S10.C. Light Scattering

Read Reichl's opening remarks.

The Raman scattering (inelastic scattering of light by vibrational waves) can be described as the Doppler shifts of the scattered light.

Reminder: in an elastic scattering, the kinetic energy (frequency) of the incident particle (light) is not changed by the scattering.

Let

λ_0 ($\boldsymbol{k}_0$) = wavelength (wave-vector) of incident light.
λ_s ($\boldsymbol{k}_s$) = wavelength (wave-vector) of sound wave.
v_s (c) = speed of sound (light) wave.
$\boldsymbol{k}$ = wave-vector of scattered light.
θ = scattering angle, i.e., angle from $\boldsymbol{k}_0$ to $\boldsymbol{k}$.

Since $c \gg v_s$, we can treat the wave front of the sound wave as stationary when applying the law of reflection, which gives

$$\Delta \boldsymbol{k} = \boldsymbol{k} - \boldsymbol{k}_0 \approx \pm 2 \frac{\boldsymbol{v}_s}{v_s} k_0 \sin \frac{\theta}{2} \qquad (10.245a)$$

where the $\pm$ sign applies when $\boldsymbol{v}_s$ is $\begin{matrix}\text{parallel}\\ \text{antiparallel}\end{matrix}$ to $\boldsymbol{k} - \boldsymbol{k}_0$.

$$\Delta k = | \boldsymbol{k} - \boldsymbol{k}_0 | \approx 2 k_0 \sin \frac{\theta}{2} \qquad (10.245)$$

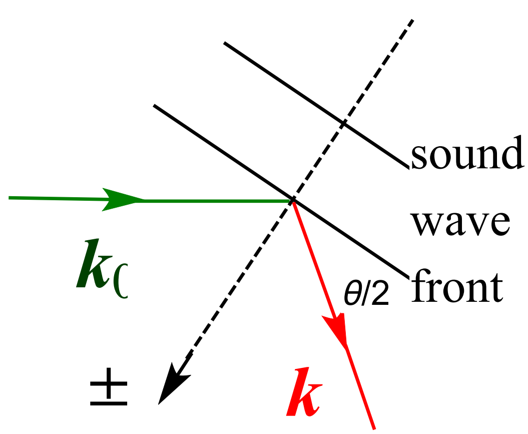

Fig.10.1. Scattering of light by a sound wave.

By the same token, neighboring sound wave fronts can be treated as stationary reflecting planes separated by a distance of λ_s when applying the Bragg's law, which gives

$$\lambda_0 \approx 2 \lambda_s \sin \frac{\theta}{2} \qquad (10.244)$$

$$\rightarrow \quad k_s \approx 2 k_0 \sin \frac{\theta}{2} \qquad \left[k = | \boldsymbol{k} | = \frac{2\pi}{\lambda} \right] \qquad (10.144a)$$

Combining (10.244-5) gives

$$\Delta k = k_s \tag{10.144b}$$

Reminder: (10.245) is true for a single wave front, while (10.144a) gives the surviving scattered light not cancelled by light reflected from neighboring wave fronts.

Now, the sound wave fronts are actually travelling with speed v_s. If we take (10.245a) as the reflection law in a system traveling with the sound wave, then an observer in the laboratory will find a Doppler shift in the frequency of the scattered light as

$$\begin{aligned}\Delta\omega &= \omega - \omega_0 \\ &= \boldsymbol{v}_s \cdot \Delta\boldsymbol{k} \\ &\approx \pm 2\, v_s \frac{\omega_0}{c} \sin\frac{\theta}{2} \qquad \text{[(10.245a) used.]}\end{aligned} \tag{10.246}$$

From the particle point of view, the Raman scattering can be interpreted as the $\begin{matrix}\text{absorption}\\ \text{emission}\end{matrix}$ of a phonon of energy $\hbar\,\omega_s = \hbar\, k_s\, v_s$ and momentum $\hbar\, \boldsymbol{k}_s$, by the incident photon $k_0^\mu = \left(\frac{\omega_0}{c},\ \boldsymbol{k}_0\right)$, which becomes the scattered photon $k^\mu = \left(\frac{\omega}{c},\ \boldsymbol{k}\right)$. (10.144b) & (10.246) are just the conservation of momentum & energy, respectively.

S10.C.1. Scattered Electric Field

We now turn to the problem of calculating the intensity of the scattered light.

To this end, light is considered as an electromagnetic (EM) wave. In particular, the incident light is a monochromatic plane wave with transverse electromagnetic field

$$\boldsymbol{E}_0(\boldsymbol{r}, t) = \boldsymbol{E}_0\, e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r} - \omega_0 t)} \qquad \boldsymbol{B}_0(\boldsymbol{r}, t) = \boldsymbol{B}_0\, e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r} - \omega_0 t)} \tag{10.247}$$

where

$$\boldsymbol{k}_0 \times \boldsymbol{E}_0 = \frac{\omega_0}{c}\boldsymbol{B}_0 \tag{10.247a}$$

The target is a fluid of volume V containing N particles, each with polarizability α. If the volume is in the shape of a cylinder, both incident & observed light beams can be arranged to be normal to the side of the cylinder. Since the tangential components of $\boldsymbol{E}$ are continuous across a boundary, $\boldsymbol{E}$ of the light beams are likewise continuous. The incident light induces in the fluid a polarization (density of dipole moment)

$$\begin{aligned}\boldsymbol{P}(\boldsymbol{r}, t) &= \alpha\,\boldsymbol{E}(\boldsymbol{r}, t)\sum_{j=1}^{N}\delta[\boldsymbol{r} - \boldsymbol{q}_j(t)] \qquad \text{[} \boldsymbol{E} = \text{total electric field.]} \\ &\approx \alpha\,\boldsymbol{E}_0(\boldsymbol{r}, t)\sum_{j=1}^{N}\delta[\boldsymbol{r} - \boldsymbol{q}_j(t)] \qquad \text{[multiple-scattering neglected.]}\end{aligned} \tag{10.248}$$

where $\boldsymbol{q}_j(t)$ is the position of the j^{th} particle at time t.

For a fluid of permeability μ and permittivity ϵ that is neutral with no free charges or currents, the Maxwell equations for the light beam inside the fluid are

$$\nabla_{\boldsymbol{r}} \cdot \boldsymbol{E} = 4\pi\rho \qquad \nabla_{\boldsymbol{r}} \cdot \boldsymbol{B} = 0$$

$$\nabla_r \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0 \qquad \nabla_r \times \boldsymbol{B} = \frac{4\pi}{c}\boldsymbol{J} + \frac{\epsilon}{c}\frac{\partial \boldsymbol{E}}{\partial t} \tag{10.249a}$$

where ρ & $\boldsymbol{J}$ are the total (now equals to the induced polarization) charge and current densities, respectively. We have also used the constituent equation

$$\boldsymbol{D} \equiv \boldsymbol{E} + 4\pi \boldsymbol{P} = \epsilon \boldsymbol{E} \tag{10.249b}$$

Reminder: a perhaps more familiar form of the augmented Ampere's law is

$$\nabla_r \times \boldsymbol{H} = \frac{4\pi}{c}\boldsymbol{J}_f + \frac{1}{c}\frac{\partial \boldsymbol{D}}{\partial t} \qquad [\, \boldsymbol{B} = \boldsymbol{H} + 4\pi \boldsymbol{M} \,]$$

where $\boldsymbol{J}_f = \boldsymbol{J} - c\nabla \times \boldsymbol{M}$ is the current density of free charges.

In terms of the potentials, we have [in Gaussian units]

$$\boldsymbol{E} = -\nabla_r \phi - \frac{1}{c}\frac{\partial \boldsymbol{A}}{\partial t} \qquad \boldsymbol{B} = \nabla_r \times \boldsymbol{A} \tag{10.249}$$

so that the homogeneous equations in (10.249a) are automatically satisfied. The inhomogeneous ones become

$$-\nabla_r^2 \phi - \frac{1}{c}\frac{\partial \nabla_r \cdot \boldsymbol{A}}{\partial t} = 4\pi\rho$$

$$\nabla_r \times (\nabla_r \times \boldsymbol{A}) = \frac{4\pi}{c}\boldsymbol{J} - \frac{\epsilon}{c}\nabla_r \frac{\partial \phi}{\partial t} - \frac{\epsilon}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} \tag{10.249c}$$

$$= \nabla_r(\nabla_r \cdot \boldsymbol{A}) - \nabla_r^2 \boldsymbol{A}$$

In the Lorentz gauge, we set

$$\nabla_r \cdot \boldsymbol{A} + \frac{\epsilon}{c}\frac{\partial \phi}{\partial t} = 0 \tag{10.249d}$$

and (10.249c) becomes

$$\nabla_r^2 \phi - \frac{\epsilon}{c^2}\frac{\partial^2 \phi}{\partial t^2} = -4\pi\rho \tag{10.251a}$$

$$\nabla_r^2 \boldsymbol{A} - \frac{\epsilon}{c^2}\frac{\partial^2 \boldsymbol{A}}{\partial t^2} = -\frac{4\pi}{c}\boldsymbol{J} \tag{10.250a}$$

Note: setting $\rho = 0 = \boldsymbol{J}$ in (10.250a-1a) shows that $c' = \dfrac{c}{\sqrt{\epsilon}}$ is the speed of light in the fluid.

Since there are no free charges,

$$\nabla_r \cdot \boldsymbol{D} = 0 \; = \nabla_r \cdot (\boldsymbol{E} + 4\pi \boldsymbol{P})$$

$$= 4\pi\rho + 4\pi\nabla_r \cdot \boldsymbol{P} \qquad [\text{ (10.249a) used. }]$$

$$\rightarrow \qquad \rho = -\nabla_r \cdot \boldsymbol{P} \tag{10.250b}$$

Conservation of charge requires

$$\frac{\partial \rho}{\partial t} + \nabla_r \cdot \boldsymbol{J} = 0$$

$$= -\frac{\partial \nabla_r \cdot \boldsymbol{P}}{\partial t} + \nabla_r \cdot \boldsymbol{J} \qquad [\text{ (10.250b) used. }]$$

$$= -\nabla_r \cdot \left(\frac{\partial \boldsymbol{P}}{\partial t} - \boldsymbol{J} \right)$$

$$\rightarrow \qquad \boldsymbol{J} = \frac{\partial \boldsymbol{P}}{\partial t} \tag{10.250c}$$

where a possible constant was dropped since there is no other source that can contribute to $\boldsymbol{J}$.

Putting (10.250b,c) into (10.250a,1a) gives

$$\nabla_{\boldsymbol{r}}^2 \phi - \frac{\epsilon}{c^2} \frac{\partial^2 \phi}{\partial t^2} = 4 \pi \nabla_{\boldsymbol{r}} \cdot \boldsymbol{P} \tag{10.251}$$

$$\nabla_{\boldsymbol{r}}^2 \boldsymbol{A} - \frac{\epsilon}{c^2} \frac{\partial^2 \boldsymbol{A}}{\partial t^2} = -\frac{4\pi}{c} \frac{\partial \boldsymbol{P}}{\partial t} \tag{10.250}$$

Since there are only one independent field $\boldsymbol{E}$ or $\boldsymbol{P}$, the system can be described by a vector potential $\boldsymbol{Z}(\boldsymbol{r}, t)$, also known as the Hertz potential, such that

$$\phi = -\nabla_{\boldsymbol{r}} \cdot \boldsymbol{Z} \tag{10.253}$$

$$\boldsymbol{A} = \frac{1}{c} \frac{\partial \boldsymbol{Z}}{\partial t} \tag{10.252}$$

Obviously, the validity of (10.252-3) hinges on subsequent consistency.

Putting (10.252-3) into (10.251) gives

$$-\nabla_{\boldsymbol{r}}^2 (\nabla_{\boldsymbol{r}} \cdot \boldsymbol{Z}) + \frac{\epsilon}{c^2} \frac{\partial^2 \nabla_{\boldsymbol{r}} \cdot \boldsymbol{Z}}{\partial t^2} = 4 \pi \nabla_{\boldsymbol{r}} \cdot \boldsymbol{P}$$

$$\rightarrow \qquad \nabla_{\boldsymbol{r}}^2 \boldsymbol{Z} - \frac{\epsilon}{c^2} \frac{\partial^2 \boldsymbol{Z}}{\partial t^2} = -4 \pi \boldsymbol{P} \tag{10.254}$$

Similarly, (10.250) gives

$$\frac{1}{c} \nabla_{\boldsymbol{r}}^2 \frac{\partial \boldsymbol{Z}}{\partial t} - \frac{1}{c} \frac{\epsilon}{c^2} \frac{\partial^2}{\partial t^2} \frac{\partial \boldsymbol{Z}}{\partial t} = -\frac{4\pi}{c} \frac{\partial \boldsymbol{P}}{\partial t}$$

$$\rightarrow \qquad \nabla_{\boldsymbol{r}}^2 \boldsymbol{Z} - \frac{\epsilon}{c^2} \frac{\partial^2 \boldsymbol{Z}}{\partial t^2} = -4 \pi \boldsymbol{P}$$

which is just (10.254). This legitimizes (10.252-3).

Solution of (10.10254) can be written in terms of the Green's function $\boldsymbol{G}(\boldsymbol{r} - \boldsymbol{r}', \ t - t')$ defined by

$$\nabla_{\boldsymbol{r}}^2 \boldsymbol{G} - \frac{\epsilon}{c^2} \frac{\partial^2 \boldsymbol{G}}{\partial t^2} = -\delta(\boldsymbol{r} - \boldsymbol{r}')\, \delta(t - t') \tag{10.254a}$$

The retarded solution of (10.254a) is [see, e.g., (12.131) of J.D.Jackson, "Classical Electrodynamics", 2nd.ed.]

$$\boldsymbol{G}(\boldsymbol{r} - \boldsymbol{r}', \ t - t') = \frac{1}{4\pi \,|\, \boldsymbol{r} - \boldsymbol{r}' \,|} \delta\left(t - t' - \frac{\sqrt{\epsilon}\, \left| \boldsymbol{r} - \boldsymbol{r}' \right|}{c} \right) \tag{10.254b}$$

where a factor $\theta(t - t')$ is omitted since it is automatically satisfied wherever the δ function is non-zero.

The retarded solution of (10.254) is

$$\boldsymbol{Z}(\boldsymbol{r}, t) = \int_{-\infty}^{\infty} d t' \int_V d \boldsymbol{r}' \frac{\boldsymbol{P}(\boldsymbol{r}', t')}{|\, \boldsymbol{r} - \boldsymbol{r}' \,|} \delta\left(t - t' - \frac{\sqrt{\epsilon}\, \left| \boldsymbol{r} - \boldsymbol{r}' \right|}{c} \right) \tag{10.255}$$

$$= \int_{-\infty}^{\infty} d\,t' \int_V d\,\boldsymbol{r}' \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} \frac{\boldsymbol{P}(\boldsymbol{r}',\,t')}{|\ \boldsymbol{r}-\boldsymbol{r}'\ |} \exp\left[i\,\omega \left(t - t' - \frac{\sqrt{\epsilon}\ |\ \boldsymbol{r}-\boldsymbol{r}'\ |}{c} \right) \right] \quad (10.256)$$

and describes the outgoing wave through [see (10.249) & (10.252-3)]

$$\boldsymbol{E} = \nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}} \cdot \boldsymbol{Z}) - \frac{1}{c^2} \frac{\partial^2 \boldsymbol{Z}}{\partial\, t^2} \quad (10.257)$$

For a low density target such as gases, $\epsilon \approx 1$ and (10.256) is applicable outside the sample. Furthermore, (10.248) also applies so that (10.256) becomes

$$\boldsymbol{Z}(\boldsymbol{r},\,t) \approx \int_{-\infty}^{\infty} d\,t' \int_V d\,\boldsymbol{r}' \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} \frac{\alpha\,\boldsymbol{E}_0\, e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0 t')}}{|\ \boldsymbol{r}-\boldsymbol{r}'\ |} \sum_{j=1}^{N} \delta[\,\boldsymbol{r}' - \boldsymbol{q}_j(t')\,] \quad (10.257a)$$

$$\times \exp\left[i\,\omega \left(t - t' - \frac{|\ \boldsymbol{r}-\boldsymbol{r}'\ |}{c} \right) \right]$$

For an observation point far away from the sample,

$$|\ \boldsymbol{r}-\boldsymbol{r}'\ | \approx r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}' + \ldots \qquad \hat{r} = \frac{\boldsymbol{r}}{r} \quad (10.258)$$

and (10.257a) simplifies to

$$\boldsymbol{Z}(\boldsymbol{r},\,t) \approx \frac{\alpha\,\boldsymbol{E}_0}{r} \int_{-\infty}^{\infty} d\,t' \int_V d\,\boldsymbol{r}' \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0 t')} \sum_{j=1}^{N} \delta[\,\boldsymbol{r}' - \boldsymbol{q}_j(t')\,] \quad (10.259)$$

$$\times \exp\left[i\,\omega \left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c} \right) \right]$$

$$= \frac{\alpha\,\boldsymbol{E}_0}{r} \int_{-\infty}^{\infty} d\,t' \int d\,\boldsymbol{r}' \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0 t')}\, n(\boldsymbol{r}',\,t') \quad (10.259a)$$

$$\times \exp\left[i\,\omega \left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c} \right) \right]$$

where

$$n(\boldsymbol{r}',\,t') = \sum_{j=1}^{N} \delta[\,\boldsymbol{r}' - \boldsymbol{q}_j(t')\,] = \text{particle density in target.} \quad (10.261)$$

and the domain of the $\boldsymbol{r}'$-integration can be extended to all spaces since $n = 0$ outside V.

In order to evaluate (10.257), need only consider

$$\boldsymbol{F} = \frac{\boldsymbol{E}_0}{r} \exp\left[i\,\omega \left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c} \right) \right] \quad (10.261a)$$

since

$$\boldsymbol{Z}(\boldsymbol{r},\,t) = \alpha \int_{-\infty}^{\infty} d\,t' \int d\,\boldsymbol{r}' \int_{-\infty}^{\infty} \frac{d\,\omega}{2\,\pi} e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0 t')}\, n(\boldsymbol{r}',\,t')\ \boldsymbol{F} \quad (10.261b)$$

Now

$$\boldsymbol{r} = x_i \qquad \hat{\boldsymbol{r}} = \frac{x_i}{r} = \frac{x_i}{\sqrt{x_j\,x_j}}$$

$$\rightarrow \quad \partial_i r = \partial_i \sqrt{x_j\,x_j} = \frac{x_i}{r} \qquad \partial_i \frac{1}{r} = -\frac{x_i}{r^3}$$

$$\partial_i(\hat{\boldsymbol{r}}\cdot\boldsymbol{r}') = \partial_i\left(\frac{x_j\,x_j'}{r}\right) = \frac{\delta_{ij}\,x_j'}{r} - \frac{x_j\,x_j'}{r^3}\,x_i = \frac{x_i'}{r} - \frac{\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{r^2}\,x_i$$

$$\partial_i(r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}') = \frac{x_i}{r} - \frac{x_i'}{r} + \frac{\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{r^2}\,x_i = \frac{x_i}{r} + O(r^{-1})$$

[x_i is of the same order as r.]

Keeping only the lowest order terms in r^{-1}, we have

$$\nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}}\cdot\boldsymbol{F}) = \partial_i(\partial_j F_j)$$

$$= \partial_i\,\partial_j\left\{\frac{E_{0j}}{r}\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right]\right\}$$

$$= -i\,E_{0j}\,\frac{\omega}{c}\,\partial_i\left\{\frac{x_j}{r^2}\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right] + O(r^{-2})\right\}$$

$$= -i\,E_{0j}\,\frac{\omega}{c}\left(\frac{\delta_{ij}}{r^2} - \frac{2\,x_j\,x_i}{r^4} - i\,\frac{\omega}{c}\,\frac{x_j\,x_i}{r^3}\right)\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right] + O(r^{-3})$$

$$= -\,E_{0j}\,\frac{\omega^2}{c^2}\,\frac{x_i\,x_j}{r^3}\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right] + O(r^{-2})$$

$$= -\,\frac{\omega^2}{c^2}\,\frac{\hat{\boldsymbol{r}}(\boldsymbol{E}_0\cdot\hat{\boldsymbol{r}})}{r}\,\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right] + O(r^{-2}) \qquad (10.261c)$$

$$\frac{\partial^2\,\boldsymbol{F}}{\partial\,t^2} = -\,\omega^2\,\frac{\boldsymbol{E}_0}{r}\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right] \qquad (10.261d)$$

Putting (10.261b-d) into (10.257) gives the electric field of the scattered light as

$$\boldsymbol{E}(\boldsymbol{r},\,t) = \alpha\int_{-\infty}^{\infty}d\,t'\int d\,\boldsymbol{r}'\int_{-\infty}^{\infty}\frac{d\,\omega}{2\,\pi}\,e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0\,t')}\,n(\boldsymbol{r}',\,t')\left[\nabla_{\boldsymbol{r}}(\nabla_{\boldsymbol{r}}\cdot\boldsymbol{F}) - \frac{1}{c^2}\,\frac{\partial^2\,\boldsymbol{F}}{\partial\,t^2}\right]$$

$$\approx \frac{\alpha}{c^2\,r}\left[\boldsymbol{E}_0 - \hat{\boldsymbol{r}}(\boldsymbol{E}_0\cdot\hat{\boldsymbol{r}})\right]\int_{-\infty}^{\infty}d\,t'\int d\,\boldsymbol{r}'\int_{-\infty}^{\infty}\frac{d\,\omega}{2\,\pi} \qquad (10.260)$$

$$\times\,e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}' - \omega_0\,t')}\,n(\boldsymbol{r}',\,t')\,\omega^2\exp\left[i\,\omega\left(t - t' - \frac{r - \hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right]$$

S10.C.2. Intensity of Scattered Light

The spectral intensity of the scattered light is defined as [c.f. (5.87) of §5.E.2]

$$I(\boldsymbol{r},\,\omega) = \lim_{T\to\infty}\frac{1}{T}\,\frac{c}{8\,\pi}\,\boldsymbol{E}(\boldsymbol{r},\,\omega\,;\,T)\cdot\boldsymbol{E}^*(\boldsymbol{r},\,\omega\,;\,T) \qquad (10.262)$$

where the factor $8\,\pi$ is due to the use of complex fields [see 6.10 of Jackson] and

$$\boldsymbol{E}(\boldsymbol{r},\,\omega\,;\,T) = \int_{-T}^{T}d\,t\,e^{i\,\omega\,t}\,\boldsymbol{E}(\boldsymbol{r},\,t)$$

$$= \int_{-\infty}^{\infty}d\,t\,e^{i\,\omega\,t}\,\boldsymbol{E}(\boldsymbol{r},\,t)\,\theta(T - |\,t\,|) \qquad (10.263)$$

Reminder: intensity of an EM wave is given by the projection of its Poynting vector on the surface it illuminates [see 7.1 of Jackson].

Putting (10.163) into (10.262) gives

$$I(\boldsymbol{r},\,\omega) = \lim_{T\to\infty}\frac{1}{T}\,\frac{c}{8\,\pi}\int_{-T}^{T}d\,t\int_{-T}^{T}d\,t'\;e^{i\,\omega\,(t-t')}\,\boldsymbol{E}(\boldsymbol{r},\,t)\cdot\boldsymbol{E}^*(\boldsymbol{r},\,t')$$

$$= \lim_{T\to\infty} \frac{1}{T}\frac{c}{8\pi}\int_{-T}^{T} dt' \int_{-T-t'}^{T-t'} d\tau\, e^{i\omega\tau}\, \boldsymbol{E}(\boldsymbol{r},\tau+t')\cdot\boldsymbol{E}^*(\boldsymbol{r},t') \qquad [\,\tau = t - t'\,]$$

$$= \frac{c}{4\pi}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T} dt'\, \boldsymbol{E}(\boldsymbol{r},\tau+t')\cdot\boldsymbol{E}^*(\boldsymbol{r},t') \qquad (10.264a)$$

If the system is ergodic [see §6.C], time averages are the same as ensemble averages. (10.264a) then becomes

$$I(\boldsymbol{r},\omega) = \frac{c}{4\pi}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\,\langle \boldsymbol{E}(\boldsymbol{r},\tau)\cdot\boldsymbol{E}^*(\boldsymbol{r},0)\rangle \qquad (10.264)$$

where the average is with respect to the equilibrium ensemble.

Putting (10.260) into (10.264) gives

$$I(\boldsymbol{r},\omega) = \frac{c}{4\pi}\left(\frac{\alpha}{c^2 r}\right)^2 \left[\boldsymbol{E}_0 - \hat{\boldsymbol{r}}\left(\boldsymbol{E}_0\cdot\hat{\boldsymbol{r}}\right)\right]^2 \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} dt' \int d\boldsymbol{r}' \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}$$

$$\times \int_{-\infty}^{\infty} dt'' \int d\boldsymbol{r}'' \int_{-\infty}^{\infty}\frac{d\omega''}{2\pi}\, e^{i\omega\tau}\, e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}'-\omega_0 t')}\,\omega'^2 \exp\left[i\omega'\left(\tau - t' - \frac{r-\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right]$$

$$\times e^{-i(\boldsymbol{k}_0\cdot\boldsymbol{r}''-\omega_0 t'')}\,\omega''^2 \exp\left[i\omega''\left(t'' + \frac{r-\hat{\boldsymbol{r}}\cdot\boldsymbol{r}''}{c}\right)\right]\langle n(\boldsymbol{r}',t')\,n(\boldsymbol{r}'',t'')\rangle$$

(10.265)

Using

$$\hat{\boldsymbol{E}}_0\cdot\hat{\boldsymbol{r}} = \cos\theta \qquad \to \qquad \left[\boldsymbol{E}_0 - \hat{\boldsymbol{r}}\left(\boldsymbol{E}_0\cdot\hat{\boldsymbol{r}}\right)\right]^2 = E_0^2\sin^2\theta$$

$$\int_{-\infty}^{\infty} d\tau\, e^{i(\omega+\omega')\tau} = 2\pi\,\delta(\omega+\omega')$$

(10.265) becomes

$$I(\boldsymbol{r},\omega) = \frac{c}{4\pi}\left(\frac{\alpha}{c^2 r}\right)^2 E_0^2\sin^2\theta \int_{-\infty}^{\infty} dt' \int d\boldsymbol{r}' \qquad (10.266)$$

$$\times \int_{-\infty}^{\infty} dt'' \int d\boldsymbol{r}'' \int_{-\infty}^{\infty}\frac{d\omega''}{2\pi}\, e^{i(\boldsymbol{k}_0\cdot\boldsymbol{r}'-\omega_0 t')}\,\omega^2 \exp\left[i\omega\left(t' + \frac{r-\hat{\boldsymbol{r}}\cdot\boldsymbol{r}'}{c}\right)\right]$$

$$\times e^{-i(\boldsymbol{k}_0\cdot\boldsymbol{r}''-\omega_0 t'')}\,\omega''^2 \exp\left[i\omega''\left(t'' + \frac{r-\hat{\boldsymbol{r}}\cdot\boldsymbol{r}''}{c}\right)\right]\langle n(\boldsymbol{r}',t')\,n(\boldsymbol{r}'',t'')\rangle$$

For an equilibrium ensemble,

$$\langle n(\boldsymbol{r}',t')\,n(\boldsymbol{r}'',t'')\rangle = \langle n(\boldsymbol{r}',t'-t'')\,n(\boldsymbol{r}'')\rangle$$

Using,

$$\int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt''\, e^{-i(\omega_0-\omega)t'}\, e^{i(\omega_0+\omega'')t''}\,\langle n(\boldsymbol{r}',t')\,n(\boldsymbol{r}'',t'')\rangle$$

$$= \int_{-\infty}^{\infty} dt''\, e^{i(\omega''+\omega)t''} \int_{-\infty}^{\infty} d\tau\, e^{-i(\omega_0-\omega)\tau}\langle n(\boldsymbol{r}',\tau)\,n(\boldsymbol{r}'')\rangle \qquad \tau = t' - t''$$

$$= \int_{-\infty}^{\infty} dt''\, e^{i(\omega''+\omega)t''}\,\langle n(\boldsymbol{r}',\Omega)\,n(\boldsymbol{r}'')\rangle \qquad \Omega = \omega_0 - \omega$$

$$= 2\pi\,\delta(\omega''+\omega)\,\langle n(\boldsymbol{r}',\Omega)\,n(\boldsymbol{r}'')\rangle$$

(10.266) becomes

$$I(\mathbf{r},\,\omega) = \frac{c}{4\,\pi}\left(\frac{\alpha}{c^2\,r}\right)^2\,E_0^2\sin^2\theta\,\int d\,\mathbf{r}'$$
$$\times \int d\,\mathbf{r}''\,e^{i\,\mathbf{k}_0\cdot\mathbf{r}'}\,\omega^2\exp\!\left[i\,\omega\,\frac{r-\hat{\mathbf{r}}\cdot\mathbf{r}'}{c}\right]$$
$$\times\, e^{-i\,\mathbf{k}_0\cdot\mathbf{r}''}\,\omega^2\exp\!\left[-i\,\omega\,\frac{r-\hat{\mathbf{r}}\cdot\mathbf{r}''}{c}\right)\Big]\langle\, n(\mathbf{r}',\,\Omega)\,n(\mathbf{r}'')\,\rangle$$
$$= \frac{c}{4\,\pi}\left(\frac{\alpha}{c^2\,r}\right)^2\,\omega^4\,E_0^2\sin^2\theta\,\int d\,\mathbf{r}'\int d\,\mathbf{r}''\,\exp\!\left[i\left(\mathbf{k}_0-\frac{\omega}{c}\,\hat{\mathbf{r}}\right)\cdot(\mathbf{r}'-\mathbf{r}'')\right]\langle\, n(\mathbf{r}',\,\Omega)\,n(\mathbf{r}'')\,\rangle$$
$$= \frac{c}{4\,\pi}\left(\frac{\alpha}{c^2\,r}\right)^2\,\omega^4\,E_0^2\sin^2\theta\,N\,S(\mathbf{k}\,;\Omega) \qquad (10.271)$$

where

$$\mathbf{k} = \mathbf{k}_0 - \frac{\omega}{c}\,\hat{\mathbf{r}} \qquad (10.271a)$$

and [see Exercise 10.4 of §10.D.2]

$$C_{n\,n}(\boldsymbol{\rho},\,\Omega) = \frac{1}{N}\int d\,\mathbf{r}\,\langle\, n(\boldsymbol{\rho}+\mathbf{r},\,\Omega)\,n(\mathbf{r})\,\rangle$$
$$= \frac{1}{N}\int d\,\mathbf{r}\int d\,\tau\,e^{-i\,\Omega\,\tau}\,\langle\, n(\boldsymbol{\rho}+\mathbf{r},\,\tau)\,n(\mathbf{r})\,\rangle \qquad (10.271b)$$

$$S\,(\mathbf{k}\,;\Omega) = \int d\,\boldsymbol{\rho}\,e^{i\,\mathbf{k}\cdot\boldsymbol{\rho}}\,C_{n\,n}(\boldsymbol{\rho},\,\Omega) \qquad (10.270)$$
$$= \frac{1}{N}\int d\,\mathbf{r}\int d\,\boldsymbol{\rho}\,e^{i\,\mathbf{k}\cdot\boldsymbol{\rho}}\,\langle\, n(\boldsymbol{\rho}+\mathbf{r},\,\Omega)\,n(\mathbf{r})\,\rangle$$

Using (7) of Exercise 10.4, we can write (10.271) as

$$I(\mathbf{r},\,\omega) = \frac{c}{4\,\pi}\left(\frac{\alpha}{c^2\,r}\right)^2\,\omega^4\,E_0^2\sin^2\theta \qquad (10.272)$$
$$\times\left\{2\,\pi\,N^2\,\delta(\Omega)\,\delta_{\mathbf{k}\,\mathbf{0}} + \langle\, n_{\mathbf{k}}(0)\,n_{-\mathbf{k}}(0)\,\rangle\left[\,\frac{\gamma-1}{\gamma}\,\frac{2\,\chi\,k^2}{\Omega^2\,+\,\chi^2\,k^4}\right.\right.$$
$$\left.\left.+\,\frac{1}{\gamma}\left(\frac{k^2\,\Gamma}{(\Omega-c\,k)^2+k^4\,\Gamma^2}+\frac{k^2\,\Gamma}{(\Omega+c\,k)^2+k^4\,\Gamma^2}\right)\right]\right\}$$

Note that I is at maximum when $\theta = 90\,°$. This is therefore the optimal observation angle since one is also out of the way of the dominant unscattered light.

The spectrum thus contains 3 peaks at

$\Omega = 0$	$\rightarrow$	$\omega = \omega_0$ (Rayleigh peak)
$\Omega \pm c\,k = 0$	$\rightarrow$	$\omega = \omega_0 \mp c\,k$ (Brillouin peaks)

The Rayleigh peak is due to elastic scattering off thermal density fluctuations.
The Brillouin peaks are due to inelastic scattering off mechanical density fluctuations (sound waves).

Since the Lorentzians are normalized to 1, the ratio of the total intensities of these two types of scattering is

$$\frac{\mathcal{I}_{\text{th}}}{\mathcal{I}_{\text{mech}}} = \gamma - 1 = \frac{C_P - c_\rho}{c_\rho} = \frac{\kappa_T\,-\,\kappa_S}{\kappa_S} \qquad (10.273)$$

As we approach the critical point,

$$c_P,\ \kappa_T \to \infty \qquad \Rightarrow \qquad \mathcal{I}_{\text{th}} \gg \mathcal{I}_{\text{mech}}$$

so that the Rayleigh peak dominates.

See Reichl’s Fig.10.4. for data obtained for CO_2 near the liquid-gas critical point.