

# 7 Molecular light scattering by pure sea water

Xiaodong Zhang

The general theory of the molecular scattering, and the scattering by water and seawater in particular, will be reviewed. For a pure liquid, free from any foreign particles, the statistical thermal motion of the molecules gives rise to the scattering of light. The resultant fluctuation of the density of the water and fluctuation in the orientations of the water molecules bring about fluctuation of the optical dielectric constant, which in turn causes scattering. For solutions such as seawater, additional scattering is due to the fluctuation of the concentration of sea salts. The latest measurements of key thermodynamic parameters of water and the development of a recent theoretical model allow the scattering by seawater to be investigated in detail as a function of temperature and salinity. The model results agree with laboratory observations within experimental error.

## 7.1 Introduction

Water is the only substance on Earth that can exist naturally in three different states as a solid (ice), liquid (water) or gas (vapor). Yet, the scattering of light by the same water molecules, but in different states is different. For example, if the intensity of light scattered at an angle of  $\theta_s$  is 100 units for a given amount of water vapor, then when the vapor condenses into liquid, the scattering intensity would be about 2 units, and when the liquid further freezes into ice, the scattering intensity would be nearly zero, as long as  $\theta_s$  is not in the direction of refraction. Generally speaking, the reduced scattering intensity results from destructive interference. For a vapor (or gases in general), each molecule acts as a scattering particle whose position is far from, and random to the others. Therefore, scattering by gases is directly additive with no interference. For pure ice (or any crystal) illuminated with light at a wavelength much greater than the separation of the lattice planes, no light is scattered, because it is always possible to pair two scattering planes so that destructive interference occurs. There are two exceptions to this general description. At the refraction direction, the scattered light is always constructive. When the wavelength ( $\lambda$ ) of the incident radiation is roughly equal to the distance ( $d$ ) separating the scattering planes, scattering can be observed at Bragg angles, defined as  $\sin(\theta_s/2) = n\lambda/2d$ , where  $n$  is an integer.

For scattering by liquid water, most of scattered light goes through destructive interference. However, Brownian motion produces transient optical inhomogeneity in the liquid, the presence of which allows a small fraction of the scattered radiation to escape destructive interference and to be observed. Fundamentally, all scattering originates from the interaction of photons with molecules; however, the treatment of scattering by gases, liquids and solids is different, as summarized in Table 7.1.

**Table 7.1.** Summary of typical treatment of scattering by water in different states

	Scattering center	Interference	Angular distribution
Gases (vapor)	Molecules in random motion	Not considered	Approx. isotropic
Liquid (water)	Small volumes in random motion <sup>1</sup>	Not considered	Approx. isotropic
	Molecules <sup>2</sup>	Considered	
Solid (ice)	Lattice planes	Considered	Refraction and reflection

<sup>1</sup> Einstein-Smoluchowski theory considering the liquid as a continuous medium with localized fluctuation in density, which can be calculated from thermodynamics (Smoluchowski, 1908; Einstein, 1910).

<sup>2</sup> Zimm (1945) considered explicitly the scattering by individual molecules and addressed the interference using the results from statistical mechanics describing the correlations between molecular separations. Zimm's molecular theory of the scattering reproduces the results of Einstein and Smoluchowski but has the advantage that it does not yield infinite scattering at the critical point.

## 7.2 General theory of scattering

### 7.2.1 Isotropic particles

Consider a plane wave polarized in the  $YZ$  plane incident upon an isotropic particle of spherical polarizability  $\alpha$  situated at the origin of the coordinate system (Fig. 7.1) in a medium of refractive index  $n$ . Only the electric field of the incident light is of interest here and its amplitude is  $E_{0Z}$ . The instantaneous electric field of incident light:  $E = E_{0Z} \cos(k_0 y - \omega_0 t)$ , where  $k_0 = 2\pi n/\lambda_0$ ,  $\lambda_0$  is the wavelength in vacuum, and  $\omega_0 = 2\pi\nu_0$  is the frequency. The electric field  $E$  interacts with electrons in an atom or molecules to induce an electric dipole moment, which oscillates at the angular frequency  $\omega_0$ . For an isotropic scatterer, for which  $\alpha$  is independent of orientation, the induced dipole moment is:

$$P_Z = \alpha E = \alpha E_{0Z} \cos(k_0 y - \omega_0 t). \quad (7.1)$$

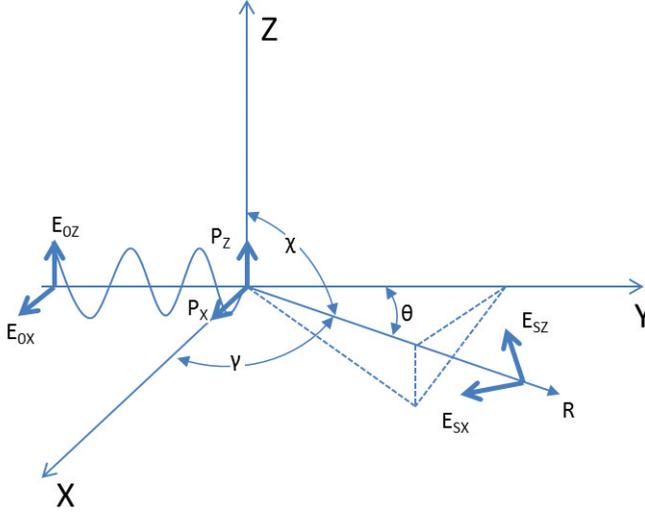


Fig. 7.1. Scattering geometry.

An oscillating dipole produces radiation, which at large distances, i.e., where  $R \gg \lambda_0$ , the electric field  $E_{SZ}$  of the scattered light is proportional to  $d^2P/dt^2 = -\omega_0^2P$  and inversely proportional to distance  $R$ ,

$$E_{SZ} = \frac{-\omega_0^2 P_Z \sin(\chi)}{4\pi\epsilon_0 c^2 R}, \quad (7.2)$$

where  $\chi$  is the angle between the induced moment  $P_Z$  and  $R$ ,  $\epsilon_0$  is the permittivity of free space, and  $c$  is the speed of light. The instantaneous irradiance,  $E_{irr} = c\epsilon_0 E^2$ . Since all measurements require times that are much longer than the oscillation period of the radiation field, the cycle averaged  $E_{irr}$  is of interest. Therefore,

$$\langle E_{irr} \rangle = c\epsilon_0 \langle E^2 \rangle = \frac{c\epsilon_0}{2} E^2. \quad (7.3)$$

The factor 0.5 in Eq. (7.3) results from averaging the term  $\cos^2(k_0 y - \omega_0 t)$  in Eq. (7.1) over sampling period that is much longer than the oscillation period of the electric field.

Combining Eqs. (7.1)–(7.3), the scattered irradiance,  $E_{irr-s}$ ,

$$E_{irr-s} = \frac{c\epsilon_0}{2} E_{0Z}^2 \left[ \frac{\omega_0^4 \alpha^2 \sin^2(\chi)}{(4\pi\epsilon_0)^2 c^4 R^2} \right]. \quad (7.4)$$

Note that the incident irradiance,  $E_{irr-i} = \frac{c\epsilon_0}{2} E_{0Z}^2$ , and therefore,

$$\frac{E_{irr-s}}{E_{irr-i}} = \frac{\omega_0^4 \alpha^2 \sin^2(\chi)}{(4\pi\epsilon_0)^2 c^4 R^2} = \frac{\pi^2 \alpha^2 \sin^2(\chi)}{\epsilon_0^2 \lambda_0^4 R^2}. \quad (7.5)$$

Similarly, for an incident wave polarized in the  $XY$  plane with electric field amplitude of  $E_{0X}$ , the ratio of scattered irradiance to the incident irradiance is

$$\frac{E_{irr-s}}{E_{irr-i}} = \frac{\pi^2 \alpha^2 \sin^2(\gamma)}{\epsilon_0^2 \lambda_0^4 R^2}, \quad (7.6)$$

where  $\gamma$  is the angle between the induced moment  $P_X$  and  $R$ . Therefore, for unpolarized incident light, the ratio of scattered irradiance to the incident irradiance would be

$$\frac{E_{irr-s}}{E_{irr-i}} = \frac{\pi^2 \alpha^2}{\epsilon_0^2 \lambda_0^4 R^2} \frac{\sin^2(\chi) + \sin^2(\gamma)}{2} = \frac{\pi^2 \alpha^2}{\epsilon_0^2 \lambda_0^4 R^2} \frac{1 + \cos^2(\theta)}{2}. \quad (7.7)$$

The second equality in Eq. (7.7) follows  $\cos^2(\chi) + \cos^2(\gamma) + \cos^2(\theta) = 1$ . Note, Eq. (7.7) can also be derived for polarized light if all the scattered light in the cone  $\theta + d\theta$  is collected regardless of the angle  $\chi$  (or  $\gamma$ ).

Equation (7.7) describes scattering by one particle. For gases, each molecule can be considered as a particle, moving randomly relative to each other. For a volume  $V$  of gas with  $N$  molecules, the ratio of scattered irradiance at scattering angle  $\theta$  to the incident irradiance is simply  $N$  multiply Eq. (7.7), i.e.

$$\frac{E_{irr-s}}{E_{irr-i}} = \frac{\pi^2 N \alpha^2}{\epsilon_0^2 \lambda_0^4 R^2} \frac{1 + \cos^2(\theta)}{2}. \quad (7.8)$$

The polarizability is not a quantity that can be determined experimentally, but from Maxwell's equation it has been shown that it is related to the dielectric constant (also called relative permittivity),  $\epsilon_r$ , and hence the square of the refractive index  $n$ ,

$$\epsilon_r = n^2 = 1 + \frac{N\alpha}{V\epsilon_0}. \quad (7.9)$$

Substituting  $N\alpha^2/\epsilon_0^2$  in Eq. (7.8) with Eq. (7.9) and applying the definition that the volume scattering function,  $\beta(\theta) = \frac{I(\theta)}{E_{irr-i}V} = \frac{1}{E_{irr-i}V} \frac{E_{irr-s}\Delta A}{\Delta\Omega} = \frac{E_{irr-s}R^2}{E_{irr-i}V}$ , where  $\Delta A$  and  $\Delta\Omega$  are the cross-sectional area and the solid angle of the scattered light,

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2 (n^2 - 1)^2}{\lambda_0^4 N_0} (1 + \cos^2\theta), \quad (7.10)$$

where  $N_0 = N/V$ , the number of particles per unit volume.

In a pure liquid, the molecules are compacted densely enough that the movement of one molecule cannot be considered totally random to others, and therefore the interference of scattered light by each molecule has to be accounted for. To overcome this challenge, Smoluchowski (1908) and Einstein (1910) developed fluctuation theory, in which fluctuations in the number of particles in a given small volume element, which is small compared with the wavelength of light, but big enough to contain a large number of molecules, result in changes in density which will produce corresponding changes in the dielectric constant. Assuming

in a sample of volume  $V$ , each small volume element is  $dV$  with an instantaneous polarizability  $\alpha_V = \bar{\alpha} + \Delta\alpha_V$ , where  $\bar{\alpha}$  represents the time average of  $\alpha_V$ ,  $\Delta\alpha_V$  the instantaneous fluctuation, the time average of which,  $\overline{\Delta\alpha_V}$ , is zero by definition. In Eq. (7.7), the scattered light is proportional to the square of polarizability; the contribution from a volume element is the time average of the  $\alpha_V^2$ . Thus,

$$\overline{(\bar{\alpha} + \Delta\alpha_V)^2} = (\bar{\alpha})^2 + \overline{(\Delta\alpha_V)^2}. \quad (7.11)$$

The contribution from  $(\bar{\alpha})^2$ , whose value does not change for the sample, cancels exactly as in perfect crystals because we can always find another element volume whose distance to the volume element being considered is such that the scattered electric fields by the two volume elements are opposite in phase and cancel each other. Therefore the net scattering in Eq. (7.7) depends only on  $\overline{(\Delta\alpha_V)^2}$ , i.e. for liquid,

$$\frac{E_{irr-s}}{E_{irr-i}} = \frac{\pi^2 \alpha^2}{\epsilon_0^2 \lambda_0^4 R^2} \frac{\sin^2(\chi) + \sin^2(\gamma)}{2} = \frac{\pi^2 \overline{(\Delta\alpha_V)^2}}{\epsilon_0^2 \lambda_0^4 R^2} \frac{1 + \cos^2(\theta)}{2}. \quad (7.12)$$

Following the same deduction from Eq. (7.7) to Eq. (7.10) for gases, but with  $\overline{(\Delta\epsilon_r)^2}$  or  $\overline{(\Delta n^2)^2} = \overline{(\Delta\alpha_V)^2}$  and  $N_0 = 1/dV$  as number of volume elements per unit volume, we have the volume scattering function for liquid,

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2 \overline{(\Delta n^2)^2} dV}{\lambda_0^4} (1 + \cos^2\theta). \quad (7.13)$$

The fluctuations of  $n_2$  is a result of fluctuations of density  $\rho$  and temperature  $T$ ,

$$\Delta n^2 = \left( \frac{\partial n^2}{\partial \rho} \right)_T \Delta \rho + \left( \frac{\partial n^2}{\partial T} \right)_\rho \Delta T. \quad (7.14)$$

But the second term is negligible compared with the first and may be neglected, so that the fluctuations in dielectric constant are expressed by

$$\overline{(\Delta n^2)^2} = \left( \frac{\partial n^2}{\partial \rho} \right)_T^2 \overline{(\Delta \rho)^2}. \quad (7.15)$$

From thermodynamic statistics (e.g., Fabelinskii, 1968),

$$\overline{(\Delta \rho)^2} = \frac{\rho^2 k_B T \beta_T}{dV}, \quad (7.16)$$

where  $k_B$  is Boltzmann constant and  $\beta_T$  the isothermal compressibility. Inserting Eqs. (7.15) and (7.16) into Eq. (7.13), we have

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2 k_B T \beta_T}{\lambda_0^4} \left( \rho \frac{\partial n^2}{\partial \rho} \right)^2 (1 + \cos^2\theta). \quad (7.17)$$

### 7.2.2 Anisotropic particles

When  $\theta = \pi/2$ , scattered light is completely polarized vertically (this would be the case in Fig. 7.1, where  $R$  is in the  $XZ$  plane), because the angle  $\gamma = 0$ , and therefore the scattered light that is horizontally polarized vanishes. However, experimental observations indicate that the scattered light at  $\theta = \pi/2$  is not completely polarized because a molecule is not an isotropic particle (with the exception of noble gases, probably) (e.g., Strutt, 1918; Cabannes, 1922). For an anisotropic particle, the induced dipole moment is not in the same direction as the electric field, i.e.,  $P_Z$  in Fig. 7.1 would not align with the  $Z$  axis. Therefore, instead of Eq. (7.1), generally,

$$\begin{pmatrix} P_X \\ P_Y \\ P_Z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_{0X} \\ E_{0Y} \\ E_{0Z} \end{pmatrix}, \quad (7.18)$$

where  $\alpha_{ij}(i, j = x, y, z)$  are elements of the polarizability tensor, and normally,  $\alpha_{ij} = \alpha_{ji}$ . Depending on the coordinate system chosen for representation, the values of  $\alpha_{ij}$  change. However, the mean polarizability  $\alpha$  defined by

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (7.19)$$

and the anisotropy  $\beta$  defined by

$$\beta^2 = \frac{1}{2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right]. \quad (7.20)$$

do not change. Also by definition,  $\beta = 0$  for isotropic particles.

In addition to movement, the orientations of molecules are random in gases or liquid. The mean values for these anisotropic elements are:

$$\overline{\alpha_{xx}^2} = \overline{\alpha_{yy}^2} = \overline{\alpha_{zz}^2} = \alpha^2 + \frac{4}{45}\beta^2, \quad (7.21)$$

$$\overline{\alpha_{xy}^2} = \overline{\alpha_{yz}^2} = \overline{\alpha_{zx}^2} = \frac{\beta^2}{15}. \quad (7.22)$$

Refer again to Fig. 7.1 and assume that the scattered light is measured in the  $XY$  plane ( $\chi = \pi/2$ ). This assumption will not lose generality because the mean states of polarizability (Eqs. (7.19) and (7.20)) do not depend on how the coordinate system is defined. The scattered light measured at the scattering angle  $\theta$ :

$$\begin{aligned} E_{VV} &\propto \overline{\alpha_{zz}^2} \\ E_{VH} &\propto \overline{\alpha_{zy}^2} \\ E_{HV} &\propto \overline{\alpha_{xz}^2} \\ E_{HH} &\propto \overline{\alpha_{xx}^2} \cos^2\theta + \overline{\alpha_{xy}^2} \sin^2\theta, \end{aligned} \quad (7.23)$$

where the first and second subscripts indicate the polarization state of incident and scattered light, respectively. For vertically polarized incident light, the scattered

light ( $E_{VV}$  or  $E_{VH}$ ) does not depend on the scattering angle  $\theta$ , for horizontally polarized incident light, the vertically polarized scattered light ( $E_{HV}$ ) does not depend on  $\theta$ , and only the horizontally polarized scattered light resulting from horizontally polarized incident light ( $E_{HH}$ ) depends on  $\theta$  through two parts:  $\overline{\alpha_{xx}^2} \cos^2 \theta$  for the contribution from  $OX$  component of the dipole moment and  $\overline{\alpha_{xy}^2} \sin^2 \theta$  for the contribution from  $OY$  component of the dipole moment. For natural unpolarized light, the total scattered light

$$E_{total} = E_{VV} + E_{VH} + E_{HV} + E_{HH} \propto \frac{45\alpha^2 + 13\beta^2}{45} \left( 1 + \frac{45\alpha^2 + \beta^2}{45\alpha^2 + 13\beta^2} \cos^2 \theta \right) \quad (7.24)$$

and the depolarization ratio is defined by ( $\theta = \pi/2$ )

$$\delta_n \left( \theta = \frac{\pi}{2} \right) = \frac{E_{VH} + E_{HH}}{E_{VV} + E_{HV}} = \frac{\overline{\alpha_{zy}^2} + \overline{\alpha_{xy}^2}}{\overline{\alpha_{zz}^2} + \overline{\alpha_{xz}^2}} = \frac{6\beta^2}{45\alpha^2 + 7\beta^2}. \quad (7.25)$$

It is apparent from Eq. (7.24), and as we have derived above, that for isotropic particles for which  $\beta = 0$ ,

$$E_{total} \propto \alpha^2 (1 + \cos^2 \theta). \quad (7.26)$$

Taking the ratio of Eq. (7.24) to Eq. (7.26) for  $\theta = \pi/2$ ,

$$\frac{E_{total}(\beta \neq 0, \theta = \pi/2)}{E_{total}(\beta = 0, \theta = \pi/2)} = \frac{45\alpha^2 + 13\beta^2}{45\alpha^2} = \frac{6 + 6\delta_n}{6 - 7\delta_n}. \quad (7.27)$$

This ratio is known as Cabannes factor (Cabannes, 1920), accounting for the increased scattering due to anisotropic nature of molecules. It should be noted that (1) both depolarization ratio and Cabannes factor are defined for  $\theta = \pi/2$ ; (2) if the incident light is polarized, then values for both parameters will be different; and (3) the Cabannes factor was originally developed for gases, but it has been shown that it holds equally well for a liquid (Prins and Prins, 1956).

As shown in Eq. (7.24), the molecular anisotropy also affects the angular distribution of scattering (King, 1923; Martin, 1923), which becomes:

$$1 + \frac{45\alpha^2 + \beta^2}{45\alpha^2 + 13\beta^2} \cos^2 \theta = 1 + \left( \frac{1 - \delta_n}{1 + \delta_n} \right) \cos^2 \theta. \quad (7.28)$$

Combinations of Eqs. (7.10) and (7.17) with Eqs. (7.27) and (7.28) lead to the volume scattering function

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2 (n^2 - 1)^2}{\lambda_0^4 N_0} \frac{6 + 6\delta_n}{6 - 7\delta_n} \left( 1 + \frac{1 - \delta_n}{1 + \delta_n} \cos^2(\theta) \right) \quad (7.29)$$

for gases, and

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2 k_B T \beta_T}{\lambda_0^4} \left( \rho \frac{\partial n^2}{\partial \rho} \right)^2 \frac{6 + 6\delta_n}{6 - 7\delta_n} \left( 1 + \frac{1 - \delta_n}{1 + \delta_n} \cos^2(\theta) \right) \quad (7.30)$$

for a pure liquid, respectively.

### 7.2.3 Liquid solutions

For a liquid solution, the fluctuation in dielectric constant has an additional contribution from the fluctuation of solute concentration. Therefore, for a liquid solution, Eq. (7.14) should be modified

$$\Delta n^2 = \left( \frac{\partial n^2}{\partial \rho} \right)_T \Delta \rho + \left( \frac{\partial n^2}{\partial T} \right)_\rho \Delta T + \left( \frac{\partial n^2}{\partial C} \right)_\rho \Delta C, \quad (7.31)$$

where  $C = m_s M_s / dV$  is the concentration of solute and  $m_s$  and  $M_s$  are the number of moles and the molecular weight of solute, respectively. The concentration fluctuation  $\Delta C$  results in changes to the mixing ratio of solute and solvent within the volume element of  $dV$ , while the total mass and hence the density remains constant. This ensures that fluctuations due to density and concentration are independent of each other, such that (neglecting the fluctuation due to temperature)

$$\overline{(\Delta n^2)^2} = \left( \frac{\partial n^2}{\partial \rho} \right)_T^2 \overline{(\Delta \rho)^2} + \left( \frac{\partial n^2}{\partial C} \right)_T^2 \overline{(\Delta C)^2}. \quad (7.32)$$

Scattering due to density fluctuations has been discussed above and for concentration fluctuation,

$$\overline{\Delta C^2} = \frac{k_B T}{\left( \frac{\partial^2 A}{\partial C^2} \right)_{T,V}}, \quad (7.33)$$

where  $A$  is the Helmholtz free energy. The change in Helmholtz free energy associated with the concentration change at constant temperature and volume is given by,

$$dA = \mu_0 dm_0 + \mu_s dm_s, \quad (7.34)$$

where  $\mu$  denotes the chemical potential, and  $m$  the number of moles. The subscripts 0 and  $s$  denote properties defined for solvent and solute, respectively. Within the volume element  $dV$ ,  $m_0$  and  $m_s$  are related by,

$$dV = m_0 V'_0 + m_s V'_s, \quad (7.35)$$

where  $V'$  denotes the partial molar volume. Since  $dV$  is held as a constant, differentiating Eq. (7.35) leads to,

$$dm_0 = -\frac{V'_s}{V'_0} dm_s. \quad (7.36)$$

The partial molar volume depends on the concentration too, but compared with the changes of concentration fluctuations of  $dm_0$  and  $dm_s$ , their changes can be

neglected. Therefore it is safe to assume that both  $V'_0$  and  $V'_s$  are constants during concentration fluctuations. Combining Eqs. (7.34) and (7.36) and the definition of  $C$ , we have

$$\left(\frac{\partial^2 A}{\partial C^2}\right)_{T,V} = \left(\frac{\partial \mu_s}{\partial C} - \frac{V'_s}{V'_0} \frac{\partial \mu_0}{\partial C}\right) \frac{dV}{M_s}. \quad (7.37)$$

Applying Gibbs–Duhem equation,

$$m_0 d\mu_0 + m_s d\mu_s = 0. \quad (7.38)$$

Eq. (7.37) becomes

$$\left(\frac{\partial^2 A}{\partial C^2}\right)_{T,V} = -\frac{dV}{CV'_0} \left(\frac{\partial \mu_0}{\partial C}\right)_{T,V}. \quad (7.39)$$

By definition, chemical potential and activity of a species are related,

$$\mu = \mu^0 + RT \ln a, \quad (7.40)$$

where  $\mu^0$  is the chemical potential in a standard state and can be considered as a constant,  $a$  is the activity, and  $R$  is the gas constant. Differentiating Eq. (7.40) and inserting the result into Eq. (7.39),

$$\left(\frac{\partial^2 A}{\partial C^2}\right)_{T,V} = -RT \frac{dV}{CV'_0} \left(\frac{\partial \ln a_0}{\partial C}\right)_{T,V}. \quad (7.41)$$

Combining Eqs. (7.41), (7.33), (7.32), (7.13), we have the volume scattering function as a function of concentration fluctuations,

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2}{N_A \lambda_0^4} \left(\frac{\partial n^2}{\partial C}\right)^2 \frac{CV'_0}{-\partial \ln a_0 / \partial C} \frac{6 + 6\delta_n}{6 - 7\delta_n} \left(1 + \frac{1 - \delta_n}{1 + \delta_n} \cos^2 \theta\right), \quad (7.42)$$

where  $N_A$  is Avogadro's number.

## 7.2.4 Seawater

Seawater is a multi-component solution with dissolved components of sea salts either in their original form or as disassociated ions. Extending Eq. (7.42), which strictly speaking, only applies to a two-component solution, to a multi-component system involves the coupling of terms among any two solutes (Brinkman and Hermans, 1949; Kirkwood and Goldberg, 1950; Stockmayer, 1950), which is difficult, if not impossible, to evaluate or measure. However, if sea salts can be considered as one hypothetical compound thermodynamically, or equivalently, the molar ratios among dissolved components of sea salts in seawater remain constant during the fluctuations of concentration, Zhang et al. (2009) showed that Eq. (7.42) can still apply for seawater accounting for the scattering due to concentration fluctuations. Since the concentration of sea salts is typically measured as salinity,  $S = C\rho$ , Eq. (7.42) can be rewritten as

$$\beta(\theta) = \frac{1}{2} \frac{\pi^2}{N_A \lambda_0^4} \frac{M_0}{\rho} \frac{S(\partial n^2 / \partial S)^2}{-\partial \ln a_0 / \partial S} \frac{6 + 6\delta_n}{6 - 7\delta_n} \left( 1 + \frac{1 - \delta_n}{1 + \delta_n} \cos^2 \theta \right), \quad (7.43)$$

where  $M_0$  is the molecular weight of pure water. It should be noted that  $S$  in Eq. (7.43) represents the mass concentration of sea salts with a unit of g/kg and it differs from the Practical Salinity Unit  $S(\text{‰})$  in both definition and values,  $S(\text{g/kg}) = 1.004 \times S(\text{‰})$  (Millero et al., 2008).

Combining Eqs. (7.30) and (7.43), we have the total volume scattering function for pure seawater,

$$\beta(\theta) = \beta_d(\theta) + \beta_c(\theta), \quad (7.44)$$

where the scattering due to density fluctuations is

$$\beta_d(\theta) = k_B T \beta_T \left( \rho \frac{\partial n^2}{\partial \rho} \right)^2 f(\lambda_0, \theta, \delta_n), \quad (7.45)$$

and the scattering due to concentration fluctuations

$$\beta_c(\theta) = \frac{M_0}{N_A \rho} \frac{S(\partial n^2 / \partial S)^2}{-\partial \ln a_0 / \partial S} f(\lambda_0, \theta, \delta_n). \quad (7.46)$$

where the function  $f$  summarizes the dependence of scattering on the wavelength of incident light in a vacuum ( $\lambda_0$ ), the angle of scattering ( $\theta$ ) and the depolarization ratio for unpolarized light ( $\delta_n$ ),

$$f(\lambda_0, \theta, \delta_n) = \frac{\pi^2}{2\lambda_0^4} \frac{6 + 6\delta_n}{6 - 7\delta_n} \left( 1 + \frac{1 - \delta_n}{1 + \delta_n} \cos^2 \theta \right). \quad (7.47)$$

For pure water with  $S = 0$ ,  $\beta_c = 0$ . It should be noted that for seawater, the density term  $\beta_d$  is different from that for pure water because  $\beta_T$ ,  $\rho$ , and  $n$  are all functions of salinity. The total scattering coefficient for seawater,  $b$ , is

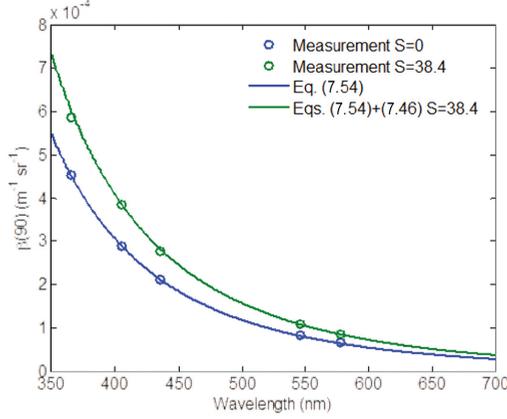
$$b = \int_0^\pi 2\pi\beta(\theta) \sin(\theta) d\theta = \frac{8\pi}{3} \frac{2 + \delta_n}{1 + \delta_n} \beta(90), \quad (7.48)$$

and the total backscattering coefficient,  $b_b$ , is

$$b_b = \int_{\pi/2}^\pi 2\pi\beta(\theta) \sin(\theta) d\theta = \frac{b}{2}. \quad (7.49)$$

### 7.3 Brief review and discussion

Morel (1966, 1968) measured the scattering by pure water and pure seawater of salinity 38.4 at five wavelengths of 366, 405, 436, 546 and 578 nm at 20°C (Fig. 7.2). Compared with the few other experimental studies of pure water (Kraut and Dandliker, 1955; Mysels and Princen, 1959; Cohen and Eisenberg, 1965; Kratochvil et



**Fig. 7.2.** Measured and modeled spectral volume scattering function at  $90^\circ$  ( $\beta(90)$ ) at  $20^\circ\text{C}$  for pure water and pure seawater of  $S = 38.4$ . For modeling,  $\delta_n = 0.039$ . The agreements between the measurements and predictions are  $-1\%$  and  $1\%$  for water and seawater, respectively, all within the experimental error of  $2\%$ .

al., 1965; Pethica and Smart, 1966; Parfitt and Wood, 1968), Morel's determinations gave the lowest values, likely an indication of the quality of the experiment as particle-free pure water is difficult to prepare. There have been no other published measurements investigating the effect of sea salts on scattering. The experimental error of these measurements was  $2\%$ .

Theoretical modeling of pure water scattering had been challenged by a lack of high-precision characterizations of the relevant thermodynamic quantities (Zhang and Hu, 2009), in particular, the density fluctuation term,  $(\partial n^2)/\partial \rho$ , and the value of depolarization ratio,  $\delta_n$ . For seawater, an additional challenge is a lack of a theoretical model explicitly formulating the effects of sea salts (Zhang et al., 2009). In the following sections, these challenges, along with some other relevant issues, are briefly reviewed and discussed.

### 7.3.1 Density derivative

From the classic Lorentz–Lorenz equation or Clausius–Mossotti relation,

$$\frac{n^2 - 1}{n^2 + 2} = \text{const.} \times \rho, \quad (7.50)$$

it can be easily derived that

$$\rho \frac{\partial n^2}{\partial \rho} = \frac{(n^2 - 1)(n^2 + 2)}{3}. \quad (7.51)$$

Inserting Eq. (7.51) into Eq. (7.30), the scattering for pure water (or due to density fluctuations alone) can be written as

$$\beta_d(\theta) = k_B T \beta_T \frac{(n^2 - 1)^2 (n^2 + 2)^2}{9} f(\lambda_0, \theta, \delta_n). \quad (7.52)$$

While Eq. (7.52) is attractive in that it unifies the scattering by gas and liquid because for gases,  $\beta_T = 1/P$ , where  $P$  is pressure, and  $n^2 + 2 \approx 3$ , it predicts poorly for water, overestimating measurements by more than 30% (Zhang and Hu, 2009). Actually, the use of the Lorentz–Lorenz equation or its variations (such as Laplace equation) failed to give a satisfactory agreement for a variety of liquids (Kerker, 1969), because the constant assumed in the Lorentz-Lorenz equation (Eq. (7.50)) is actually a function of temperature (Eisenberg, 1965; Beysens and Calmettes, 1977). Upon reviewing the earlier studies, Morel (1974) suggested the density derivative be replaced with the pressure derivative, i.e.,  $\left(\rho \frac{\partial n^2}{\partial \rho}\right)_T = \frac{2n}{\beta_T} \left(\frac{\partial n}{\partial P}\right)_T$ , which can be measured relatively more easily. With this,

$$\beta_d(\theta) = \frac{4k_B T n^2}{\beta_T} \left(\frac{\partial n}{\partial P}\right)_T^2 f(\lambda_0, \theta, \delta_n). \quad (7.53)$$

Equation (7.53) has also been used by Shifrin (1988) and Buiteveld et al. (1994) to estimate scattering by pure water. Using the most recent experimental results, estimates by Buiteveld et al. (1994) agree with Morel’s measurements for pure water with a relative difference of 6%.

However, the refractive index of water is least sensitive to the change in pressure as compared to  $T$ ,  $\lambda$ , and  $S$  (Austin and Halikas, 1974), making estimates of  $\partial n/\partial P$  very sensitive to errors in the function of  $n(P)$ . The advancement in theory and experimental observation of the refractive index of water has led to the improved modeling of density derivative. Zhang and Hu (2009) evaluated three of the latest theoretical estimates of  $[\rho(\partial n^2/\partial \rho)_T]$  by Proutiere et al. (1992), Niedrich (1985), and Eisenberg (1965), respectively and found that the use of any of them improved the prediction of pure water scattering, all within an experimental error of 2%. With Proutiere et al.’s (1992) derivation of  $[\rho(\partial n^2/\partial \rho)_T]$ ,

$$\beta_d(\theta) = k_B T \beta_T \left\{ (n^2 - 1) \left[ 1 + \frac{2}{3} (n^2 + 2) \left( \frac{n^2 - 1}{3n} \right)^2 \right] \right\}^2 f(\lambda_0, \theta, \delta_n). \quad (7.54)$$

along with the better characterization of other parameters, the prediction using Eq. (7.54), shown in Fig. 7.2, agrees with Morel’s measurement with a relative difference of  $-1\%$ .

Equation (7.54) offers an apparent numerical advantage over Eq. (7.53): the density derivative is represented theoretically as a function of the refractive index of water, which can be measured with relatively high precision (typically  $10^{-5}$  but up to  $10^{-7}$  in Tilton and Taylor, (1938)); on the other hand, with no analytical forms existing,  $(\partial n/\partial P)_T$  can only be approximated as  $\Delta n/\Delta P$ , which is difficult to measure because of very low sensitivity and nonlinearity of function  $n(P)$ .

### 7.3.2 Depolarization ratio

Kratohvil et al. (1965) compiled historical values determined for the depolarization ratio of water, which ranged from 0.06 to 0.21. This wide range of values was an indication that the measurements of depolarization are very sensitive to stray

light. For example, stray light that is 10% of  $\beta(90)$  would create a 50% change in the measured depolarization ratio (Pethica and Smart, 1966). Kratochvil et al. (1965) suggested a value of 0.108, which was the mean of their measurements. Morel (1974) and Shifrin (1988) used a value of 0.091, as measured by Pethica and Smart (1966) at 436 nm. Buiteveld et al. (1994) used a value of 0.051, measured by Farinato and Rowell (1976) at 514.4 nm. Jonasz and Fournier (2007) recommended a value of 0.039, which was determined by Farinato and Rowell (1976) after filtering out stray light using a 0.46 nm bandpass filter.

We recommend using the value of 0.039 for the depolarization ratio because the potential contamination of stray light has been removed. The theoretical results shown in Fig. 7.2 were all estimated using 0.039 for  $\delta_n$ . No published values for the depolarization ratio for water have been reported since Farinato and Rowell (1976). However, uncertainties in the depolarization ratio value remain. As far as scattering by seawater is concerned, the two main issues are: the spectral dependence of the value, and whether and how the value varies with salinity.

Table 7.2 summarizes the reported spectral values of  $\delta_n$  and not only are the values different, but their spectral dependence is not consistent either. For example,  $\delta_n$  reported in Raman and Rao (1923) and in Cohen and Eisenberg (1965) decreases with wavelength, but this spectral behavior is reversed in Kratochvil et al. (1965) and Pethica and Smart (1966). We still do not know how the depolarization varies spectrally. There also no published studies evaluating the effect of salinity on the depolarization ratio. Therefore, until further research is conducted, we must assume a constant value for the range of wavelengths of interest to ocean optics and for the natural range of salinity. This value is 0.039.

**Table 7.2.** The literature values of  $\delta_n$  for water determined at different wavelengths

Authors	$\lambda_0(\text{nm})/\delta_n$
Raman and Rao (1923)	Violet, blue, green, yellow, red 0.21, 0.155, 0.107, 0.106, 0.094
Cohen and Eisenberg (1965)	436, 546 0.087, 0.076
Kratochvil et al. (1965)	436, 546 0.107, 0.115
Pethica and Smart (1966)	436, 546 0.091, 0.109

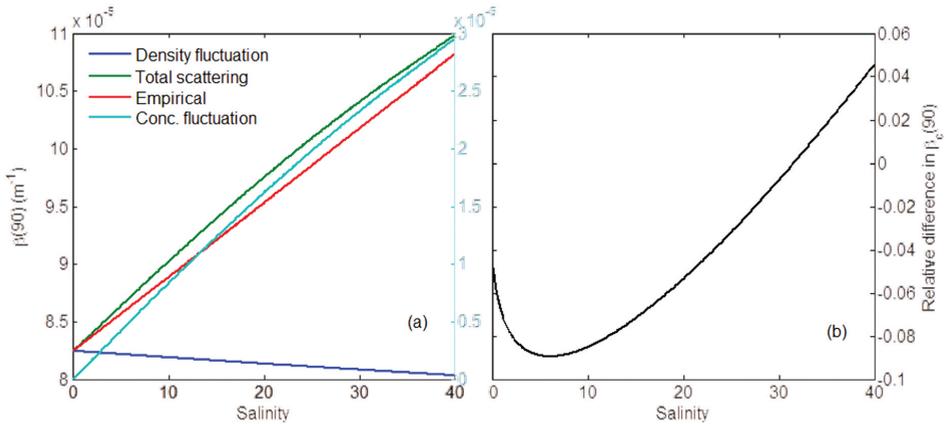
### 7.3.3 Effects of sea salts

From Morel's (1968) measurements, which remain the only experimental determination of scattering by pure seawater, the scattering by pure seawater at a salinity of 38.4 increases about 30% relative to that by pure water. Based on this, Boss

and Pegau (2001) suggested an empirical model adjusting the seawater scattering linearly with salinity,

$$\beta(\theta) = \beta_{pw}(\theta) \left( 1 + \frac{0.3}{38.4} S \right), \quad (7.55)$$

where  $\beta_{pw}$  represent the scattering by pure water. Results using the empirical model of Eq. (7.55) and the theoretical models of Eqs. (7.54) and (7.46) are compared in Fig. 7.3(a). These results suggest scattering as a function of with salinity is not linear, and that Eq. (7.55) would underestimate the theoretical values for a majority of oceanic waters. As validation, the theoretically modeled pure seawater scattering for  $S = 38.4$  is shown in Fig. 7.2 and agrees with Morel's measurements with a relative difference of 1%.



**Fig. 7.3.** (a) Theoretically and empirically modeled total scattering and its components as a function of salinity; (b) Relative error (Eq. (7.57) / Eq. (7.46) - 1) in modeling concentration fluctuations by assuming seawater is ideal. In both (a) and (b),  $\lambda = 546$  nm and  $T = 20^\circ\text{C}$ .

The effects of sea salts on scattering arise from two factors: changes in the density fluctuations (Eq. (7.55)) and additional fluctuations in concentration (Eq. (7.46)). The magnitude of the former is relatively small (about 2.6% decrease as  $S$  increases from 0 to 40), because of contradicting influences of sea salts on  $\beta_T$  (decreasing with  $S$ ) and on  $n$  and  $\rho$  (both increasing with  $S$ ). The effect of the latter is significant. As can be seen from Eq. (7.46) and Fig. 7.3 (a), this increase in scattering is mainly due to the linear term  $S$ , modified by nonlinear changes in  $\rho$  and  $a_0$ . The nonlinearity arises because seawater is an electrolyte solution, which is not ideal, regardless how dilute its concentration.

Assuming that seawater is ideal,  $a_0 = 1 - X_{ss}$ , where  $X_{ss}$  is the molar fraction of sea salts and  $X_{ss} = m_{ss}/(m_0 + m_{ss})$ , where  $m$  represents molar amount and subscript  $ss$  represents sea salts, we have

$$-\frac{\partial \ln a_0}{\partial S} = \frac{M_0}{M_{ss}} \frac{1 - X_{ss}}{(1 - S)^2} \approx \frac{M_0}{M_{ss}}. \quad (7.56)$$

Inserting Eq. (7.56) into Eq. (7.46), we have

$$\beta_c(\theta) = \frac{M_{ss}S}{N_A\rho} \left( \frac{\partial n^2}{\partial S} \right)^2 f(\lambda_0, \theta, \delta_n), \quad (7.57)$$

which was proposed by Debye (1944) and used in Morel (1974) and in Jonasz and Fournier (2007) to model the scattering due to concentration fluctuations in pure seawater. Equation (7.57) would underestimate scattering due to concentration fluctuations at salinities  $< 31$  with difference up to  $-9\%$  and overestimate scattering at higher salinities (Fig. 7.3 (b)).

### 7.3.4 Other relevant issues

#### 7.3.4.1 Spectral dependence

The spectral dependence of scattering by seawater has been characterized by  $s$  as in  $(\lambda/\lambda_a)^s$ . A value of  $-4.32$  has often been used (e.g., Gordon and Morel, 1983) and was first reported by Morel (1974) with an anchor wavelength  $\lambda_a = 436$  nm. Twardowski et al (2007) and Shifrin (1988) reported a value of  $-4.17$  based on fitting to Eq. (7.53). The value of  $s$  would also change with salinity, ranging from  $-4.286$  to  $-4.306$  for a  $S$  from 0 to 40 with  $\lambda_a = 450$  nm based on Eqs. (7.54) and (7.46). Historically,  $s$  was used to scale the measured scattering by Morel (1974) (which was only available at 5 wavelengths, e.g., Fig. 7.2) to other wavelengths. Given that the scattering by pure water and pure seawater can now be modeled spectrally, the use of  $s$  should be limited.

#### 7.3.4.2 Temperature dependence

Water, the most common molecule on Earth, has several ‘anomalous’ properties that are relevant to scattering: maximum  $\rho$  near  $4^\circ\text{C}$  (Vedamuthu et al., 1994), minimum  $\beta_T$  near  $46^\circ\text{C}$  (Vedamuthu et al., 1995), and maximum  $n$  near  $0^\circ\text{C}$  (Cho et al., 2001). It should be expected that through the combined effects of these parameters, the scattering by water may also behave anomalously. For pure water, Cohen and Eisenberg (1965) measured the scattering for  $T = 5^\circ\text{C}$  to  $65^\circ\text{C}$  at two wavelengths of 436 and 546 nm and found a scattering minimum at  $\sim 22^\circ\text{C}$ . Modeled scattering by pure water using Eq. (7.54) and Buiteveld et al (1994) equation are compared with the measurements of Cohen and Eisenberg (1965) in Fig. 7.4. Predictions based on Eq. (7.54) agree with the measurements within 1.4% at both wavelengths. The scattering estimated using Eq. (7.54) varies with the temperature nonlinearly with a minimum at  $24.64^\circ\text{C}$  (denoted as  $T_{min}$  hereafter). The scattering decreases by 4.25% between  $0^\circ\text{C}$  and  $T_{min}$  and increases by 7% between  $T_{min}$  and  $70^\circ\text{C}$ . The  $T_{min}$  is close to the value of  $22^\circ\text{C}$  estimated by Cohen and Eisenberg (1965), however, differs significantly with the estimates by Buiteveld et al. (1994), who found a maximum near  $15^\circ\text{C}$ . They used Eq. (7.53), which is valid theoretically, but suffers from the relatively large uncertainty in modeling  $(\partial n/\partial P)_T$ . Fig. 7.4 reaffirms the advantage in using Eq. (7.54) against Eq. (7.53). The value of  $T_{min}$  also increases with salinity, reaching  $27.49^\circ\text{C}$  at 40 (Zhang and Hu, 2010).

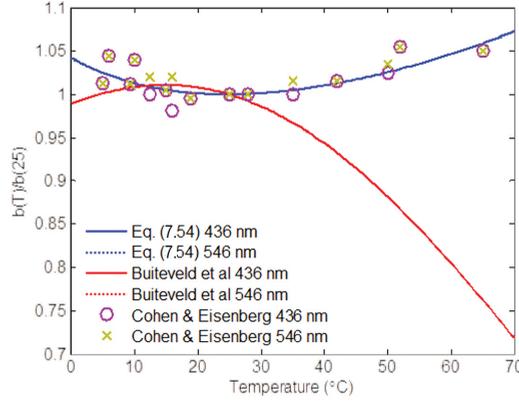


Fig. 7.4. (a) Scattering by pure water normalized at  $T = 25^\circ\text{C}$  as a function of temperature.

### 7.3.4.3 Polarization

So far, the focus of this review has been on natural, unpolarized light. If the incident light is polarized, the depolarization ratio and the Cabannes factor will be different, as well as the angular dependence. For incident illumination that is vertically polarized, from Eqs. (7.21) to (7.23)

$$E_{total} = E_{VV} + E_{VH} \propto \frac{45\alpha^2 + 7\beta^2}{45} \quad (7.58)$$

$$\delta_V = \frac{E_{VH}}{E_{VV}} = \frac{\overline{\alpha_{zy}^2}}{\alpha_{zz}^2} = \frac{4\beta^2}{45\alpha^2 + 4\beta^2} \quad (7.59)$$

$$\text{Cabannes factor} = \frac{E_{total}(\beta \neq 0)}{E_{total}(\beta = 0)} = \frac{45\alpha^2 + 7\beta^2}{45\alpha^2} = \frac{3 + 3\delta_V}{3 - 4\delta_V}. \quad (7.60)$$

For incident illumination that is horizontally polarized,

$$E_{total} = E_{HV} + E_{HH} \propto \frac{2\beta^2}{15} \left( 1 + \frac{45\alpha^2 + \beta^2}{6\beta^2} \cos^2\theta \right) \quad (7.61)$$

$$\delta_H = 1 \quad (7.62)$$

and the Cabannes factor is not defined. Depolarization ratios for different polarization states satisfy the Krishnan relationship (Fabelinskii, 1968),

$$\delta_n = \frac{1 + \frac{1}{\delta_H}}{1 + \frac{1}{\delta_V}} = \frac{2\delta_V}{1 + \delta_V} \quad (7.63)$$

Farinato and Rowell (1976) measured  $\delta_V$  for pure water, with values of 0.020 or 0.026, with or without a stray light filter, respectively. These values are lower than earlier experimental results, e.g., 0.032 and 0.058 as reported in Kratochvil et al.

(1965), who also measured  $\delta_H$ , with values ranging from 1.00 to 1.05, very close to the theoretical value.

## 7.4 Conclusions

Light scattering by pure seawater is a physical quantity of critical importance to *in situ* ocean optics and remote sensing. Since the density fluctuation theory was established one century ago by Smoluchowski (1908) and Einstein (1910), a great deal of progress has been made leading to a significant improvement in our understanding of these processes. Recent advancements in both theoretical and experimental characterizations of key thermodynamic parameters have allowed us to model scattering within the experimental error of measurements (Zhang and Hu, 2009; Zhang et al., 2009). The measurements of Morel (1966, 1968) for pure water and pure seawater scattering at one salinity still are the best values for validating theory. Despite our progress, there are still uncertainties that need to be further constrained. We still do not know whether and how the depolarization ratio varies spectrally and/or with salinity. It seems that additional experimental efforts, particularly those addressing the uncertainty with respect to the depolarization ratio, are needed. The Matlab codes used to generate Figs. 7.2 to 7.4 can be downloaded from the author's website, <http://www.und.edu/instruct/zhang>.

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