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Experimental Study of Rayleigh Scattering Related to Concentration Fluctuations in Binary Solutions: Evidence of a Departure from Ideality

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The simultaneous determination of the two spectra of entropy and concentration fluctuations in a binary solution yields the Rayleigh ratio related to the concentration fluctuations. The results are in good agreement with the theoretical predictions. The departure from ideality of the solution is given by the evaluation of the term $\partial\mu/\partial c$.

The spectrum of the light scattered quasielastically by a binary system is composed[1,2] of two Lorentzian curves, both centered on the frequency of the incident light; the narrower of these curves corresponds to the light scattered by concentration fluctuations, the broader to entropy fluctuations at constant pressure. The spectral density of the whole spectrum is thus composed of two terms given by the dynamical structure factor

$$S(q,\omega)=\left(\frac{\partial\epsilon}{\partial C}\right)_{P,T}^{2}\langle\Delta C^2\rangle_{TP}\frac{1}{\pi}\frac{2Dq^2}{(Dq^2)^2+\omega^2}+\left(\frac{\partial\epsilon}{\partial T}\right)_{C,P}^{2}\frac{kT^2}{\rho C_p}\frac{1}{\pi}\frac{2\chi q^2}{(\chi q^2)^2+\omega^2}. \quad (1)$$

C is the weight concentration; $\langle\Delta C\rangle^2$, the mean square value of the fluctuations of C; D, the mass diffusion coefficient; χ, the coefficient of thermal diffusivity; q, the scattering vector; and ϵ, the dielectric constant at optical frequency.

The intensity of the light scattered by the concentration fluctuations and by the entropy fluctuations is proportional[3] to the integral over all frequencies of the first and second terms of $S(q,\omega)$, respectively (area of the corresponding optical spectrum). These integrals are, for concentration fluctuations,

$$I_c=(\partial\epsilon/\partial C)_{T,P}{}^2\langle\Delta C^2\rangle_{TP};$$

and for entropy fluctuations,

$$I_E=(\partial\epsilon/\partial T)^2kT^2/\rho C_p.$$

In a previous paper[4] we showed that the two terms of $S(q,\omega)$ give rise to two spectra which can be easily separated. The simultaneous measurement of these two spectra then gives the ratio of the light scattered by the two kinds of fluctuations. As the scattering factor corresponding to I_E is well known and easily computable (at least in the case of dilute solutions), the intensity of the light scattered by the concentration fluctuations can be deduced. We determined it for the three following solutions: benzene-acetone, benzene-chloroform, and carbon disulfide–acetone.

Theoretical determination of the term I_C in the case of an ideal solution. (1) Determination of $(\partial\epsilon/\partial C)$. –This term can be obtained by differentiation of the Lorentz-Lorenz formula, which in the case of a mixture can be written

$$\frac{\epsilon-1}{\epsilon+2}=\frac{4\pi}{3}\rho\left[C\frac{\alpha_1}{m_1}+(1-C)\frac{\alpha_2}{m_2}\right],$$

where $\rho=[C/\rho_1+(1-C)/\rho_2]^{-1}$ is the density of the mixture, m_i is the mass of the molecule, α_i is the molecular polarizability, and $\epsilon=n^2$, n being the refractive index of the solution. The subscript 1 refers to the solute and the subscript 2 refers to the solvent. The derivative of this formula gives

$$\left(\frac{\partial\epsilon}{\partial C}\right)_{P,T}=\frac{4\pi}{3}\frac{(\epsilon+2)^2}{3}\rho\left[\frac{\alpha_1}{m_1}-\frac{\alpha_2}{m_2}-\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}\left(\frac{1}{\rho_1}-\frac{1}{\rho_2}\right)\right]. \tag{2}$$

We checked the validity of this formula in the case of the three mixtures studied below by measuring the slope of the curve giving the variation of the refractive index versus the concentration of solute. Table I gives the experimental values for weak concentrations of solute compared with that deduced from (2). One can notice a very good agreement between experimental and theoretical values.

(2) Determination of $\langle\Delta C^2\rangle$ and of I_C. —The mean square value of concentration fluctuations of the solute can be expressed by

$$\langle\Delta C^2\rangle_{T,P}=kT(\partial\mu/\partial C)_{P,T}{}^{-1},$$

where μ is the chemical potential of the solution. In the case of mass diffusion in an ideal solution, the adequate chemical potential is

$$\mu_C=\rho[\mu_1/M_1-\mu_2/M_2],$$

where μ_1 and μ_2 are the chemical potentials of the solute and the solvent, respectively.[5] $\mu_1=RT\ln x+\mu_{01}$ and $\mu_2=RT\ln(1-x)+\mu_{02}$, x being the molar concentration.

From this we have for the general expression for μ_C, taking into account that $x=(M/M_1)C$ and $M=[C/M_1+(1-C)/M_2]^{-1}$,

$$\mu_C=RT\rho\left[\frac{1}{M_1}\ln\frac{M}{M_1}C-\frac{1}{M_2}\ln\frac{M}{M_2}(1-C)\right]+\rho\left[\frac{\mu_{01}}{M_1}-\frac{\mu_{02}}{M_2}\right].$$

By differentiation[6] relative to C, we obtain for $\partial\mu/\partial C$

$$\frac{\partial\mu}{\partial C}=RT\left\{\rho\left[\frac{1}{C(1-C)}\frac{M_1C+M_2(1-C)}{M_1M_2}-\frac{(1/M_1-1/M_2)^2}{C/M_1+(1-C)/M_2}\right]-\rho^2\left[\frac{1}{\rho_1}-\frac{1}{\rho_2}\right]\left[\frac{1}{M_1}\ln\frac{M}{M_1}C-\frac{1}{M_2}\ln\frac{M}{M_2}(1-C)\right]\right\}. \tag{3}$$

The most important term of this expression is

$$\frac{\partial\mu}{\partial C}\cong\frac{RT}{C(1-C)}\rho\frac{M_1C+M_2(1-C)}{M_1M_2};$$

the remaining terms represent few percents of this one. Getting thus the value of $\partial\mu/\partial C$, we deduce the value of $\langle\Delta C^2\rangle$ and of I_C.

Experimental results. —We performed this study by means of optical mixing spectroscopy. The experimental apparatus has been described in a previous paper.[7] In Fig. 1 is shown an example of a heterodyne spectrum relative to the two types of fluctuations.

(1) Entropy fluctuations of dilute solutions. —We systematically compared the spectra corresponding to entropy fluctuations of dilute solutions having benzene as solvent with those obtained with pure benzene. Within our experimental accuracy (~10%) the linewidths corresponding to entropy fluctuations of benzene plus 10% weight acetone and of benzene plus 10% weight chloroform are the same as for pure benzene, i.e.,

$$(\Lambda/\rho C_p)_{\text{diluted mixture}}=(\Lambda/\rho C_p)_{\text{pure solvent}}.$$

Under these conditions no appreciable error is

Table I. Experimental and theoretical value of $d\epsilon/dc$.

Solvent-solute	$(\partial\epsilon/\partial C)_{\text{expt}}$	$(\partial\epsilon/\partial C)_{\text{theor}}$
Benzene-acetone	-0.45 ± 0.02	-0.466
Benzene-chloroform	-0.1196	-0.106
Carbon disulfide-acetone	-1.40	-1.357

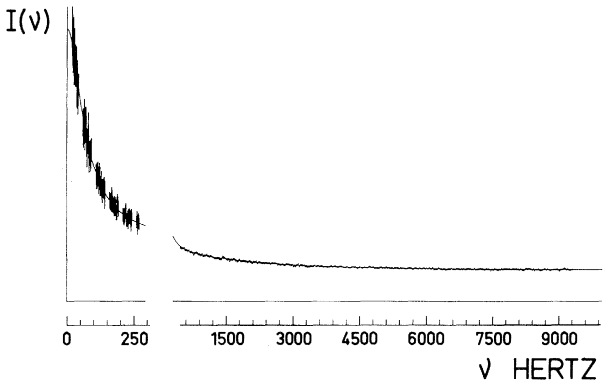

FIG. 1. Spectrum of light scattered by a benzene-acetone mixture (10% by weight of acetone). The narrow spectrum is the average of 20 scans, each made with $\Delta\nu=3$ Hz and 1-sec time constant. The broad spectrum is the average of 100 scans, each made with $\Delta\nu=50$ Hz and 0.08-sec time constant.

Table II. Experimental results relative to the absolute intensity scattered by concentration fluctuations.

Mixture (solvent-solute)	C (wt%)	x (mole%)	$(I_C/I_E)_{\rm expt}$	R_C (10^{-6}cm^{-1})	$\dfrac{(\partial\mu/\partial C)_{\rm exp}}{(\partial\mu/\partial C)_{\rm theor\,ideal}}$
Benzene-acetone	10	13	$1.14^{+0.2}_{-0.2}$	1.1 ± 0.15	0.06 ± 0.1
Benzene-chloroform	10	6.75	$0.13^{+0.02}_{-0.05}$	$>0.07, <0.14$	$>0.65, <1.25$
Carbon disulfide–acetone	8	10	$4.8\ ^{+1}_{-1}$	8.3 ± 1.4	0.35 ± 0.07

made in taking the parameters of the solution equal to those of the pure solvent in order to calculate the term I_E.

(2) Ratio of intensities of the light scattered by the two kinds of fluctuations.—The computer processing of the spectra gives directly the ratio I_C/I_E. The total intensity of the quasielastic spectrum corresponding to entropy fluctuations is proportional to I_E with

$$I_E = (\partial\epsilon/\partial T)^2 kT^2/\rho C_p$$

and this term can be calculated by means of various coefficients found in the literature.[8] From the experimental ratio $(I_C/I_E)_{\rm exp}$ we have deduced the Rayleigh ratio R_C for concentration fluctuations and $(\partial\mu/\partial C)$. It is then interesting to compare the value of this term with that obtained on the assumption of ideality of solutions [formula (3)]. Table II summarizes the average experimental values obtained for various solutions (room temperature).

Discussion.—The results, obtained for each mixture are examined separatively, in connection with its particular properties.

(a) Benzene-acetone solution.—This solution was chosen because the light-scattering properties of the solvent are well known and the difference between the reduced polarizabilities of the two molecules is important. Thus the light scattering due to concentration fluctuations is relatively strong and its level is well above that of the background scattering: The discrepancy between the experimental results and the values corresponding to an ideal solution is thus significant. However because of the lack of other thermodynamical information on this solution, we cannot compare our value of $(\partial\mu/\partial C)$ with values deduced from other experimental techniques.

(b) Benzene-chloroform solution.—This solution exhibits at room temperature a very small deviation from Raoult's law and thus it can be considered as nearly ideal. Unfortunately the difference between the reduced polarizabilities of the two kinds of molecules is very small and the resulting scattering is comparable to that due to small particles of dust present in air in the neighborhood of the scattering cell containing the solution. This fact explains the poor accuracy of the corresponding experimental results. Nevertheless we can consider that the theoretical value is consistent with the experimental one.

(c) Carbon disulfide-acetone.—In this case a large and significant discrepancy can be noticed between the experimental value of $(\partial\mu/\partial C)$ and that calculated on the assumption of ideality of the solution. Indeed the solution studied is nonideal at room temperature, as shown by a strong positive deviation from Raoult's law.[8] In the case of such a nonideal solution,

$$\mu_1 = RT\ \ln a_1,$$

$$\mu_2 = RT\ \ln a_2,$$

a_1 and a_2 being the activities of solute and solvent, respectively, and

$$\frac{\partial\mu}{\partial C} = RT\left\{\left(\frac{\ln a_1}{M_1} - \frac{\ln a_2}{M_2}\right)\frac{\partial\rho}{\partial C} + \rho\left(\frac{1}{M_1}\frac{d\ln a_1}{dC} - \frac{1}{M_2}\frac{d\ln a_2}{dC}\right)\right\}.$$

For dilute solutions $\ln a_2 \approx 0$ and $d\ln a_1/dC \gg d\ln a_2/dC$. So, we have

$$\frac{\partial\mu}{\partial C} = RT\left\{+\frac{\rho}{M_1}\frac{d\ln a_1}{dC} - \frac{\ln a_1}{M_1}\rho^2\left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)\right\}. \qquad (4)$$

From the tables giving the partial vapor pressure of this solution[9] at 50°C, we have deduced the curve of a_1 vs C, and so, for $C = 0.08$, we calculated $d\ln a_1/dC = 6.3$; hence we obtained $(\partial\mu/\partial C)_{\rm computed} = 350$ J/cm^3, whereas in the case of an ideal solution $(\partial\mu/\partial C)_{\rm theor} = 757$ J/cm^3. The result of our measurements is $(\partial\mu/\partial C)_{\rm expt} = 260 \pm 40$ J/cm^3; this value is compatible with that obtained from formula (4), the discrepancy observed being probably due to the difference in the temperature of the two measurements.

Conclusion.—We performed, for the first time to our knowledge, quantitative measurements of Rayleigh ratio relative to the light scattered by concentration fluctuations in dilute solutions. With similar concentrations the experimental data obtained for the Rayleigh ratio show a great difference from one solution to one another (two orders of magnitude between benzene-chloroform and carbon disulfide–acetone solutions). The results obtained are in reasonably good agreement with those expected, for a nearly ideal solution as well as for a nonideal solution. Thus, the experimental method which we used seems to be useful for the study of deviation from ideality of the solutions.

We wish to thank Dr. Calmettes for many helpful discussions on this subject.

Note added in proof.—Some attempts to measure the activity coefficients of a solution have been made (Refs. 8 and 9) using the Rayleigh-to-Brillouin scattering intensity ratio. But this last method seems more complicated and requires the evaluation of more parameters than in our measurements, and seems less conclusive, according to the authors themselves.

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Experimental Observation of Drift Instabilities in a Collisionless Plasma

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Pressure-gradient–driven drift waves have been identified in a collisionless ($n_0 = 10^{10}$ cm^{-3}, $T_e = 10$ eV), 5.4-m-long, hydrogen plasma. Measurements show large but finite parallel wavelengths and short transverse wavelengths as predicted by the theory. For these wavelengths, computations give the maximum linear theoretical growth rate.

A low-β, collisionless, inhomogeneous plasma contained in a magnetic field $\vec{B}_0$ will be unstable to low-frequency electrostatic oscillations.[1] Gradient-driven waves propagate in a direction almost perpendicular to the magnetic field but have a large phase velocity parallel to $\vec{B}_0$, allowing a strong coupling with the parallel motion of the electrons (inverse Landau damping). The experiments reported herein were directed towards the identification of spontaneous oscillations arising in a hydrogen plasma as collisionless drift waves. The frequencies, wave numbers, and density versus potential phase shift of the instabilities have been measured and compared with computations of the linear dispersion relation.

The experimental work has been performed on the ODE device. ODE is a 5.4-m-long vacuum chamber immersed in a homogeneous magnetic field $B_0 \leq 3.5$ kG. The steady hydrogen plasma is produced by two sources[2] symmetrically located at both ends of the machine (Fig. 1). Compared with other experiments used in studies of both collisional[3] and collisionless[4] drift instabilities, this device has the following characteristics: (1) All collision frequencies are lower than the frequencies of the observed instabilities by at least a factor of 10; (2) there are no metallic end plates which would quantify the parallel wavelength to the machine length; and (3) the length of the column, 5.4 m, permits the development of large parallel wavelengths.

Most of the measurements (density n_0, electron temperature T_e, plasma potential, and waves) were performed using spherical coaxially shielded Langmuir probes (0.5 mm in diameter). The wave potential was detected with a high-impedance (10^8 Ω) capacitive probe. The ion temperature ($T_i = 2 \pm 0.4$ eV) was measured both by spectroscopy (Doppler broadening of H$_\beta$) and with a gridded probe. On the axis of the plasma column T_e is equal to 14 eV and n_0 increases linearly with the source current between 10^9 and 10^{10} cm^{-3}. Both n_0 and T_e exhibit a Gaussian