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## Critical Opalescence: The Rayleigh Linewidth\*

HERMAN Z. CUMMINS AND H. L. SWINNEY

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Debye's derivation of the Ornstein-Zernike modification of Einstein's theory of critical opalescence is reviewed. It is shown that Debye's free-energy function leads to a modification of the Landau theory for the width of the Rayleigh line which is equivalent to the results of Fixman, Botch, and Felderhof. This equivalence is utilized to predict the magnitude of the departure of Rayleigh linewidths from the Landau prediction by comparison with the results of angular-scattering intensity measurements. It is thus shown that in light-scattering experiments, pure fluids should obey the Landau theory quite accurately, whereas critical mixtures should show significant departures from the Landau prediction.

## I. INTRODUCTION

THE Einstein-Smoluchowski theory of critical opalescence assumed that fluctuations in neighboring volume elements are uncorrelated. This led to the prediction that the scattered light intensity is independent of angle and that the differential scattering cross section approaches infinity as the critical temperature is approached along the critical isochore. Later Ornstein and Zernike considered the effect of correlations between neighboring volume elements. They predicted an angular dissymmetry in the scattering intensity and that the differential scattering cross section approaches a finite value (except for forward scattering) as the critical point is approached. In most cases the experimental data fit the Ornstein-Zernike scattering equation more closely than the Einstein equation.

An alternative to the Ornstein-Zernike approach to the effect of correlations was later presented by Debye. Debye accounted for correlations by the addition to the free-energy expression of a term proportional to the square of the density gradient.<sup>1-3</sup> Fixman has shown that the Ornstein-Zernike and Debye approaches are equivalent.<sup>4</sup> We follow the Debye approach, which leads to the scattering equation most directly and with fewest assumptions.

Recently another aspect of critical opalescence has become experimentally accessible as a result of techniques which permit measurements of extremely narrow linewidths.<sup>5</sup> Experiments using these techniques

have shown that the width of the Rayleigh line decreases as the critical temperature is approached.<sup>6-10</sup> These experiments have been interpreted in terms of a formula derived by Landau.<sup>11</sup> Like Einstein's derivation of the scattering cross section, Landau's derivation of the Rayleigh linewidth neglects the effect of correlations between neighboring volume elements. Fixman and Botch<sup>12</sup> (and more recently Mountain<sup>13</sup> and Felderhof<sup>14</sup>) have proposed a modified linewidth formula (hereafter referred to as Fixman's modification) which includes the effect of correlations. We show how Debye's modification of the free energy leads to the linewidth expression of Botch and Fixman. It is seen that the multiplicative correction terms involved in the scattering cross section and linewidth expressions are identical. Since, as Fixman has shown, the Debye and Ornstein-Zernike approaches are a necessary consequence of one another, the modified expression for the linewidth is as valid as the Ornstein-Zernike formula for the scattering cross section.

The free-energy approach to the effect of correlations emphasizes the fact that the divergence of the scattered light intensity in Einstein's theory and of the fluctuation relaxation time in Landau's theory both result from the vanishing of a thermodynamic "restoring force" associated with the fluctuation. The

<sup>6</sup> S. S. Alpert, Y. Yeh, and E. Lipworth, *Phys. Rev. Letters* **14**, 486 (1965).

<sup>7</sup> S. S. Alpert, D. Balzarini, R. Novick, L. Seigel, and Y. Yeh, *Proc. Intern. Conf. Quantum Electronics 3rd*, San Juan, Puerto Rico, 253 (1966).

<sup>8</sup> L. R. Wilcox, *Bull. Am. Phys. Soc.* **11**, 344 (1966).

<sup>9</sup> N. C. Ford, Jr., and G. B. Benedek, *Proc. Conf. Phenomena Neighborhood Critical Points*, Washington D.C., April, 1965 (to be published); *Phys. Rev. Letters* **15**, 649 (1965).

<sup>10</sup> J. A. White, J. S. Osmundson, and B. H. Ahn, *Phys. Rev. Letters* **16**, 639 (1966).

<sup>11</sup> L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1960), Secs. 94-95; L. Landau and G. Placzek, *Physik. Z. Sowjetunion* **5**, 172 (1934).

<sup>12</sup> M. Fixman, *J. Chem. Phys.* **33**, 1363 (1960); W. Botch and M. Fixman, *ibid.* **42**, 199 (1965); W. D. Botch, "Studies of Some Critical Phenomena," Ph.D. dissertation, University of Oregon, 1963, p. 63.

<sup>13</sup> R. D. Mountain, *Rev. Mod. Phys.* **38**, 205 (1966), Eq. (33).

<sup>14</sup> B. U. Felderhof, *J. Chem. Phys.* **44**, 602 (1966), Eq. (9.6).

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<sup>1</sup> P. Debye, *J. Chem. Phys.* **31**, 680 (1959). A similar suggestion had been made previously by Landau concerning the dependence of the free energy of binary alloys on the gradient of the order parameter [cf. L. Landau, *Physik. Z. Sowjetunion* **12**, 123 (1937)].

<sup>2</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958), Sec. 116.

<sup>3</sup> M. E. Fisher, *J. Math. Phys.* **5**, 944 (1964).

<sup>4</sup> M. Fixman, *J. Chem. Phys.* **33**, 1357 (1960).

<sup>5</sup> H. Z. Cummins, N. Knable, and Y. Yeh, *Phys. Rev. Letters* **12**, 150 (1964).

addition of the Debye term to the free energy thus introduces a new nonlocal force which serves to limit both the size of the fluctuations and their relaxation time. Having established this association we see that the magnitude of the Fixman correction can be predicted from the slope of plots of the angular scattering intensity distribution, and we give some numerical estimates based on recent experiments.

II. SCATTERING CROSS SECTION

Before discussing the linewidth calculation we review the results for the cross section for scattering from density fluctuations in a continuous medium. The magnitude of the fluctuations is obtained using thermodynamic fluctuation theory. First we expand the free energy in terms of the density and retain only the lowest nonzero term; this approach yields the Einstein formula for the scattering cross section. Then we introduce Debye's density-gradient term into the free energy; this leads to the Ornstein-Zernike scattering formula.

Let a plane monochromatic lightwave ( $I_0, \omega_0, \mathbf{K}_0$ ) polarized perpendicular to the scattering plane ( $\mathbf{K}_0, \mathbf{K}_s$ ) traverse a sample of volume  $V$  characterized by a local isotropic dielectric constant  $\epsilon(\mathbf{r}, t)$ . Assume that (1) the time dependence of  $\epsilon$  can be ignored (quasi-static approximation), and (2)  $\epsilon$  may be expressed as a function of the density  $\rho$  alone. Hence,  $\langle(\delta\epsilon)^2\rangle = (\partial\epsilon/\partial\rho)^2 \langle(\delta\rho)^2\rangle$ . Then, neglecting multiple scattering, the Rayleigh factor or the differential scattering cross section per unit volume,  $\sigma(\theta)$  (the intensity of light scattered per unit solid angle per unit volume per incident intensity  $I_0$ ), is given by<sup>15</sup>

$$\sigma(\theta) = (\pi^2/\lambda_0^4) V (\partial\epsilon/\partial\rho)^2 |\delta\rho_{\mathbf{K}}|^2, \tag{1}$$

where

$$\delta\rho_{\mathbf{K}} = V^{-1} \int_V (\rho - \rho_0) \exp(-i\mathbf{K}\cdot\mathbf{r}) d\mathbf{r},$$

$$\rho = \rho_0 + \sum_{\mathbf{K}} \delta\rho_{\mathbf{K}} \exp(i\mathbf{K}\cdot\mathbf{r}),$$

and

$$K = |\mathbf{K}_s - \mathbf{K}_0| = 2K_0 \sin\frac{1}{2}\theta = (4\pi n/\lambda_0) \sin\frac{1}{2}\theta.$$

( $\rho$  is the density,  $\lambda_0$  is the vacuum wavelength of the incident light, and  $n$  is the refractive index of the medium.) The Fourier component  $\delta\rho_{\mathbf{K}}$  of the density fluctuation  $\delta\rho = \rho - \rho_0$  can be evaluated using thermodynamic fluctuation theory where the probability of fluctuation is given by<sup>2</sup>

$$W(\delta x) \propto \exp(-\Delta F_t/kT), \tag{2}$$

where  $\Delta F_t$  is the change in the appropriate total free energy associated with the fluctuation  $\delta x$  in  $x$ .

Following Einstein, we write<sup>2</sup>

$$F(\rho) = F(\rho_0) + \frac{1}{2}(\partial^2 F/\partial\rho^2)(\rho - \rho_0)^2$$

$$= F(\rho_0) + \frac{1}{2}a(\rho - \rho_0)^2, \tag{3}$$

where  $F$  is the free energy per unit volume. Then, since

$$\Delta F_t = \int_V [F(\rho) - F(\rho_0)] d\mathbf{r},$$

we have

$$\Delta F_t = \frac{1}{2}a \int_V (\rho - \rho_0)^2 d\mathbf{r} = \frac{1}{2}aV \sum_{\mathbf{K}} |\delta\rho_{\mathbf{K}}|^2.$$

Since each term in the sum involves only one  $\delta\rho_{\mathbf{K}}$ , the fluctuations of different  $\mathbf{K}$  are independent. Hence for any given  $\mathbf{K}$ ,  $\Delta F_t(\rho_{\mathbf{K}}) = \frac{1}{2}aV |\delta\rho_{\mathbf{K}}|^2$ , and

$$W(\rho_{\mathbf{K}}) \propto \exp[-aV |\delta\rho_{\mathbf{K}}|^2/kT], \tag{4}$$

which is a Gaussian with variance

$$\langle |\delta\rho_{\mathbf{K}}|^2 \rangle = kT/aV. \tag{5}$$

Now from Eq. (3),  $a = (\partial^2 F/\partial\rho^2)_T$ , and, from thermodynamics,

$$(\partial^2 F/\partial\rho^2)_T = \rho^{-1}(\partial P/\partial\rho)_T = (\rho^2\beta_T)^{-1}, \tag{6}$$

where  $\beta_T$  is the isothermal compressibility. Therefore we have

$$\langle |\delta\rho_{\mathbf{K}}|^2 \rangle = kT\rho^2\beta_T/V. \tag{7}$$

Thus

$$\sigma(\theta) = (\pi^2/\lambda_0^4) (\partial\epsilon/\partial\rho)^2 kT\rho^2\beta_T, \tag{8}$$

which is Einstein's result. Fisher<sup>16</sup> has shown that any theory which assumes that the free energy expressed as a function of density and temperature is nonsingular at the critical point leads to the prediction that the compressibility diverges along the critical isochore as a simple pole. That is,  $\beta_T \propto |T - T_c|^{-1}$  (where  $T_c$  is the critical temperature); hence  $\sigma(\theta)$  diverges as  $|T - T_c|^{-1}$ . The cause of this divergence in  $\sigma(\theta)$  is the vanishing of  $(\partial^2 F/\partial\rho^2)_T$  which in this approximation makes the free energy independent of  $\rho$ .

The effect of correlations can be introduced directly into the Einstein thermodynamic theory by including a term which is proportional to  $|\nabla\rho|^2$  in the free-energy expression, as was first shown by Debye,<sup>1,4</sup>

$$F - F(\rho_0) = \frac{1}{2}a(\rho - \rho_0)^2 + \frac{1}{2}b |\nabla\rho|^2. \tag{9}$$

This gives  $\Delta F_t = \frac{1}{2}V \sum_{\mathbf{K}} (a + bK^2) |\delta\rho_{\mathbf{K}}|^2$ . Hence

$$\langle |\delta\rho_{\mathbf{K}}|^2 \rangle = kT[V(a + bK^2)]^{-1}. \tag{10}$$

<sup>15</sup> This equation is implicit in Einstein's original paper [A. Einstein, Ann. Physik **33**, 1275 (1910)], although it is not stated in this form. It is frequently used in the present form in the Russian literature [cf. V. L. Ginzberg, Soviet Phys.—Usp. **5**, 649 (1963), Eq. (12) [Usp. Fiz. Nauk **77**, 621 (1962)]].

<sup>16</sup> See Ref. 3, p. 945.

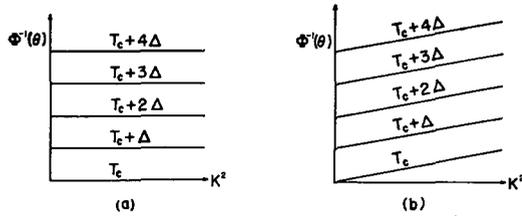


FIG. 1. The function  $\Phi^{-1}(\theta)$ : the angle-dependent part of the reciprocal scattering cross section  $\sigma^{-1}(\theta)$  and the Rayleigh linewidth function  $\Delta\omega_1/K^2$ . [ $K = (4\pi n/\lambda_0) \sin \frac{1}{2}\theta$ .] Graph 1(a) depicts the angular dependence of  $\sigma^{-1}(\theta)$  and  $\Delta\omega_1/K^2$  predicted by the Einstein and Landau theories, respectively. Einstein:  $\Phi^{-1}(\theta) = a = (\rho^2\beta_T)^{-1}$ . Graph (b) depicts the angular dependence of  $\sigma^{-1}(\theta)$  and  $\Delta\omega_1/K^2$  predicted by the Ornstein-Zernike-Debye and Fixman-Boch-Felderhof theories, respectively. Ornstein-Zernike,  $\Phi^{-1}(\theta) = kTR^2\rho^{-1}(\kappa^2 + K^2)$ ; Debye,  $\Phi^{-1}(\theta) = a + bK^2 = (\rho^2\beta_T)^{-1} + kTR^2\rho^{-1}K^2$ .

Therefore, for the Debye theory the Rayleigh factor is

$$\sigma(\theta) = (\pi^2/\lambda_0^4) (\partial\epsilon/\partial\rho)_T \rho^2 kT (a + bK^2)^{-1}. \quad (11)$$

The Ornstein-Zernike approach to the effect of correlations leads to<sup>3</sup>

$$\sigma(\theta) \propto [R^2(\kappa^2 + K^2)]^{-1}, \quad (12)$$

where  $R$  is a measure of the range of the "direct correlation" and is assumed to be nonsingular in the critical region, and  $\kappa$ , the inverse correlation length, is given by

$$\kappa = (kT\rho R^2\beta_T)^{-\frac{1}{2}}. \quad (13)$$

Thus  $\kappa \rightarrow 0$  as  $T \rightarrow T_c$  along the critical isochore. By comparing the Debye result, Eq. (11), to the equivalent Ornstein-Zernike result, Eq. (12), we find

$$(a/b) = \kappa^2. \quad (14a)$$

Using Eqs. (6), (13), and (14a), we obtain

$$b = (a/\kappa^2) = (\rho^2\beta_T)^{-1} (kT\rho R^2\beta_T) = kTR^2\rho^{-1}. \quad (14b)$$

Hence

$$a + bK^2 = kTR^2\rho^{-1}(\kappa^2 + K^2). \quad (14c)$$

*Summary.* For all three theories we can write:

$$\sigma(\theta) = (\pi^2/\lambda_0^4) (\partial\epsilon/\partial\rho)_T \rho^2 kT \Phi(\theta), \quad (15)$$

where for the Einstein theory

$$\Phi(\theta) = a^{-1} = \rho^2\beta_T = (\rho/kTR^2)\kappa^{-2}, \quad (16a)$$

for the Debye theory

$$\Phi(\theta) = (a + bK^2)^{-1} = [(\rho^2\beta_T)^{-1} + kTR^2\rho^{-1}K^2]^{-1}, \quad (16b)$$

and for the Ornstein-Zernike theory

$$\Phi(\theta) = (\rho/kTR^2)[\kappa^2 + K^2]^{-1}. \quad (16c)$$

For small  $K/\kappa$ , (16b) and (16c) reduce to the Einstein expression (16a). Plots of  $\Phi^{-1}(\theta)$  vs  $K^2$  predicted by the three theories are shown in Fig. 1. Plots of reciprocal scattering intensity vs  $K^2$  (or  $\theta^2$ ) are called O-Z

plots. The O-Z or Debye prediction—a series of parallel sloping lines with the  $K=0$  intercept proportional to  $T - T_c$  as shown in Fig. 1(b)—has recently been shown to be almost perfectly fulfilled for x-ray scattering in argon by Thomas and Schmidt.<sup>17</sup>

### III. LANDAU-PLACZEK THEORY

In the preceding section the free-energy function used was the Helmholtz free energy, which is a function of density and temperature. Since it is usually true that  $(\partial\epsilon/\partial T)_\rho \ll (\partial\epsilon/\partial\rho)_T$ , the total fluctuation in  $\epsilon$  (and hence the total light scattering) arises from the single term  $(\partial\epsilon/\partial\rho)_T \langle (\delta\rho)^2 \rangle$ . In discussing the spectrum of the scattered light this choice is not convenient since both the Rayleigh (quasielastic) and Brillouin (inelastic) components are combined in a single term. A more appropriate choice for the free-energy function is the enthalpy  $H(S, P)$ , since the isobaric entropy fluctuations  $\delta S_P$  and the isentropic (adiabatic) pressure fluctuations  $\delta P_S$  are responsible, respectively, for the Rayleigh and Brillouin components.<sup>11</sup>

#### A. Rayleigh Component

The probability of an entropy fluctuation at constant pressure is

$$W(\delta S_P) \propto \exp(-\Delta H/kT).$$

In the quadratic approximation

$$\Delta H = \frac{1}{2}(\partial^2 H/\partial S^2)_P (\delta S)_P^2,$$

but from thermodynamics

$$(\partial^2 H/\partial S^2)_P = (\partial T/\partial S)_P = T/C_P,$$

where  $C_P$  is the heat capacity per unit volume. Hence

$$W(\delta S_P) \propto \exp[-(\delta S)_P^2/2kC_P], \quad (17)$$

so that

$$\langle (\delta S)_P^2 \rangle = kC_P. \quad (18)$$

The associated isobaric density fluctuation is

$$(\delta\rho)_P = (\partial\rho/\partial S)_P (\delta S)_P, \quad (19)$$

but

$$\left(\frac{\partial\rho}{\partial S}\right)_P = \left(\frac{\partial\rho}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial\rho}{\partial T}\right)_P \frac{T}{C_P}$$

and

$$(\partial\rho/\partial T)_P = \rho^2(\beta_T - \beta_S)(C_P/TV),$$

where  $\beta_S$  is the adiabatic compressibility. Hence we have

$$\langle (\delta\rho)_P^2 \rangle = [T\rho^2(\beta_T - \beta_S)/C_P V] \langle (\delta S)_P^2 \rangle,$$

which becomes upon substitution of Eq. (18)

$$\langle (\delta\rho)_P^2 \rangle = kT\rho^2(\beta_T - \beta_S)/V. \quad (20)$$

<sup>17</sup> J. E. Thomas and P. W. Schmidt, J. Chem. Phys. **39**, 2506 (1963).

**B. Brillouin Components**

The probability of a pressure fluctuation at constant entropy is

$$W(\delta P_S) \propto \exp(-\Delta H/kT).$$

In the quadratic approximation

$$\Delta H = \frac{1}{2}(\partial^2 H/\partial P^2)_S (\delta P)^2,$$

but from thermodynamics,

$$(\partial^2 H/\partial P^2)_S = (\partial V/\partial P)_S = -V\beta_S.$$

Hence

$$W(\delta P_S) \propto \exp[-(\delta P)^2 V\beta_S/2kT], \tag{21}$$

so that we have

$$\langle(\delta P)^2\rangle = kT/V\beta_S. \tag{22}$$

The corresponding isentropic density fluctuation is

$$(\delta\rho)_S = (\partial\rho/\partial P)_S (\delta P)_S. \tag{23}$$

Since

$$(\partial\rho/\partial P)_S = \rho\beta_S,$$

we have

$$\langle(\delta\rho)^2\rangle = (\rho\beta_S)^2 \langle(\delta P)^2\rangle = \rho^2 kT\beta_S/V. \tag{24}$$

The intensity  $I_R$  of the Rayleigh line is proportional to  $\langle(\delta\rho)^2\rangle$ , while the sum of the two Brillouin intensities,  $2I_B$ , is proportional to  $\langle(\delta\rho)^2\rangle$ . Thus the sum  $(I_R+2I_B)$  is proportional to

$$\langle(\delta\rho)^2\rangle + \langle(\delta\rho)^2\rangle = kT\rho^2\beta_T/V, \tag{25}$$

which is equal to the total  $\langle(\delta\rho)^2\rangle$  derived from the Helmholtz free energy in Sec. II [Eq. (7)]. It should be noted that in Sec. II we discussed a single Fourier component of the density fluctuation  $\delta\rho_K$  for the entire volume whereas in the present section we are considering the total fluctuation in the local density  $\delta\rho$ . The fact that  $\langle|\delta\rho_K|^2\rangle$  and  $\langle(\delta\rho)^2\rangle$  are equal when correlations are neglected is most easily demonstrated by comparing the results of thermodynamic calculations (cf. Secs. 111 and 116 of Ref. 2).

The intensity ratio  $I_R/2I_B$  is given by

$$I_R/2I_B = \langle(\delta\rho)^2\rangle/\langle(\delta\rho)^2\rangle = (\beta_T - \beta_S)/\beta_S, \tag{26}$$

which is the Landau-Placzek ratio.<sup>11,18</sup> In the critical region  $\beta_T \gg \beta_S$ , so that in the limit  $T \rightarrow T_c$  Expression (20) for  $\langle(\delta\rho)^2\rangle$  and Expression (7) for  $\langle(\delta\rho)^2\rangle$  become equal. Hence in the limit  $T \rightarrow T_c$  the Rayleigh intensity equals the total intensity.

**IV. RAYLEIGH LINEWIDTH**

The width of the Rayleigh line is determined by the time constant with which the isobaric entropy fluctua-

<sup>18</sup> For recent discussions of the Landau-Placzek ratio including comparison with experiment, see: H. Z. Cummins and R. W. Gammon, *J. Chem. Phys.* **44**, 2785 (1966) and also Ref. 13.

tions relax.<sup>11</sup> As we have noted, the magnitude of a fluctuation is controlled by the probability function

$$W(\delta x) \propto \exp(-\Delta F_t/kT). \tag{2}$$

In the critical region the minimum work  $\Delta F_t$  required to produce a given fluctuation  $\delta x$  becomes progressively smaller so that  $\langle(\delta x)^2\rangle$  diverges.

Relaxation of the fluctuation is controlled fundamentally by the thermodynamic "force"<sup>19</sup>

$$\Omega = (1/T)(\partial F/\partial x). \tag{27}$$

For those nonpropagating fluctuations which can decay locally (such as fluctuating polarization in ferroelectrics) the decay is described by a simple kinetic equation of the type<sup>20</sup>

$$\dot{x} = -\gamma\Omega, \tag{28}$$

where  $\gamma$  is a phenomenological kinetic coefficient. For those nonpropagating fluctuations which must decay by transport, relaxation requires that there be a gradient of the local force  $\nabla\Omega$ . The relaxation process is then governed by a transport equation of the type<sup>21</sup>

$$\mathbf{J}_x = -\Psi\nabla\Omega. \tag{29}$$

The Rayleigh line is produced by isobaric entropy fluctuations. As we have seen the appropriate free energy is the enthalpy  $H$ , and

$$\begin{aligned} (H-H_0)_P &= \frac{1}{2}(\partial^2 H/\partial S^2)_P (S-S_0)^2 \\ &= \frac{1}{2}(T/C_P)(S-S_0)^2. \end{aligned} \tag{30}$$

Therefore, we have for the thermodynamic "force,"

$$\Omega = (1/T)(\partial H/\partial S) = (1/C_P)(S-S_0). \tag{31}$$

Thus

$$\nabla\Omega = C_P^{-1}\nabla S, \tag{32}$$

and

$$\mathbf{J}_S = -(\Psi/C_P)\nabla S. \tag{33}$$

Equation (33) is equivalent to

$$\mathbf{J}_Q = -\Psi\nabla T, \tag{34}$$

so that  $\Psi$  is just the thermal conductivity  $\Lambda$ .

Thus Eq. (33) becomes

$$\mathbf{J}_S = -(\Lambda/C_P)\nabla S. \tag{35}$$

But  $\nabla \cdot \mathbf{J}_S = -(\Lambda/C_P)\nabla^2 S$  and  $\nabla \cdot \mathbf{J}_S = -(\partial S/\partial t)$ , so

$$(\partial S/\partial t) = (\Lambda/C_P)\nabla^2 S. \tag{36}$$

<sup>19</sup> See Ref. 2, Secs. 22 and 119.

<sup>20</sup> L. D. Landau and I. M. Khalatnikov, *Dokl. Akad. Nauk SSSR* **96**, 469 (1954).

<sup>21</sup> Note that in this section we assume that only one variable need be considered in order to avoid introducing an additional term in the relaxation and transport equations. Since the relevant variables are entropy and pressure, this is equivalent to assuming isobaric conditions throughout in accord with the Landau-Placzek theory.

Now suppose that

$$S(t) = S_0 + S_K(t) \exp(i\mathbf{K} \cdot \mathbf{r}). \quad (37)$$

Then

$$(\partial S_K / \partial t) = -(\Lambda / C_P) K^2 S_K(t) = -(\Lambda K^2 / \rho c_P) S_K(t),$$

where  $c_P = (C_P / \rho)$ . Hence

$$S_K(t) = S_K(0) \exp(-t/\tau), \quad (38)$$

where

$$\tau = \rho c_P / \Lambda K^2, \quad (39)$$

which is the Landau result.<sup>11</sup> Thus, an isobaric entropy fluctuation with wave vector  $\mathbf{K}$  will follow a simple exponential decay law with characteristic time constant  $\tau$ .

The resultant spectrum of the Rayleigh line is thus a Lorentzian of half-width at half-maximum

$$\Delta\omega_{\frac{1}{2}} = 1/\tau = \Lambda K^2 / \rho c_P. \quad (40)$$

The divergence of the relaxation time ( $\tau \rightarrow \infty$  as  $T \rightarrow T_c$ ) is thus seen to result directly from the disappearance of the thermodynamic "force"  $\Omega = (\rho c_P)^{-1}(S - S_0)$  and is therefore directly analogous to the divergence of  $\sigma(\theta)$  in the Einstein theory.

In the spirit of Debye's modification of Einstein's free-energy Expression (9) we may make a similar modification of Eq. (30). Thus

$$(H - H_0)_P = (T/2\rho c_P)(S - S_0)^2 = \frac{1}{2}a'(S - S_0)^2$$

is replaced by

$$(H - H_0)_P = \frac{1}{2}a'(S - S_0)^2 + \frac{1}{2}b'|\nabla S|^2. \quad (41)$$

Since

$$\Omega = T^{-1}(\partial H / \partial S) = T^{-1}a'(S - S_0)$$

is replaced by

$$\Omega = T^{-1}(a' + b'K^2)(S - S_0), \quad (42)$$

where we have taken  $(S - S_0) = S_K \exp(i\mathbf{K} \cdot \mathbf{r})$ .

Since  $\tau \propto \Omega^{-1}$ , the  $\tau$  of the Landau equation [Eqs. (38) and (39)] is multiplied by  $a'/(a' + b'K^2)$  and thus

$$\Delta\omega_{\frac{1}{2}} = [(a' + b'K^2)/a'](\Lambda K^2 / \rho c_P). \quad (43)$$

The quantities  $a$  and  $b$  in the Debye theory (Sec. II) are associated with total density fluctuations while  $a'$  and  $b'$  in the present section refer only to the isobaric component of the density fluctuations which generate the Rayleigh line; nevertheless, the *ratio*  $a'/b'$  can be taken as equal to  $a/b$ . Hence we have

$$\Delta\omega_{\frac{1}{2}} = (\Lambda K^2 / \rho c_P)[1 + (b/a)K^2]. \quad (44)$$

Since

$$a/b = \kappa^2, \quad (14a)$$

we have

$$\Delta\omega_{\frac{1}{2}} = (\Lambda K^2 / \rho c_P)[1 + (K^2/\kappa^2)], \quad (45)$$

which is equivalent, in the neighborhood of the critical point, to the Fixman modification as given by Botch<sup>12</sup> (see also Mountain<sup>13</sup> and Felderhof<sup>14</sup>). The Fixman

modification was originally derived from the hydrodynamic equations, which were modified by the inclusion of a term describing the effect of density correlations; the resultant linewidth expression was

$$\Delta\omega_{\frac{1}{2}} = \frac{\Lambda K^2}{\rho c_P} \left[ \frac{1 + (K^2/\kappa^2)}{1 + (c_V K^2 / c_P \kappa^2)} \right]. \quad (46)$$

However, in the neighborhood of the critical point  $c_P \gg c_V$ , so that (46) becomes identical to (45).

Using Eq. (6) we can rewrite Eq. (44):

$$\begin{aligned} \Delta\omega_{\frac{1}{2}} &= (\Lambda K^2 / \rho c_P) a^{-1}(a + bK^2) \\ &= (\Lambda K^2 \rho^2 \beta_T / \rho c_P)(a + bK^2). \end{aligned} \quad (47)$$

Since  $\beta_T$  and  $c_P$  both diverge (classically) as  $|T - T_c|^{-1}$ ,

$$\Delta\omega_{\frac{1}{2}}/K^2 = \text{const}(a + bK^2).$$

Summarizing, we can write

$$\Delta\omega_{\frac{1}{2}}/K^2 = (\Lambda / \rho c_P)(\rho^2 \beta_T) \Phi^{-1}(\theta), \quad (48)$$

where  $\Phi^{-1}(\theta)$  is given in Fig. 1 with 1(a) representing Landau's result and 1(b) representing Fixman's modification.

## V. NUMERICAL ESTIMATES

The thermodynamic theory of Sec. IV is ultimately subject to the same criticisms as the Debye theory, since the power series expansion for the free energy may not converge for temperatures arbitrarily close to  $T_c$ . However, the Fixman modification should represent experimentally determined Rayleigh linewidths more accurately than the Landau theory, just as the O-Z-Debye theory represents the scattering cross section more accurately than the Einstein theory.

As we have seen, both the reciprocal scattering cross section  $\sigma^{-1}(\theta)$  and the half-width of the Rayleigh line divided by  $K^2$ ,  $(\Delta\omega_{\frac{1}{2}}/K^2)$ , are proportional to the quantity  $\Phi^{-1}(\theta)$ , which is given by

$$\Phi^{-1}(\theta) = (\rho^2 \beta_T)^{-1} + kTR^2 \rho^{-1} K^2. \quad (49)$$

Since  $\beta_T \propto |T - T_c|^{-1}$ ,  $\Phi^{-1}(\theta)$  will itself be proportional to the quantity

$$|T - T_c| + \xi_\lambda \sin^2 \frac{1}{2} \theta, \quad (50)$$

where  $\xi_\lambda$  has the dimensions of temperature and scales with wavelength as  $\lambda^{-2}$ . The significance of the "temperature"  $\xi_\lambda$  can be seen by examining the O-Z plot of Fig. 1(b). The total range of  $K^2$  represents a variation of  $\sin^2 \frac{1}{2} \theta$  from 0 to 1. Thus the maximum change in  $\Phi^{-1}(\theta)$  with  $\theta$  (measured at fixed  $T$ ) is equal to the change in  $\Phi^{-1}(\theta)$  at fixed  $\theta$  produced by a change in the temperature equal to  $\xi_\lambda$ .

If  $\xi_\lambda$  is large, the slope of the isotherms will be large, so the O-Z modification for  $\sigma(\theta)$  and the Fixman modification for  $\Delta\omega_{\frac{1}{2}}/K^2$  will be important.

If  $\xi_\lambda$  is small (e.g., less than 1 mdeg C), the modifications will be small, and the scattering cross section

TABLE I. Approximate value of the constant  $\xi_{6328}$  appearing in  $\Phi^{-1}(\theta) = \text{const}(|T - T_c| + \xi_\lambda \sin^2 \frac{1}{2}\theta)$ .

System	Investigator	$\xi_{6328}(10^{-3} \text{ }^\circ\text{C})$	Comments
Argon	Thomas and Schmidt <sup>a</sup>	0.8	$\lambda = 0.71 \text{ \AA}$
39.4 wt % <i>n</i> -decane + $\beta, \beta'$ -dichloroethyl ether	Chu <sup>b</sup>	47	$n_{6328} = 1.43$
40.6 wt % <i>n</i> -dodecane + $\beta, \beta'$ -dichloroethyl ether	Chu and Kao <sup>c</sup>	74	$n_{6328} = 1.43$

<sup>a</sup> See Ref. 17, Fig. 10. For argon at the critical point  $n_{6328} \approx 1.09$ .<sup>b</sup> See Ref. 23, Fig. 8.<sup>c</sup> See Ref. 24, Fig. 1.

and the Rayleigh linewidth should be very well described by the Einstein and Landau theories, respectively. In the limit  $\xi_\lambda \rightarrow 0$ , the slope of the isotherms in the O-Z plot [Fig. 1(b)] disappears, and the plot becomes identical with the Einstein plot [Fig. 1(a)].

### A. Pure Fluids

Very few angular-scattering intensity measurements in pure fluids have been reported which are free of uncertainties associated with multiple scattering and related experimental difficulties. The best experimental data comes from small-angle x-ray scattering. Thomas and Schmidt<sup>17</sup> have reported small-angle x-ray-scattering results in argon which are in almost perfect agreement with the O-Z theory. Their Fig. 10 is an O-Z plot for various temperatures at the critical pressure (48.3 atm); their isotherms resemble the theoretical isotherms of our Fig. 1(b) and closely fit the function

$$\Phi^{-1}(\theta) = \text{const}[|T - T_c| + (5.1 \times 10^4) \sin^2 \frac{1}{2}\theta]. \quad (51)$$

Thus for  $\lambda = 0.71 \text{ \AA}$ ,  $\xi = 5.1 \times 10^4$ , while for  $\lambda_0 = 6328 \text{ \AA}$ , in argon,  $\lambda \approx 5750 \text{ \AA}$ , and  $\xi \approx 8 \times 10^{-4}$  (since  $\xi$  scales as  $\lambda^{-2}$ ). Therefore

$$\Phi^{-1}(\theta)_{\lambda=6328} = \text{const}[|T - T_c| + (8 \times 10^{-4}) \sin^2 \frac{1}{2}\theta]. \quad (52)$$

Thus for  $\lambda_0 = 6328 \text{ \AA}$  the maximum variation in either  $\sigma^{-1}(\theta)$  or  $\Delta\omega_{\frac{1}{2}}/K^2$  produced by scanning  $\theta$  over the entire range  $0^\circ$  to  $180^\circ$  should be approximately equal to the variation observed at any *fixed* angle by changing the temperature by 0.8 mdeg C.

For temperatures within a few millidegrees of the critical temperature the experimental difficulties due to convection, density gradients, and multiple scattering are quite severe. Thus, at least for argon, departures from the Einstein and Landau theories are probably too small to be observable in light-scattering experiments.

Although experimental results for other single-component systems are less complete than for argon, we mention some recent experimental evidence which suggests that carbon dioxide is characterized by a parameter  $\xi$  which is not significantly larger than that of argon:

(1) Preliminary results of angular light-scattering

measurements in  $\text{CO}_2$  by Sengers, McIntyre, and Wims show no significant slope of the O-Z isotherms.<sup>22</sup>

(2) Measurements of the Rayleigh linewidth vs angle at fixed  $T$  in  $\text{CO}_2$  by Wilcox, Alpert, and Yeh<sup>8</sup> show no measurable departures from the Landau equation in the immediate vicinity of the critical temperature.

### B. Liquid Mixtures

In contrast to the pure fluid situation, nonhorizontal isotherms in the O-Z plots for critical liquid mixtures have been frequently observed. In Table I we list the value of  $\xi_{6328}$  in millidegrees for two mixtures, taken from the results and Chu and Kao.<sup>23,24</sup> The argon value is also included for comparison. In most cases  $\xi_{6328}$  is large enough to produce an easily measurable slope of the O-Z isotherms; therefore, for liquid mixtures, measurements of the Rayleigh linewidth should be expected to show significant departures from the Landau equation.<sup>25</sup>

Although two experimental determinations of Rayleigh linewidths in critical mixtures have been reported,<sup>6,10</sup> departures from the Landau theory indicating the possible presence of a Fixman modification term were not adequately explored. Additional linewidth measurements in critical mixtures would therefore be of value, particularly for those mixtures known from angular-scattering experiments to exhibit large  $\xi$  values.

## VI. CONCLUSIONS

It has been demonstrated that the reciprocal scattering cross section  $\sigma^{-1}(\theta)$  and the Rayleigh linewidth function  $\Delta\omega_{\frac{1}{2}}/K^2$  are both proportional to the O-Z function:

$$\Phi^{-1}(\theta) \propto (|T - T_c| + \xi_\lambda \sin^2 \frac{1}{2}\theta), \quad (50)$$

where  $\xi_\lambda$  is a constant with the dimensions of a temperature which depends on wavelength as  $\lambda^{-2}$ . In the limit  $\xi_\lambda \rightarrow 0$  the O-Z isotherms are horizontal straight lines, and the scattering cross section and Rayleigh linewidth are given by the Einstein and Landau

<sup>22</sup> J. V. Sengers (private communication).<sup>23</sup> B. Chu, *J. Chem. Phys.* **41**, 226 (1964).<sup>24</sup> B. Chu and W. P. Kao, *J. Chem. Phys.* **42**, 2608 (1965).<sup>25</sup> See comment by P. Debye, *Phys. Rev. Letters* **14**, 783 (1965).

theories, respectively. For nonzero  $\xi_\lambda$  the isotherms have nonzero slope which modifies the scattering cross section and the linewidth equation in accordance with the Ornstein-Zernike-Debye theory and the Fixman theory, respectively.

Analysis of x-ray-scattering data for argon and preliminary experimental light-scattering data for CO<sub>2</sub> has led us to predict that critical opalescence in pure fluids observed with light should show extremely little departure from the Einstein and Landau predictions, since  $\xi_\lambda$  for argon with  $\lambda_0 = 6328 \text{ \AA}$  is less than  $10^{-3} \text{ }^\circ\text{C}$ . Critical liquid mixtures, however, exhibit considerable slope of the isotherms—presumably because the correlation length increases more rapidly as  $T \rightarrow T_c$  for

critical mixtures than for pure fluids—and  $\xi_\lambda$  is in some cases on the order of  $10^{-1} \text{ }^\circ\text{C}$ . Departures of the Rayleigh linewidth from Landau's equation—in accordance with the modification proposed by Fixman—should therefore be experimentally detectable in the case of liquid mixtures since the change in  $\Delta\omega_i/K^2$  produced by scanning  $\theta$  from  $0^\circ$  to  $180^\circ$  will be equivalent to changing  $T$  (with  $\theta$  fixed) by nearly  $10^{-1} \text{ }^\circ\text{C}$ .

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## Kinetics of Growth of Multicomponent Chains

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A theory is presented by which the rate of growth and composition (including all pair and higher distributions) of a chain growing in a multicomponent system may be calculated. Each position in the chain may be occupied by any of the components of the system. Only nearest-neighbor interactions are assumed and the rate constants  $\alpha^{ij}$  for addition of Species  $j$  to a chain ending in Species  $i$ , and  $\beta^{ij}$ , for the removal of Species  $j$  from a chain ending in  $i$ ,  $j$  are assumed known and independent of chain length, except for those referring to the first step of the chain, which are distinct. The full kinetic equations for the growth of such chains are formulated and a solution obtained for steady-state conditions. It is shown that when the matrix of  $\alpha^{ij}/\beta^{ij}$  is indecomposable and primitive a solution of the equations which is independent of chain length always exists for sufficiently long chains and computational methods for obtaining this solution for a relatively large number of components (of the order of 10) are presented. In addition, the relationship of  $\alpha^{ij}/\beta^{ij}$  to the energetics of the system is derived.

### INTRODUCTION

**I**N systems consisting of several components there are a number of kinetic problems which may be formulated as the kinetics of growth of a "mixed chain," i.e., a chain whose  $\nu$ th unit may be any of the components of the system. Examples of such systems are (1) a mixture of monomers which polymerize to form a copolymer, (2) a mixture of several components which crystallize to form a solid solution, the chain in this case being a crystal strip growing at, say, a screw dislocation edge, (3) a polymer melt or solution crystallizing to form a chain-folded crystal, the chain being a strip growing on the edge of the crystal and the "components" being the possible lengths of the segments of molecules between folds.

In these problems it is desirable to be able to calculate the rate of growth of the chain as a function of the relevant parameters of the system, the average composition of the chain at various rates of growth, and the various pair and higher distributions. For the copolymer case this has been done, but the back-

reaction has not specifically been taken into account.<sup>1</sup> For the case of crystallization in a binary system, the problem has been formulated by Chernov<sup>2</sup> and solved for certain specialized conditions. The polymer crystallization problem has been formulated and solved by Price<sup>3</sup> for equilibrium conditions but not for conditions of finite growth rate.

It is our purpose to develop a method by which in principle any such problem may be solved, and by which in practice a relatively large number of components (of the order of 10) may be handled. A preliminary account has already been given.<sup>4</sup>

### FORMULATION OF THE PROBLEM

We consider a system of  $n$  components and consider an ensemble of chains  $\nu$  units long growing in this

<sup>1</sup> See, for example, P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, N.Y., 1953), Chap. 5.

<sup>2</sup> A. A. Chernov, *Colloq. Intern. Centre Natl. Rech. Sci. (Paris)* **152**, 1 (1965).

<sup>3</sup> F. P. Price, *J. Chem. Phys.* **35**, 1884 (1961).

<sup>4</sup> E. A. DiMarzio, J. I. Lauritzen, Jr., and E. Passaglia, *Bull. Am. Phys. Soc.* **10**, 354 (1965).