) \rangle$$

Its spatial and temporal FT is what is measured in a light scattering experiment that measures the scattered intensity as a function of frequency.

The relevant frequency for the time Fourier transform is

$$\omega_f - \omega_i$$

and the relevant wave vector is

$$\mathbf{k}_f - \mathbf{k}_i$$

where these are the scattered and initial wave vectors of the light *in the material*.

Thus, except for other geometric, sensitivity, and resolution factors related to the experimental apparatus the quantity measured is the space-time Fourier transform of

$$\frac{\omega^4}{c^4} \langle (\mathbf{n}_f \cdot \delta \epsilon(\mathbf{r}, t) \cdot \mathbf{n}_i) (\mathbf{n}_f \cdot \delta \epsilon(\mathbf{0}, 0) \cdot \mathbf{n}_i) \rangle$$

This explains why the sky is blue and sunsets are red. For a low density gas, it turns out that the correlation function is very short ranged in distance and hence is very insensitive to wave vector hence to the wave vector of the incident light. This result then predicts that blue light will be scattered by the atmosphere much more strongly than, for example, yellow light.

Scattering geometries. The incident and scattering vectors determine a plane, called the scattering plane. It is also the plane that passes through the source, the scattering region, and the detector. The four possible intensities that can be measured are called I_{VV} , I_{VH} , I_{HV} , and I_{HH} , where H and V refer to ‘horizontal’ and ‘vertical’. ‘Horizontal’ means ‘in the scattering plane’ and ‘vertical’ means ‘perpendicular to the scattering plane. This refers to the direction of the polarizers, with the first subscript referring to the polarization of the incident light and the second referring to the polarization filter in front of the detector.

I_{VV} is usually called polarized light scattering, since the detected scattered light has the same polarization as the incident light. I_{VH} and I_{HV} are usually called depolarized light scattering.

Fluctuations studied by light scattering. Light scattering is used to study:

- density fluctuations
- composition fluctuations
- orientational alignment fluctuations

Because of the nature of the light scattering process, the wave vectors studied correspond to wave lengths that are typically large compared with molecular lengths. Long wave length fluctuations are expected to decay according to hydrodynamic laws.

Review. The basic principle involved is something we derived early in the course using linear response theory.

Suppose we have two dynamical variables A and B . Imagine a field that couples to B . Turn it on and let system equilibrate in the presence of the

field. Then turn off the field. Observe the return of $\langle A \rangle_{ne}$ to its equilibrium value. We showed

$$\langle A(t) \rangle_{ne} = \int_t^\infty dt' \chi_{AB}(t')$$

and

$$\frac{d}{dt} \langle A(t) \rangle_{ne} = -\chi_{AB}(t)$$

We also showed

$$\chi_{AB}(t) = -\frac{1}{k_B T} \Theta(t) \frac{d}{dt} C_{AB}(t)$$

Therefore

$$\frac{d}{dt} \langle A(t) \rangle_{ne} = \frac{1}{k_B T} \Theta(t) \frac{d}{dt} C_{AB}(t)$$

and

$$\langle A(t) \rangle_{ne} = \frac{1}{k_B T} C_{AB}(t) \quad \text{for } t > 0$$

The left side can be calculated from the appropriate hydrodynamic equations, if A is the right types of variable for using hydrodynamics on the left. We then need to invent a field that couples to B , use this to determine the zero time situation for the hydrodynamic description, solve the hydrodynamic equations, and this gives the correlation function of interest.

This is analogous to two things we have already discussed.

- concentration fluctuations of reactants and products of chemical reactions decay according to the chemical rate equations, which contain rate constants.
- concentration fluctuations of trace components decay according to Fick's law, which contains self diffusion coefficients.

In each case, the study of the dynamics of fluctuations can in principle provide information about the values of the constants that appear in these equation.

The hydrodynamic laws appropriate for density fluctuations are the Navier-Stokes equations of hydrodynamics. The parameters in these equations include the adiabatic speed of sound, the kinematic viscosity, the heat capacity, and the thermal diffusivity.

0.0.1 Density fluctuations - Rayleigh-Brillouin spectrum

Density fluctuations occur in all liquids, including the simplest, and can be studied on long wave lengths by light scattering.

Consider a one component system that is a dense liquid. Its thermodynamic state is characterized by two intensive properties, e.g. density and temperature. Its dielectric constant $\hat{\epsilon}(\omega)$ is in principle a function of these two quantities. Thus we might express it as $\hat{\epsilon}(\omega; \rho, T)$, where T is the temperature. Throughout the following discussion, we will omit the ω arguments for simplicity.

If there are fluctuations of density and temperature in the material, then we have a fluctuating dielectric constant.

$$\hat{\epsilon}(\mathbf{r}, t) = \hat{\epsilon}_0 + \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \delta \rho(\mathbf{r}, t) + \left(\frac{\partial \epsilon}{\partial T} \right)_\rho \delta T(\mathbf{r}, t)$$

In many liquids studied, the dielectric constant is much more sensitive to density than temperature. I.e.

$$\left(\frac{\partial \epsilon}{\partial T} \right)_\rho \approx 0$$

So we have

$$\hat{\epsilon}(\mathbf{r}, t) = \hat{\epsilon}_0 + \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \delta \rho(\mathbf{r}, t)$$

The fluctuations in dielectric constant are simply related to the fluctuations in the density. Moreover, there is nothing about a density fluctuation that destroys the isotropy of the system. So this is a fluctuation in the diagonal elements of the dielectric constant matrix. Thus the correlation function of interest is

$$\frac{\omega^4}{c^4} \left[\left(\frac{\partial \epsilon}{\partial \rho} \right)_T \right]^2 (\hat{n}_f \cdot \hat{n}_i)^2 \langle \delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{0}, 0) \rangle$$

For a monatomic liquid, the $\delta \rho$ that appears here, and the resulting correlation function, are the same as what appears in the theory of neutron scattering or x-ray scattering or electron scattering. There are two major differences here, compared with those situations.

- The wave vector of interest for this experiment is much smaller than for the other scattering experiments.
- The prefactors are different. Instead of scattering lengths or atomic form factors or Fourier transforms of electron densities, we get the square of the derivative of ϵ with respect to density, factors related to the wavelength of the light, and the dot product of the incident and detected polarizations. Notice that this will contribute to the polarized I_{VV} but not the depolarized I_{VH} or I_{HV} .

$$\hat{\rho}(\mathbf{k}, t) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \delta\rho(\mathbf{r}, t)$$

$$\langle \delta\rho(\mathbf{r}, t) \delta\rho^*(\mathbf{r}, 0) \rangle$$

Behavior at $t = 0$ from x-rays, neutrons

graph of $S(k)$, large peak at about $2\pi/\sigma$, small fluctuations at small k . Explanations in terms of compressibility.

Behavior of $S(k, t)$ for large k . Decay, sometimes plateau, for $k \approx 2\pi/\sigma$. Smaller k see oscillations.

Rayleigh-Brillouin spectrum. Central peak at $\delta\omega = 0$. Satellite peaks.

E.g. argon at 85K, $\lambda \approx 5000\text{\AA}$, 90° scattering. Side peaks separated by about 3GHz from central peak. HWHH ≈ 0.2 GHz for side peaks, 0.1 for central peak.

There is a detailed theory. Qualitative discussion.

Low wavelength density fluctuations at equilibrium behave according to hydrodynamic equations.

Relevant equations are for: density fluctuations, velocity fluctuations, temperature fluctuations. Linearized Navier-Stokes equations. Contain various thermodynamic quantities, like specific heat; various transport coefficients, like thermal conductivity.

Imagine writing down equations, setting up an initial condition with a sinusoidal variation of density with position. Solve. What would you find?

An initial fluctuation in density generate velocity fluctuations and temperature fluctuations. If velocity is zero and temperature is constant but density

varies, the pressure varies. This causes a nonzero velocity in the fluid. Flow is accompanied by local expansion and contraction. This does work against the surrounding fluid, leading to temperature fluctuations. So something that is initially a pure density fluctuation with wave vector \mathbf{k} ends up being a complicated combination of density, velocity, and temperature fluctuations, all with the same wave vector, however, since the hydrodynamic equations are linear in the fluctuating variables.

How do these fluctuations decay? Sound waves actually propagate and get damped. The mechanism of damping involves viscosity which decreases the amplitude of the velocity field and thermal conductivity, which decreases the amplitude of the variation temperature field. Both effects are small but nonzero for small k . Temperature fluctuations don't propagate, but they are damped.

Linearized hydrodynamics predicts (let $q = \Delta k = |\mathbf{k}_f - \mathbf{k}_i|$):

- central peak
 - centered at $\Delta\omega = 0$
 - HWHH = $D_T q^2$, D_T = thermal diffusivity, contains λ = thermal conductivity, c_P = specific heat at constant pressure, ($D_T = \lambda/m\rho_0 c_P$)
- Brillouin doublet
 - centered at $\Delta\omega = \pm c_S q$, c_S = adiabatic sound velocity
 - HWHH = Γq^2 , Γ = acoustic attenuation coefficient, contains η_s = shear viscosity, η_v = bulk viscosity, thermal conductivity, c_V = specific heat at constant volume

Qualitative discussion. Spectrum is the time Fourier transform of a correlation function.

A line in a spectrum at nonzero frequency corresponds to a part of time correlation function that oscillates at that frequency and decays slowly. The location of the line gives the frequency of the oscillation. The width of the line gives the time constant for the decay.

Brillouin doublet corresponds to sound waves whose frequency is $c_S q$ and whose decay time goes as q^2 . This is why the lines can be observed at all.

A line in a spectrum at zero frequency corresponds to a part of the time correlation function that does not oscillate but that just decays slowly. The width of the line gives the time constant of the decay.

The result of the latter is a line centered at $\delta\omega = 0$.

You never see sharp lines centered on zero frequency in absorption spectra, since there what is measured is the absorption, and that has an additional power of ω as well as the Fourier transform of the relevant correlation function. Thus, anything you see is peaked at an at least slightly nonzero frequency.

If you look at low frequency in other types of absorption, you can see absorption, but you never see lines that correspond to the Brillouin spectra. Why? Two reasons.

- Density changes do not affect dipole moment, which is what absorption of electromagnetic radiation is coupled to.
- Light scattering sets wave vector as well as resolves frequency.

Another perspective: lines in spectra often correspond to normal modes of vibration of the material. You are used to thinking about normal modes as being properties of a molecule. Sound waves are in effect normal modes of vibration of an entire liquid. They have a spectrum that is continuous, but by using the wave vector specificity provided by light scattering, the lines can be observed. Typically for a line spectrum, the location, width, and shape are important, and all of these can be investigated and understood for Brillouin spectra.

The Brillouin doublets are essentially a Raman spectrum of these normal modes. There is a Stokes line and anti-Stokes line.

0.0.2 Depolarized scattering by nonspherical molecules

A contribution to $\delta\epsilon$ of the form

$$\delta\hat{\epsilon}_{xy}(\mathbf{r}) = (\text{const}) \sum_{i,j=1}^N \hat{u}_x(i)u_y(j)$$

The sum is over all molecules in a region centered at \mathbf{r} large enough to have a dielectric constant. The correlation function of this includes terms such

as

$$\langle u_x(i, t)u_y(j, t)u_x(i, 0)u_y(j, 0) \rangle$$

and

$$\langle u_x(i, t)u_y(i, t)u_x(i, 0)u_y(i, 0) \rangle$$

For the time scales of interest it is only rotational motion that is important, so we won't keep track of the positional degrees of freedom.

Gives contributions to I_{HV} .

Get self terms and two molecule terms. The two molecule terms do not factor unless the two molecules are in fact uncorrelated. It is generally regarded as not a good approximation to assume they are uncorrelated.

Self terms decay to zero on the time scale for rotational relaxation in the fluid. Same thing is true for the two molecule terms, but the relative importance is not completely understood.

What is usually observed is a single line centered at $\Delta\omega = 0$. Approximately Lorentzian in shape, or perhaps several Lorentzians. Can extract a relaxation time.

Simplest theory, orientational Brownian motion or orientational diffusion. Leads to a correlation function that decays. Line at zero frequency. Used to study rotational relaxation.

For some molecules a spectrum with a dip is observed.

Suppose we considered sound waves that for some reason were highly damped. End up with either two overlapping lines or one merged line centered at zero frequency.

Possibility of transverse waves in liquids. Also called shear waves.

Physical picture and comparison with longitudinal sound waves.

Known in solids. Don't exist in normal liquids at very long wave lengths. We know this experimentally, because they have never been observed. We know this theoretically, because if they did exist at long wavelengths they would represent possible solutions of the hydrodynamic equations for normal liquids. But these equations do not have solutions that represent transverse waves.

Indications that they can exist at short wavelengths in liquids, but they are highly damped.

If they existed, what would you see in the scattering? Orientational density can couple to transverse motion. Oscillatory or damped oscillatory behavior of the waves would lead to oscillatory or damped oscillatory decay of the correlation function for orientational fluctuations. Look in I_{VH} or I_{HV} , since the dielectric constant fluctuations have off diagonal elements and contributions from polarized light scattering would not appear. For some liquids, in ordinary light scattering regime, see a central peak with a dip. Interpreted as overdamped shear waves.

0.0.3 Composition fluctuations

Binary mixture. $\partial\epsilon/\partial c_A \neq 0$. See correlation function

$$\langle c_A(\mathbf{r}, t) c_A(\mathbf{0}, 0) \rangle$$

Decays as

$$\exp(-q^2 D t)$$

FT is a line centered at $\Delta\omega = 0$. Width proportional to $q^2 D$. $D =$ mutual diffusion constant. Can be used to measure mutual diffusion coefficients in liquids.

0.1 Decay of fluctuations

For equilibrium systems, the decay of fluctuations at long times (and long wavelengths), has the time dependence predicted by the hydrodynamic equations that apply even far from equilibrium. Any fluctuations that influence the local dielectric constant can affect the light scattering. Hydrodynamic theory can be used to interpret the results.

E.g. chemical reactions, concentration of trace species, concentration fluctuation in binary mixtures, density fluctuations in liquids, orientational fluctuations in liquids.

Experimental measurements of correlation functions of fluctuations at equilibrium can give information about parameters that relate to nonequilibrium

situations - rate constants, diffusion constants, rotational relaxation times, sound attenuation coefficients, thermal diffusivity.

1 Molecular polarizability theory of light scattering

Molecular approach focuses on the molecules rather than the dielectric constant.

Most appropriate for dilute solutions of the species of interest. (Must always recognize however that the solvent also contributes to the scattering.)

Dielectric constant theory: \mathbf{E} and \mathbf{P} . Replace latter by $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$. These are macroscopic fields.

Assumptions of the molecular polarizability theory.

- A molecule i in a material feels the macroscopic electric field $\mathbf{E}(\mathbf{r}_i, t)$ at its location.
- A molecule i has a polarizability tensor $\hat{\alpha}(i)$, such that the dipole moment of the molecule is

$$\mu(i, t) = \hat{\alpha}(i, t) \cdot \mathbf{E}(\mathbf{r}_i, t)$$

- $\hat{\alpha}(i, t)$ depends on the internal coordinates at time t (orientation, conformational coordinates, but not position.)

These assumptions are not quite true, but they are often used. They neglect:

- internal field effects
- collision induced effects

The assumptions lead to an essentially correct description of some but not all the phenomena seen in light scattering.

The total induced dipole moment of the sample as a function of position is

$$P(\mathbf{r}, t) = \sum_i \hat{\alpha}(i, t) \cdot \mathbf{E}(\mathbf{r}_i, t) \delta(\mathbf{r} - \mathbf{r}_i)$$

The induced dipole moment in the sample varies from place to place and from time to time and is the origin of the scattered light, just as in the dielectric constant theory.

As in the generic scattering theory, we find that the relevant correlation function is that of

$$\sum_i \hat{\mathbf{n}}_f \cdot \hat{\alpha}(i, t) \cdot \hat{\mathbf{n}}_i \delta(\mathbf{r} - \mathbf{r}_i(t))$$

Note that both the positional and internal coordinates appear here. Let's abbreviate this as

$$\sum_i \hat{\alpha}_{fi}(i, t) \delta(\mathbf{r} - \mathbf{r}_i(t))$$

The Fourier transform of this in space is

$$\sum_i \hat{\alpha}_{fi}(i, t) e^{i\mathbf{k} \cdot \mathbf{r}_i(t)}$$

This approach is especially useful for dilute solutions where the molecules are statistically independent. Then the cross terms between different molecules is not important. The relevant correlation function is

$$\left\langle \sum_i \hat{\alpha}_{fi}(i, t) e^{i\mathbf{k} \cdot \mathbf{r}_i(t)} \hat{\alpha}_{fi}(i, 0) e^{i\mathbf{k} \cdot \mathbf{r}_i(0)} \right\rangle = \sum_i \left\langle \hat{\alpha}_{fi}(i, t) \hat{\alpha}_{fi}(i, 0) e^{i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))} \right\rangle$$

It becomes even simpler when the internal degrees of freedom and the translational degrees of freedom are uncorrelated.

Discussion of the meaning of this.

Then we have, for a system with one kind of scatterer.

$$\sum_i \left\langle \hat{\alpha}_{fi}(i, t) \hat{\alpha}_{fi}(i, 0) \right\rangle \left\langle e^{i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))} \right\rangle$$

Let

$$F_s(\mathbf{k}, t) \equiv \left\langle e^{i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))} \right\rangle$$

This is often called the intermediate scattering function.

The other factor in the sum depends on internal coordinates, e.g. rotational, conformational.

Meaning of intermediate.

Incidentally, for some kinds of detection, it can be measured directly in the time domain.

Hydrodynamic theory of this function

$$F_s(\mathbf{k}, t) = \exp(-q^2 Dt)$$

Provides a way of measuring diffusion coefficients of macromolecules, which can be related to the size of the molecules. Look in the polarized spectrum, which will always be nonzero. Must deal in some way with the other factor. How you do this is very system dependent.

Simplest case is spherical molecules for which the polarizability does not fluctuate. Then look in the polarized spectrum

Next case is molecules that relax internally very quickly. Note that diagonal elements don't deal with fluctuations. Internal correlation function goes to a nonzero constant.

Next simplest case is molecules that rotate very slowly on the time scale of diffusion. (Not clear this is ever applicable.)

In more general case, you have to think carefully about the meaning of the signal you are seeing. It may be dominated by diffusion or by one or more internal degrees of freedom.

1.1 Dilute solution of linear molecules

1.1.1 Polarizability of linear molecule

Tensor in molecule fixed frame

symmetry axis is x

$$\epsilon_{xx} = \epsilon_{||}$$

others

$$\epsilon_{\perp}$$

Define

$$\alpha = \frac{1}{3}(\alpha_{||} + 2\alpha_{\perp})$$

Define

$$\beta = \alpha_{||} - \alpha_{\perp}$$

Then in molecule fixed frame

$$\hat{\alpha} = \alpha \hat{\mathbf{I}} + \beta (\text{a tensor})$$

In lab frame

$$\hat{\alpha} = \alpha I + \beta (\text{a tensor that depends on orientation})$$

Correlation function of an component of α

$$\begin{aligned} \hat{\alpha}_{fi} &= \alpha \hat{\mathbf{u}}_i \cdot \hat{\mathbf{I}} \cdot \mathbf{u}_i + \beta (\text{something dependent on orientation}) \\ &= \alpha \hat{\mathbf{u}}_i \cdot \mathbf{u}_i + \beta (\text{something dependent on orientation}) \end{aligned}$$

Average of the last term is zero. First term does not fluctuate.

$$\langle \hat{\alpha}_{fi}(i, t) \hat{\alpha}_{fi}(i, 0) \rangle = \alpha^2 \hat{\mathbf{u}}_i \cdot \mathbf{u}_i + \beta^2 (\text{something that goes to zero for long times})$$

1.1.2 Rotational diffusion of linear molecules

Diffusion

$$\frac{\partial c}{\partial t} = D \nabla^2 c$$

In spherical polar coordinates

$$\nabla^2 = \left(\frac{1}{r} \frac{\partial}{\partial r} r \right)^2 + \frac{1}{r^2 \sin^2 \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \phi^2} \right) = -\hat{I}^2$$

Points diffusing on the surface of a sphere. Physical meaning.

Debye equation for rotational diffusion.

$$\frac{\partial c(\mathbf{u}, t)}{\partial t} = -D_r \hat{I}^2 c(\mathbf{u}, t)$$

D_r often called the rotational diffusion constant.

1.1.3 Light scattering by dilute solution of linear molecules

Now have everything needed to calculate the spectrum.

I_{VV} = two Lorenzians at zero frequency

1. relative amplitude α^2 , HWHH $q^2 D$.
2. $4\beta^2/45$, $6D_r + q^2 D$
3. $\beta^2/15$, $6D_r + q^2 D$

Lots of assumptions went into this. Dilute, independence of rotation and translation, translational diffusion, rotational diffusion. Usually satisfied for dilute solutions of cylindrically symmetric molecules.

1.2 More complicated molecules

Get several exponentials from the rotation, not just one. Can be difficult to extract the individual relaxation times