

Equation (B2) shows clearly that the Bogoliubov theory is a weak-coupling version of the Feynman theory of liquid helium.<sup>11</sup> Moreover, Eq. (14) shows that it is not necessary to go through any kind of canonical transformation of plane-wave creation and annihilation operators in order to

explicitly calculate  $E_B(\vec{k})$  and thus  $S_B(\vec{k})$ . As Mihara and Puff suggest,<sup>1</sup> once the initial ansatz is made (in this case, that the dynamic structure factor corresponds to a single excitation frequency), the sum rules completely determine the energy spectrum for the liquid.

<sup>1</sup>N. Mihara and R. D. Puff, *Phys. Rev.* **174**, 221 (1968).

<sup>2</sup>R. P. Feynman, *Phys. Rev.* **94**, 262 (1954).

<sup>3</sup>N. N. Bogoliubov, *J. Phys. (USSR)* **11**, 23 (1947).

<sup>4</sup>E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Chap. 8.

<sup>5</sup>Throughout this paper we use units such that  $\hbar=1$  and assume the liquid to be confined to unit volume.

<sup>6</sup>T. Davison and E. Feenberg, *Phys. Rev.* **171**, 221 (1968).

<sup>7</sup>A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Appendix II.

<sup>8</sup>R. D. Puff, *Phys. Rev.* **137**, A406 (1965). See also

A. A. Abrikosov, L. P. Gor'kov, and I. -E.

Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963), pp. 151 f.

<sup>9</sup>The even-moment sum rules elude us here because the dynamic structure factor is an odd function of  $\omega$ . Indeed, direct computation of the coefficients of  $\delta(\omega)$ ,  $\delta^{(2)}(\omega)$ , etc., shows that they are identically zero.

<sup>10</sup>This is also because the dynamic structure factor is an odd function of the frequency. See Ref. 8 for details.

<sup>11</sup>This fact was first pointed out by A. Miller, D. Pines, and P. Nozières, *Phys. Rev.* **127**, 1452 (1962).

## Radiation Pressure Theory of Thermal Diffusion in Liquids

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An analysis of the nature of heat in the condensed phases leads to the conclusion that the transport of thermal energy must be accompanied by the development of a "radiation pressure." In line with this conclusion, a force must act on the particles dissolved or suspended in a liquid when a temperature gradient is established in absence of convection. The direction of the force is parallel to the temperature gradient, and its orientation depends on the thermal conductivities and speed of sound both within the liquid and the particles. On this basis a physical explanation of the thermodiffusive phenomena in the condensed phases is advanced.

### INTRODUCTION

Since the time of its discovery by C. Ludwig<sup>1</sup> and C. Soret,<sup>2-5</sup> the phenomenon of thermal diffusion in liquids has never ceased to puzzle theoretical physicists. The hypothesis that the variation of osmotic pressure with temperature was the physical basis of thermal diffusion in liquids goes back to the time of Van't Hoff<sup>6</sup>; his early theory was disproved by the experiments of Arrhenius.<sup>7,8</sup> Also inadequate to explain the

complex behavior of liquid solutions and mixtures when crossed by a flow of heat, in conditions of gravitational equilibrium, were the many theories put forward, among others, by Wereide,<sup>9</sup> who tried in 1914 to generalize Einstein's theory of Brownian motion for a system at nonuniform temperature; by Chapman,<sup>10,11</sup> who worked along similar lines with more refined methods; and by Porter,<sup>12</sup> who applied to thermal diffusion the kinetic theory of diffusion worked out by E. Meyer for the case of a gas.

One common feature of all these theories is the assumption of a gas kinetic model – crude in some cases, sophisticated in others – as the basis upon which the theory is constructed. This approach stems from the great success met by simple kinetic models in explaining osmotic pressure, diffusion, and Brownian movements in liquids, and the complete success of the gas kinetic theory in explaining the behavior of thermal diffusion within matter in the gaseous state (see, for instance, the article by G. Dickel<sup>13</sup>).

In the present paper we question the validity of a gas kinetic model as the starting point for a theory of thermal diffusion in liquids, and we develop a thermal-radiation-pressure theory of thermodiffusive phenomena. We make no mention of the interesting and successful phenomenological theories of thermodiffusive phenomena, nor of the theories based on nonequilibrium thermodynamics, because none of them gives insight into the physical mechanism of interaction between the flux of thermal energy and the materials crossed by it, which mechanism is the object of the present study.

#### NATURE OF THERMAL AGITATION IN LIQUIDS

Since the cause of thermal diffusion in a solution is the flow of heat produced by a temperature gradient in the liquid, the first step towards a physical explanation of thermodiffusion consists in an understanding of the nature of heat in a liquid. If one assumes that a liquid behaves like a condensed gas, then the sum of the individual kinetic energies of the particles constitutes the total thermal energy of the liquid, and the transfer of kinetic energy mediated by collisions among the particles is the elementary mechanism responsible for the flow of heat. Following this approach, thermal diffusion phenomena can be considered as a consequence of asymmetry in the average distribution of collisions that are produced by the existence of a thermal gradient.

If, on the other hand, a liquid is assumed to behave as a melted solid, potential energy also plays a role; in fact, in the disordered lattice of a liquid, the heat content consists of the sum of both the kinetic and potential energies of collective oscillatory disturbances that are ceaselessly propagating within it. The liquid is to be considered as the seat of elastic waves of all frequencies within certain physical limiting values, which propagate within the liquid mass in all directions. The flow of heat along the direction of a thermal gradient consists of an excess flow of undulatory energy in that direction. In this context, thermal diffusion phenomena can be considered as a consequence of the mechanical interaction of thermal elastic waves and matter.

Concerning the nature of heat in liquids, P.

Debye<sup>14</sup> extended to liquids his theory of specific heats of solids by introducing the condition that only longitudinal waves propagate in liquids, the transverse waves being absent, owing to lack of rigidity. According to this theory, conclusions are obtained for monoatomic liquids very similar to those that are reached for monoatomic solids.

A theoretical difficulty raised by L. Brillouin<sup>15</sup> was that, following Debye's argument, one is forced to assume a higher-frequency limit for thermal waves for a given substance in the liquid state than in the solid. On the other hand, if one keeps the same limiting Debye frequency ( $\nu_D$ ) for both the liquid and solid states, namely,

$$\nu_D = v_l (3N/4\pi V)^{1/3}, \quad (1)$$

[where  $v_l$  is the phase velocity of elastic waves (of frequency  $\nu_D$ ) in the liquid,  $N$  is Avogadro's number, and  $V$  the molar volume (volume occupied by a gram-atom in our case)], one is left with too small a total number of normal modes to accommodate all the  $3N$  degrees of freedom of the gram-atom. Brillouin<sup>15</sup> suggested that the excess degrees of freedom are occupied by transverse vortex movements, implying only kinetic energy. (We observe here that the concept of roton, developed by Landau, is already contained in this work of Brillouin.) Alternative ways to settle the question of the unoccupied degrees of freedom in the liquid could lie in assuming either the existence of transverse waves within pseudo-solid micro-domains or of strongly damped viscosity waves.

We must remember that another fundamental consequence of Debye's theory is that, in the limiting case of very low temperatures, the specific heats of substances which can still exist in the liquid state should obey the famous law of proportionality to the third power of the absolute temperature, in analogy to the case of solids for which

$$C_V \approx \frac{12}{5} \pi^4 R(T/\Theta)^3, \quad (2)$$

where  $R$  is the gas constant and  $\Theta$  is the "Debye temperature" of the substance.

Let us now look at the experimental reality to check the theoretical predictions. If one plots the specific heats of monoatomic liquids against the reduced temperature defined by

$$t = (T - T_c)/(T_c - T_m), \quad (3)$$

where  $T_m$  is the melting point temperature,  $T_c$  the critical point temperature, and  $T$  is the temperature at which the specific heat is measured; then, as observed by Bauer and co-workers,<sup>16</sup> different substances behave in a remarkably similar way, the specific heats approach-

ing very closely the theoretical value of  $C_V = 3R$  at  $0 \leq t \leq 0.4$ . At higher values of the reduced temperature  $t$  (nearer to the critical temperature),  $C_V$  approaches the value  $2R$ . As one can see, Brillouin's criticism of Debye's theory seems to be sustained by the experimental behavior of specific heats of monoatomic liquids, and thus the question of the form taken by that part of the thermal agitation not consisting of longitudinal waves is left open to further speculation. The idea that longitudinal waves are the principal form taken by the heat content of liquids is, however, confirmed by these observations. The investigation of specific heat at temperatures close to absolute zero, as in the case of the two isotopes  $\text{He}^3$  and  $\text{He}^4$ , lends further support to the concept of the undulatory nature of heat in liquids. Measurements of the specific heat of  $\text{He}^4$  in the temperature range  $0.25-1^\circ\text{K}$ , carried out first by Pickard and Simon and more recently by Kramers, Wesscher, and Gorter,<sup>17</sup> proved that, below  $0.8^\circ\text{K}$ , Debye's law (2) was surprisingly well obeyed, with a value of  $\Theta \approx 15.5^\circ\text{K}$ . The best available measurements give<sup>18</sup>  $C_V = 0.02T^3 \times J/g^\circ\text{K}$  at temperatures below  $0.6^\circ\text{K}$ .

Direct evidence of the existence of longitudinal waves ceaselessly propagating in all directions in liquids at room temperature was finally obtained through the study of the interaction of these waves with light. In a general theoretical study of the interaction of thermal waves with light, Brillouin<sup>19</sup> predicted the existence of a detectable Doppler shift in the light waves crossing a liquid, produced by thermal waves. The refractive index changes associated with these waves will scatter an appreciable amount of light at angle  $\varphi$  to an incident parallel light beam of optical frequency  $\nu_0$  only for the acoustic plane wave satisfying the Bragg condition for reflection. The Doppler shift  $\Delta\nu$  of scattered light will be given by

$$\Delta\nu/\nu_0 = \pm 2(v_l/C_{\text{liq}}) \sin \frac{1}{2} \varphi, \quad (4)$$

where  $v_l$  is the velocity of the thermal waves in the liquid and  $C_{\text{liq}}$  is the velocity of light of frequency  $\nu_0$  in the same. The frequency shift  $\Delta\nu$  is equal to the frequency  $\nu_s$  of the elastic wave responsible for the scattering. Early experiments by Meyer and Ramm,<sup>20</sup> Raghavendra-Rao<sup>21</sup> and others gave poor results due to lack of a suitable monochromatic light source, but the advent of lasers, providing an intense beam of light that is strictly monochromatic and comprised in a very narrow angle, has now made it possible to obtain reliable quantitative verifications of expression (4) together with measurements of  $\Delta\nu = \nu_s$  and  $v_l$  in a number of liquids.<sup>22-27</sup>

To conclude, it is now possible to consider the existence of longitudinal elastic thermal waves in liquids as a well-established fact. The spec-

trum of these waves seems to extend from the longest wavelengths compatible with the dimensions of the vessel up to much smaller waves, the limit being the mode in which immediately neighboring atoms vibrate in opposition of phase. Of this whole spectrum, only frequencies up to  $10^{10}$  Hz (wavelengths of  $\approx 0.15\mu$  in water) have been experimentally investigated with the methods described above. Within this region the velocity of propagation of the waves does not change very much with frequency and is in general close to, but a little higher than, the speed of the usual elastic longitudinal waves in the acoustical and ultrasonic ranges of the spectrum. One interesting point open to further investigation is whether this is true also in the  $10^{10}-10^{12}$  Hz region, where relaxation phenomena are to be expected.

#### FORCES GENERATED BY THE FLOW OF HEAT ON PARTICLES SUSPENDED IN LIQUIDS

According to the discovery of Rayleigh, elastic waves exert dynamic actions on emitting, absorbing, or reflecting surfaces; therefore thermal waves also, being elastic high-frequency acoustic radiation, must exert such a "radiation pressure" along their paths. The dynamic actions exerted by acoustical radiation on a surface depend on the mutual orientation of the surface relative to the propagation vector of the waves, and therefore it would be more appropriate to speak of a radiation stress tensor rather than a radiation pressure. These problems have been extensively studied by Brillouin<sup>28-31</sup>; here we shall confine ourselves to the simple concept of radiation pressure to develop a theory of thermal diffusion in liquids.

Let us consider the schematic drawing of a thermal diffusion cell (Fig. 1). If  $T_1$  and  $T_2$  are the temperatures at which the hot and cold plates are maintained and  $a$  is their distance, when the steady state is reached there will be a thermal gradient

$$(T_1 - T_2)/a = \Delta T/a = dT/dx$$

and a flow of heat in the liquid given by

$$dQ/dT = K_l S dT/dx, \quad (5)$$

where  $S$  is the cross section of the liquid traversed by the flow of heat and  $K_l$  is the thermal conductivity of the liquid. The flow of momentum per unit of surface associated with the flow of heat will be

$$(1/Sv_l) dQ/dT = p_l = (K_l/v_l) dT/dx, \quad (6)$$

$v_l$  being the phase velocity of the waves (see, for instance, Ref. 31). Let us now consider a cylindrical particle of cross section  $\sigma$  and height  $h$ ,

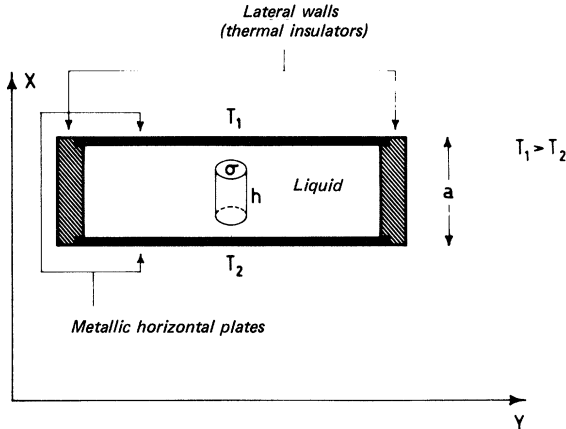


FIG. 1. Schematic drawing of a thermal diffusion cell. The thermal gradient is parallel to the  $X$  axis. A cylindrical particle of height  $h$  and cross section  $\sigma$  is suspended in the liquid.

suspended in the liquid as in Fig. 1. If  $K_p$  and  $v_p$  are the thermal conductivity and the velocity of the thermal waves in the material of which the particle is made, then

$$p_p = (K_p/v_p) dT/dx \tag{7}$$

will be the flow of momentum associated with the flow of heat in the particle. Now  $p_l$  and  $p_p$  both have the dimensions of a pressure, and the force exerted on the particle by the thermal energy flowing from the liquid into the particle through its upper surface  $\sigma$ , assuming that the downward direction of the  $x$  axis is positive, will therefore be

$$f' = \tau_{l,p}^2 (K_l/v_l - K_p/v_p) \sigma dT/dx = \frac{4\rho_l u_l \rho_p u_p}{(\rho_l u_l + \rho_p u_p)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \sigma \frac{dT}{dx}; \tag{8}$$

$\tau_{l,p}$  being the characteristic coefficient of transmission of elastic waves from the liquid surrounding the particle to the material of which the particle is made. This coefficient is, as usual, given by a combination of the acoustic impedances  $\rho u$  of the media,  $\rho$  being the density and  $u$  the group velocity of the waves in each medium, with the usual meaning of subscripts. At the lower surface of the particle, the force acting on the particle will be

$$f'' = -\tau_{p,l}^2 (K_p/v_p - K_l/v_l) \sigma dT/dx = \frac{4\rho_l u_l \rho_p u_p}{(\rho_l u_l + \rho_p u_p)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \sigma \frac{dT}{dx}; \tag{9}$$

the minus sign on the first expression arising from our convention on the orientation of the  $x$  axis, or, in other words,  $f''$  represents the reaction on the particle of the energy leaving it.

The total force exerted on the particle by the thermal energy flowing through it is therefore

$$F_1 = f' + f'' = \frac{8\rho_l u_l \rho_p u_p}{(\rho_l u_l + \rho_p u_p)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \sigma \frac{dT}{dx}, \tag{10}$$

and this force will be positive (i. e., directed downward) if

$$K_l/v_l > K_p/v_p$$

and negative (i. e., directed upward) if

$$K_l/v_l < K_p/v_p.$$

The first term, corresponding to  $\tau^2$ , will vary between 2 and 0, the highest value being obtained for  $\rho_l u_l = \rho_p u_p$  and the lowest for  $\rho_p u_p = 0$ ; that is, for a particle unable to transmit energy through itself. An empty box with thin rigid walls would be impervious to the flow of heat and the condition  $\rho_p u_p = 0$  would apply, so that the force  $F_1$  would vanish.

One is immediately led to inquire whether, in the case of such an "adiabatic" particle, there would be any effect produced by heat flowing in the surrounding liquid. An answer to this question would also lead to an evaluation of the effect on the "conductive" particle considered above of that amount of thermal energy which is reflected by its surfaces.

Both  $K_l$  and  $v_l$  in Eq. (6) are temperature-dependent quantities and furthermore, in more general conditions  $dT/dx$  may be temperature-dependent and position-dependent, too, if steady-state conditions are not established. In general, therefore, a net force  $F_2$  will act on the "adiabatic particle," such force being given by

$$F_2 = \left[ \left( \frac{K_l}{v_l} \frac{dT}{dx} \right)_{\text{sup}} - \left( \frac{K_l}{v_l} \frac{dT}{dx} \right)_{\text{inf}} \right] \sigma, \tag{11}$$

the subscripts sup and inf representing the values of the term  $(K_l/v_l) dT/dx$  at the upper and lower surfaces of the particle. For the case of the conductive particle this force will be

$$F_2 = \left[ \left( r_{l,p}^2 \frac{K_l}{v_l} \frac{dT}{dx} \right)_{\text{sup}} - \left( r_{l,p}^2 \frac{K_l}{v_l} \frac{dT}{dx} \right)_{\text{inf}} \right] \sigma = \left[ \left( \frac{(\rho_p u_p - \rho_l u_l)^2}{(\rho_p u_p + \rho_l u_l)^2} \frac{K_l}{v_l} \frac{dT}{dx} \right)_{\text{sup}} \right]$$

$$-\left[ \frac{(\rho_p u_p - \rho_l u_l)^2}{(\rho_p u_p + \rho_l u_l)^2} \frac{K_l}{v_l} \frac{dT}{dx} \right]_{\text{inf}} \sigma, \quad (12)$$

$$= cS \frac{(F_1 + F_2)D}{KT_{\text{av}}} + DS \frac{dc}{dx}. \quad (15)$$

and the total force  $F_T$  acting on the conductive particle will result from the sum of  $F_1 + F_2$ . As will be seen later, however, the force  $F_2$  is very often much smaller than  $F_1$  and can be neglected.

#### THERMAL DIFFUSION IN LIQUIDS AS A CONSEQUENCE OF RADIATION PRESSURE: THE CASE OF MACROMOLECULAR SOLUTIONS

Up till now we have not considered the size of the particles because, in principle, the above considerations can apply to particles of any size, both molecular and macroscopic.

However, let us now consider particles small enough not to sediment appreciably under the action of the earth's gravitational field (macromolecules or ultramicroscopic molecular aggregates). If originally they are uniformly distributed in the liquid contained in the thermodiffusion cell of Fig. 1, then as soon as the thermal gradient

$$dT/dx = (T_1 - T_2)/a$$

is established throughout the cell, the flow of heat will originate, as we have shown, forces like  $F_1$  and  $F_2$  acting on the particles, so that the latter will start drifting towards one of the two plates along the direction of the thermal gradient. This thermal sedimentation is counteracted by ordinary diffusion which tends to redistribute the particles uniformly in the liquid. The flow of matter caused by thermal diffusion across the section  $S$  of the cell will be

$$\left( \frac{dm}{dt} \right)_{\text{therm}} = cSv_x = cS \frac{F_T}{f} = cS \frac{(F_1 + F_2)D}{KT_{\text{av}}}, \quad (13)$$

where  $f$  is the friction coefficient of the particles,  $v_x$  is their drift velocity,  $c$  is the concentration ( $\text{g/cm}^3$ ),  $D$  is the ordinary diffusion coefficient,  $T_{\text{av}}$  is the mean of the temperature of the plates, and  $K$  is Boltzmann's constant. Because of ordinary diffusion the flow of matter in the opposite direction will be

$$\left( \frac{dm}{dt} \right)_{\text{diff}} = -DS \frac{\partial c}{\partial x} = -DS \frac{dc}{dx}, \quad (14)$$

so that the net flow of matter will be

$$\left( \frac{dm}{dt} \right)_{\text{total}} = \left( \frac{dm}{dt} \right)_{\text{therm}} - \left( \frac{dm}{dt} \right)_{\text{diff}}$$

At equilibrium

$$\int_0^a [(F_1 + F_2)/KT_{\text{av}}] dx = - \int_{c_i}^{c_s} dc/c, \quad (16)$$

where  $c_i$  and  $c_s$  are the equilibrium concentrations near the upper and lower plates, respectively. From (16) the following equation can be derived:

$$c_i/c_s = \exp[(F_1 + F_2)a/KT_{\text{av}}]. \quad (17)$$

Comparing this expression with the equivalent one arrived at by the phenomenological theory of thermal diffusion<sup>22</sup>:

$$c_i/c_s = \exp(s \Delta T), \quad (18)$$

where  $s$  is the Soret coefficient of the particles, and remembering our Eq. (10) for  $F_1$  and dropping the term  $F_2$  in the expression for  $F_T$  (since generally it is much smaller than  $F_1$ ) one obtains

$$s \Delta T = \left[ \frac{8\rho_l u_l \rho_p u_p}{(\rho_p u_p + \rho_l u_l)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \frac{\sigma}{KT_{\text{av}}} \right] \frac{dT}{dx} a$$

$$= \left[ \frac{8\rho_l u_l \rho_p u_p}{(\rho_p u_p + \rho_l u_l)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \frac{\sigma}{KT_{\text{av}}} \right] \Delta T. \quad (19)$$

It is easily seen that the term in square brackets in the second member has the dimensions of ( $^{\circ}\text{C}^{-1}$ ), precisely as the Soret coefficient ( $s$ ). Alternatively, since  $s$  is defined as the ratio of the thermal diffusion coefficient  $D'$  ( $\text{cm}^2/\text{sec}^{\circ}\text{C}$ ) to the ordinary diffusion coefficient  $D$  ( $\text{cm}^2/\text{sec}$ ), and remembering the relation between the friction and diffusion coefficients of the particles  $f$  and  $D$ , one can also write

$$D' = \frac{8\rho_l u_l \rho_p u_p}{(\rho_p u_p + \rho_l u_l)^2} \left( \frac{K_l}{v_l} - \frac{K_p}{v_p} \right) \frac{\sigma}{f}, \quad (20)$$

which gives the analytical expression of the thermal diffusion coefficient  $D'$  in terms of the force  $F_1$ . It is easy to write the expressions for  $s$  and  $D'$  in terms of the complete expression of the force  $F_T$  exerted by the flow of thermal energy on the particles.

One interesting feature of the expressions for  $s$  and  $D'$  [Eqs. (19) and (20)] is their proportionality to the cross section  $\sigma$  of the particles. If the particles are supposed to have a shape different from that of right cylinders, this feature would still be retained. Let us then take into consideration one consequence of this propor-

tionality of the Soret coefficient  $s$  to the cross section  $\sigma$  of the particles. Since the cross section

$$\sigma = Ar^2 = A(M/\rho)^{2/3},$$

where  $A$  is a proportionality constant,  $r$  is the "radius" or an equivalent dimension of the particles,  $\rho$  is the density of the material of the particles and  $M$  is the molecular mass, then it follows that

$$s = HM^{2/3}, \quad (21)$$

where  $H$  is another proportionality constant dependent from the geometry and density of the particles. This last expression (21) can easily be checked by doing a series of experiments of thermodiffusion with particles of a polymer of progressively increasing molecular weight. We remember here that dependence of thermal diffusion on the mass of the particles cannot be predicted by the phenomenological theories of thermal diffusion, mass being not even a parameter in them.

The only existing published data on the values of Soret coefficients obtained in thermal diffusion with polymer substances in an apparatus of the kind schematically represented in Fig. 1 are those of Emery and Drickamer<sup>33</sup> and they are in very good agreement with the theoretical predictions of Eq. (21). In Fig. 2 it can be seen how the data for polystyrene molecules of five molecular weights ranging from 10 000 to 338 000 in toluene fit the theoretical curve. Other data on the behavior of macromolecular substances in thermal diffusion experiments are those of Debye and Bueche<sup>34</sup> and Langhammer,<sup>35-38</sup> who all used the thermogravitational method. Comparison of the data of these authors with our theory is complicated by the very strong concentration dependence of the Soret coefficient and the difference in the apparatus employed: the results of Debye and Bueche and Langhammer, however, fit our theories closely enough. The only other existing data on the behavior of macromolecular substances in a thermogravitational column are those recently obtained by Gaeta and Cursio,<sup>39</sup> where the results obtained with the two kinds of ribosomal particles [the only results suitable for comparison with (21)] also fit the theory.

Equation (19) has another interesting feature: The value of the Soret coefficient  $s$  can be positive or negative depending on the sign of the term  $(K_l/v_l - K_p/v_p)$ . This means that macromolecular materials can be expected to migrate either towards the hot or the cold wall depending on the relative values of the thermal conductivities and the speed of sound in the material of the

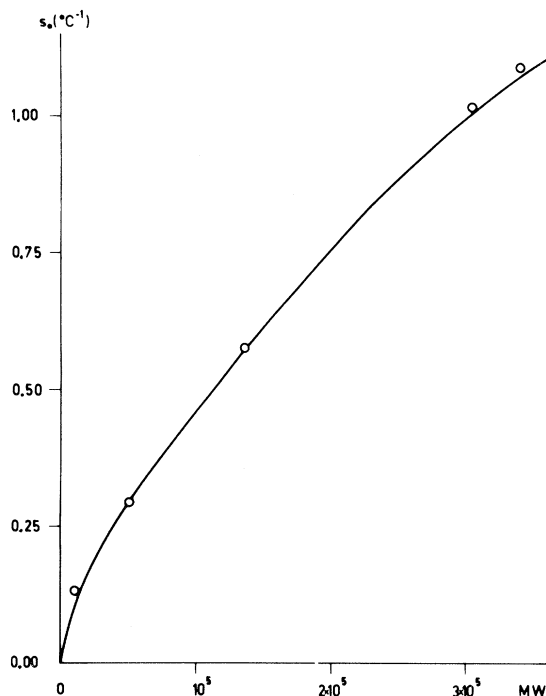


FIG. 2. Experimental values of Soret's coefficient for various cuts of polystyrene molecules, obtained by Emery and Drickamer<sup>33</sup> (the five points being represented by circles). The curve drawn as a full line represents the function  $s = HM^{2/3}$  proposed by us; the value of  $H$  has been obtained by fitting the expression to the third experimental point. A better fit could be obtained by deriving the parameter  $H$  from the curve of the family which could best be superimposed to all five experimental points.

particles and the surrounding liquid. This is a fundamental feature of the theory, in contrast to all other theoretical predictions based on kinetic models, and is a point open to an unambiguous experimental check.

It is difficult to compare the numerical values of Soret coefficients calculated from (19) and experimental values because of lack of data on thermal conductivities and velocity of sound in macromolecular materials, and because of complications arising from the solvation of the particles. A crude estimate from the few available data for bulk materials shows that expression (19) yields the right order of magnitude for  $s$  and that the contribution of the force  $F_2$  [Eq. (12)] is negligible.

#### EXTENSION OF THE THEORY TO SOLUTIONS OF SMALL MOLECULES AND IONS

In the preceding paragraph we have dealt with the special case of relatively large particles contained in a liquid made up of much smaller mole-

cules. The reasons for this will become evident when treating the case of solutions of small molecular-weight solutes, which we shall now briefly discuss.

No mention has previously been made of the relationship between the wavelength of elastic thermal waves and the dimensions of the particles. This is an important point, inasmuch as all our preceding considerations implicitly assume that the particles have diametral dimensions greater than the wavelength of the elastic waves interacting with them. Because of the distribution of energy in a Debye spectrum of thermal waves, most of the energy is concentrated in the highest frequency range (in water, for instance, in the  $10^{11}$ – $10^{12}$  Hz region, corresponding to wavelengths ranging from the order of 100 Å down to perhaps 3 or 4 Å). This means that macromolecules having molecular weights of  $10^5$ – $10^7$  can be considered already "large particles" in terms of their diametral dimensions relative to the wavelengths of the greatest part of the thermal energy. These considerations justify our simple radiation-pressure theory of thermal diffusion of macromolecules in liquid solutions, and indeed this was the idea which induced us to perform experiments<sup>39</sup> with such complex materials.

The same physical mechanism must underlie the thermodiffusion of small molecules and ions in liquid solutions, but the difficulties met with when one tries to extend the theory to this case are of two kinds: the lack of a sufficient knowledge of the distribution of thermal waves in the high-energy region of the spectrum, and the need for a more detailed description of the interactions of the thermal waves with the particles.

However, the general features of the behavior of small dissolved molecules and ions in thermal diffusion in liquids is readily explainable on the basis of the radiation pressure theory. For instance, the very peculiar behavior of the benzene-*n*-heptane system studied by Bierlein *et al.*<sup>40</sup> and not explained until now, is readily understandable on the basis of the radiation pressure theory. Indeed the values of the  $K/v$  ratios of the two compounds and their temperature and composition dependence in the solution are such that an inversion point in the thermodiffusive behavior is readily predictable, just as was found by the authors of the paper quoted. The same can be said concerning the various other liquid mixtures which exhibit inversion of the sense of migration of the components when the composition of the mixture varies beyond a certain point (for instance, water-acetone solutions, etc.).

One extreme but instructive case is that of ions in superfluid liquid He<sup>4</sup>. As is well known, this system was used by Careri and his co-workers to study superfluidity. The "heat flush" ex-

periment,<sup>41</sup> in which a stream of thermal excitations interact with ions generated in the liquid by irradiation, can be considered as an example of thermal diffusion, showing that both the phononic (or longitudinal acoustic wave component) and the rotonic (or quantized vortex component) of the thermal excitations interact with the ions in the liquid. More detailed information on the interactions between the "gas" of thermal excitations and the ions was obtained by studying the ionic recombination in superfluid liquid He<sup>4</sup> at various temperatures.<sup>42,43</sup> This showed that the ions are pushed around in the liquid (this time in a state of thermal equilibrium) in a kind of Brownian motion, by collisions with the phononic and rotonic excitations existing in superfluid helium. These results demonstrate that a more refined theory of thermal diffusion can be formulated on the basis of the ideas expressed above.

#### CONCLUSIONS

A simple radiation-pressure theory of thermal diffusion in liquids provides a plausible physical explanation of this puzzling phenomenon. In the case of macromolecules or supermolecular particles, the conclusions reached by the radiation pressure theory are qualitatively, and – in the few cases in which the parameters entering in the formulas are known – even quantitatively, satisfactory.

Some predictions made by the theory are not unexpected and are confirmed by the existing data (i. e., the molecular weight dependence of Soret coefficients in solutions of high polymers); some are completely unexpected and are now being actively studied in this Laboratory. The inversion of the direction of migration of macromolecules in the thermal gradient has already been proved to have taken place in at least one case in the conditions predicted by the theory.<sup>44</sup>

In order to proceed further, a more refined theory and new data on thermal conductivities and the velocity of sound in various materials (together with the temperature-dependence of these parameters) are needed, as well as an extension of the study of the spectrum of thermal excitations in liquids by means of Brillouin effect. We hope to be able to develop such a theory before long, and to furnish further evidence on the validity of the line of thought presented here.

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