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Phonons in liquids, Onsager's reciprocal relations, and the heats of transport

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We continue the study of liquids considered as composed by two interacting subsystems: a population of particles, weakly bound to the sites of a disordered lattice, and a "gas" of phonons. The interactions among the material particles and the wave packets are mediated by "thermal radiation forces," a special class of inertial effects. When the liquid system is a solution, the application of a temperature or a concentration gradient breaks the symmetry of one of the two subsystems, producing an excess of phonon-solute collisions and performing work on the particles, at the expense of the thermal energy of the wave packets. The heats of transport of thermal diffusion, isothermal diffusion, and Soret equilibrium may be statistically calculated from the energy balance of these collisions. The expressions arrived at by this approach are coincident with the ones obtained by nonequilibrium thermodynamics, although for our derivation Onsager reciprocal relations are not required. It is also argued that, within the frame of the phonon theory, transport processes in liquids may be treated in general by means of the classical Boltzmann transport equation, applied to phonon-particle interactions rather than to particle-particle collisions.

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I. INTRODUCTION

Should a liquid be considered as a condensed gas or a molten solid? On one hand, it is a system of particles subject to random motions hindered by the close proximity of nearby neighbors, as a dense gas. On the other hand, the average distances among particles in liquids are practically the same as in solids, and therefore the force field in which they move also has the same average intensity, imposing similar constraints to their individual motions. Therefore translational thermal motions in condensed fluids are collective oscillatory modes (phonons), propagating with the velocity of sound.

The existence of phonons in liquids was first proposed by Debye in 1912 [1]. Subsequently fundamental studies on various aspects of the problem were contributed by Brillouin [2,3], among others. It was shown that thermodynamic equilibrium properties could be accounted for in terms of the phonon theory. However, no way could be devised to deal with nonequilibrium thermodynamic properties within this frame, not even rather simple transport phenomena such as diffusive and osmotic flow, which are easily interpreted in terms of the gas-kinetic approach. The difficulty resided at a fundamental level, consisting in the lack of a mechanism by which phonons could exchange momentum with material particles. Phonons indeed were considered only to reversibly transfer oscillatory energy, without developing forces on material particles. Therefore there was no ground for a phonon theory of matter transport in the condensed phases and consequently processes such as diffusion and heat transport could only be treated by means of Fick and Fourier equations, using the continuum properties.

But is it conceivable that phonons carry and eventually exchange momentum with material particles? The expression generally used to calculate the momentum carried by electromagnetic waves cannot be applied to phonons. Indeed the relation

$$p=\left[\frac{h\nu}{c}\right]_{\text{e.m.}} \tag{1}$$

derives from the notion that the velocity of light is the maximum velocity of transmission of energy-carrying signals. Obviously the velocity of sound is not maximal in the same sense, and no equivalent of Eq. (1) can be obtained on the grounds of an analogy with the photon. The notion of momentum carried by electromagnetic waves, however, was developed independently from relativistic arguments, on the basis of Maxwell's equations, and similar arguments may be used in the case of phonons.

The existence of radiation pressure due to elastic waves was demonstrated by Rayleigh [4,5] at the beginning of the century. Many authors have investigated the problem [6–12]. The coupling between momentum and acoustic energy fluxes was mentioned by Borgnis [8] and by Johansen [10].

We have dealt with the problem of the coupling of fluxes of thermal energy and momentum [13] and subsequently proposed a mechanism of mutual exchange of energy and momentum among individual phonons and material particles in liquids [14].

The arguments used until now in relation to the problem of radiation pressure and momentum transport connected with the propagation of elastic waves and of thermal energy in liquids have never been reviewed in a systematic way. It is useful to recall some relevant points, for a clearer understanding of the following.

(1) When an acoustic beam propagates across the boundary between two adjoining media, the energy densities E_1 and E_2 are different and a pressure difference $\Delta P = E_1 - E_2$ appears across the boundary [4,5].

(2) In a harmonic perturbation the averages of the amplitudes of oscillation ξ and those of their time derivatives $\dot{\xi}$ vanish, while the averages of the squares ξ^2 and $\dot{\xi}^2$ do not. Thus in wave propagation there is transport of energy but not of momentum [15]. Whenever the properties of the medium change along the path of the perturbation the harmonic character is disturbed and the effect of the anharmonic terms that appear is that of making the averages of ξ and $\dot{\xi}$ nonvanishing. Momentum transport therefore couples with transport of energy and radiation pressure effects appear [15]. A temperature or a concentration gradient may thus lead to anharmonicity and to momentum transport coupled with wave propagation.

(3) It is also possible to derive the principle of inertia of acoustic energy directly from Euler's equations, if attention is paid to the second-order terms of acoustics [16].

(4) The extension of these notions to heat flux has been proposed on the basis of a physical argument [17], and also derived from the principles of statistical mechanics [13]. Compelling evidence has been found on the existence of phonons in dense fluids [18–23], heat flow consisting in the diffusion of high-frequency wave packets along the temperature gradient. This gradient constitutes the driving force for phonon drift and, at the same time, it also creates conditions for anharmonicity along the path of the heat flux, owing to thermal expansion of the liquid. Anharmonicity induces the coupling of energy and momentum flow, as in the case of acoustic waves, giving rise to a gradient of radiation pressure parallel to the temperature gradient. In the case of heat flow two approaches were used that led to coincident analytical expressions for either momentum flux and radiation pressure due to the nonisothermal state of the liquid. One consisted in an extension of the Boltzmann-Ehrenfest theorem, the other in the analysis, by the methods of continuous-field hydrodynamics, of the changes of momentum flux across the boundary between adjoining media having different constitutive properties. Supporting experimental evidence is available and has been critically discussed [13].

(5) The macroscopic formulation of the theory of thermal radiation forces holds that when a surface S in a nonisothermal liquid is crossed by a heat flux J_q it is also crossed by a flux of momentum $J_p = J_q/u = -(K/u)(dT/dr)$ where K and u are thermal conductivity and sound velocity and (dT/dr) is the temperature gradient normal to S. If S is a physical boundary, across which the constitutive properties of the medium change, then a thermal radiation force $\mathbf{f}^{\mathrm{th}}$ develops on S, given by [13]

$$f^{\mathrm{th}} = SH^* \left[\left| \frac{K}{u} \frac{dT}{dr} \right|_{trans} - \left| \frac{K}{u} \frac{dT}{dr} \right|_{cis} \right] , \tag{2}$$

having indicated by (*cis*) the medium lying in front of S and by (*trans*) the medium beyond S. The sense of $\mathbf{f}^{\mathrm{th}}$ is such that the media on the two sides of S are pressed one against the other, or pulled apart, depending on whether the "*trans*" medium has a higher, or respectively, lower $H^*(K/u)$ than the other. The constant H^* is a numerical proportionality factor dependent on the acoustical impedances of the "*cis*" and "*trans*" media.

(6) This macroscopic formulation has been subsequently extended by us to the microscopic level, i.e., to individual phonon-particle interactions in the fluid [14]. These interactions occur also in an isothermal fluid, in the course of the propagation of the wave packets ceaselessly moving with the velocity of sound. A phonon, sweeping through a portion of the liquid having properties different from its surroundings, may exchange energy and momentum with an "obstacle." For such an exchange to occur, however, some conditions must be fulfilled, the most obvious being relative to the dimensions of the obstacle. When its diameter is smaller than the phonon's wavelength, the interaction probability decreases, as also occurs in the case of electromagnetic waves.

From this microscopic point of view S must be substituted by the phonon-particle cross section σ_p^{ph}, accounting for the dimensions of the particle and also for the probability that the wave packet interacts with the obstacle. Accordingly, the temperature gradient is the one due to the local fluctuation generated by the propagating phonon [14].

A large solute particle suspended in a liquid may receive energy and momentum from a phonon, or may transfer these quantities to the phonon, through the processes schematically represented in Fig. 1. A small solute molecule or a solvated ion may also undergo the same collisional events, but with a smaller *a priori* probability.

On the basis of this model, we have recently proposed a unified theory of thermomechanical and mechanothermal effects in liquid solutions [13,14], based on the consideration of the conservation of momentum in the collisional events mediated by thermal radiation forces. To complete the description, the energy balance of events of types 1(a) and 1(b) [shown, respectively, in Figs. 1(a) and 1(b)] should now enter into the analysis of diffusive phenomena in isothermal and nonisothermal liquids.

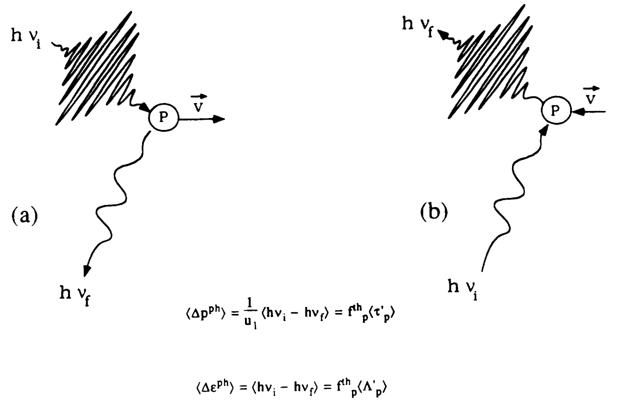

FIG. 1. The event represented in (a), in which an energetic phonon transfers energy and momentum to a particle, is commuted upon time reversal into the one represented in (b) where a particle transfers energy and momentum to a phonon. The particle of mass m_p changes velocity, and the phonon is frequency shifted by the amount $(\nu_i - \nu_f)$. Commuting (t) into $(-t)$ either of the two processes is transformed into the opposite one.

II. DIFFUSION AND THERMAL DIFFUSION IN A SYSTEM OF PHONONS AND MATERIAL PARTICLES

We will consider the energy exchanges among phonons and particles, by which vibrational energy of the wave packets is commuted into particle motion and vice versa.

In an event of type 1(a), an impinging phonon develops a thermal radiation force f_p^{th} on a material particle. The expression of f_p^{th}, defined in [14], represents a special case of Eq. (2), applied to a molecule or ion (p), suspended in a liquid (l). We consider the phonon as a wave packet, so that it is necessary to specify the time interval $\langle \tau'_p \rangle$ taken by the phonon-particle interaction. During it, momentum $\langle \Delta p^{\text{ph}} \rangle = f_p^{\text{th}} \langle \tau'_p \rangle$ is transmitted to the particle, which is displaced along a distance $\langle \Lambda'_p \rangle$. The energy exchanged, $\langle \Delta \varepsilon^{\text{ph}} \rangle = h \langle \nu_i - \nu_f \rangle = f_p^{\text{th}} \langle \Lambda'_p \rangle$, is eventually dissipated against resistance to particle motion in the liquid. The total duration of the process is $\langle \tau_p \rangle$, during which the particle travels along a total length $\langle \Lambda_p \rangle$ (see Appendix).

In an event of type 1(b) a material particle exerts a force f_p^{th} on a phonon, transferring momentum and energy to the latter. The phonon is then shifted to a higher frequency, the whole process being the opposite of the one of type 1(a), from which, on the other hand, it becomes indistinguishable upon time reversal.

In an isothermal liquid the phonons move at random, their wave vectors being isotropically oriented in space. The total content of thermal energy per unit of volume of the liquid is [14]

$$q_l^{\text{ph}} = m^* \rho_l (C_V)_l T \ , \tag{3}$$

ρ_l and $\langle C_V \rangle_l$ being density and specific heat at constant volume, and m^* a constant, dependent on the nature of the liquid, given by

$$m^* = m \frac{\int_0^{\Theta/T} \rho_l (C_V)_l dT}{\rho_l (C_V)_l T} = m f[\Theta/T] \ , \tag{4}$$

where Θ is the Debye temperature of the substance and m represents the fraction of the total heat content corresponding to collective oscillatory molecular motions; $f[\Theta/T]$ may be shown to range from 0.2 at $T \ll \Theta$, to 1 at $T \gg \Theta$ [24,25].

The phonons "collide" with regions of the medium where the intermolecular potential is altered, i.e., at the boundary between two different substances or on a solvated solute particle, or also at the limit between two differently structured local domains in the liquid. Each phonon propagates along an average distance $\langle \Lambda_l \rangle$, during a time interval $\langle \tau^0 \rangle$, at the end of which it interacts with an obstacle, exchanging with it energy and momentum.

During free flight the wave packets may be considered as local heat currents flowing through a section σ^{ph}, that should be possible to determine on a phenomenological basis. Phonon diffusivity causes the displacement in the isothermal liquid of equal numbers of wave packets per unit of time in each sense, across an arbitrarily oriented surface S of unit area. From Eq. (3) it is possible to define the intensity of each of the two opposite diffusive heat fluxes across S:

$$\langle J_q^{\text{ph}} \rangle = \frac{q_l^{\text{ph}}}{6} \frac{\langle \Lambda_l \rangle}{\langle \tau^0 \rangle} = -K_l \left\langle \frac{\delta T}{\delta r} \right\rangle \ , \tag{5}$$

$\langle \delta T / \delta r \rangle$ being the "virtual" local temperature gradient, normal to S, that, applied across a distance $\langle \Lambda_l \rangle$ to the liquid of thermal conductivity K_l, would produce the heat flux $\langle J_q^{\text{ph}} \rangle$. This heat flux $\langle J_q^{\text{ph}} \rangle$ results from $N^{\text{ph}}/6$ individual phonons flowing through S in either sense per second, each being a local heat current $\langle j_q^{\text{ph}} \rangle$ lasting a short time $\langle \tau^0 \rangle$ and flowing through a small fraction σ^{ph} of S.

If according to Onsager [26] we assume that the kinetic and thermodynamic approaches must exactly agree in the mean, we may use the macroscopic value of K_l also when dealing with local heat fluxes due to propagation of individual phonons between two successive interactions. Therefore each elementary heat current produces a temperature gradient of the same average intensity $\langle \delta T / \delta r \rangle$ through a small part of S, and during a short time interval $\langle \tau^0 \rangle$.

The local heat currents generate forces on the obstacles with which they interact at the end of the phonon free paths. Observable effects of these microscopic, random events appear in the form of mass fluxes, when an anisotropy is introduced in a liquid solution by applying to it a concentration or a temperature gradient [13,14].

We will now explore the aspects of energy exchanges among phonons and solute particles in dilute solutions. The considerations developed in the following may be applied to very dilute ionic, molecular, and macromolecular solutions, since only in this case may the values of $\langle \Lambda_l \rangle$, $\langle \tau^0 \rangle$, and $\langle \delta T / \delta r \rangle$ be assumed practically coincident with those of the pure solvent, independently calculated [14]. The amount of energy lost by an impinging phonon,

$\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$, is subsequently dissipated through various mechanisms, which will be considered in detail later on.

When a temperature gradient is applied, for instance along z, the solute thermodiffusive drift velocity is $\langle v_d^{\mathrm{th}} \rangle = D_p^{\mathrm{th}} dT/dz$. Let $\langle \nu_p \rangle$ be the number of collisions per second with phonons experienced by a solute particle at $T \equiv T_0$ in the isothermal liquid. In the presence of a temperature gradient the particle shall experience $\langle \nu_p \rangle /6 + \langle d\nu_p \rangle$ interactions with wave packets coming from $+z$, and $\langle \nu_p \rangle /6 - \langle d\nu_p \rangle$ from the opposite sense, so that the total number of collisions per second and per particle, within the linear range, remains the same as in the isothermal condition. It may be assumed that, as long as linear conditions are fulfilled,

$$6\frac{\langle d\nu_p \rangle}{\langle \nu_p \rangle} = \frac{dT/dz}{\langle \delta T/\delta z \rangle} \ . \tag{6}$$

The rationale of Eq. (6) is that macroscopic and microscopic heat conduction obey the same phenomenological relations, with identical coefficients. Accordingly, a temperature gradient dT/dz is expected to generate a flux of phonons that is the fraction $dT/dz/\langle \delta T/\delta z \rangle$ of the one corresponding to the local, microscopic heat currents $\langle j_q^{\mathrm{ph}} \rangle$ owing to phonon diffusivity. Equation (6) thus gives the ratio of the number of phonons per second sweeping past a solute particle owing to the applied gradient to the one due to the random motions of collective thermal excitations.

Solute particles therefore will experience $2\langle d\nu_p \rangle$ collisions in excess in one of the two senses and execute as many jumps per second of average length $\langle \Lambda_p \rangle$ in excess in the same sense. The average drift velocity (thermodiffusive drift) along z will be

$$\langle v_d^{\mathrm{th}} \rangle = D_p^{\mathrm{th}} \frac{dT}{dz} = 2\langle d\nu_p \rangle \langle \Lambda_p \rangle = \frac{\langle \Lambda_p \rangle \langle \nu_p \rangle}{3} \frac{dT/dz}{\langle \delta T/\delta z \rangle} \ , \tag{7}$$

after introducing the value of $\langle d\nu_p \rangle$ deduced from Eq. (6). The coefficient of thermal diffusion D_p^{th} may thus be expressed as

$$D_p^{\mathrm{th}} = \frac{\langle \Lambda_p \rangle \langle \nu_p \rangle}{3\langle \delta T/\delta z \rangle} \tag{8}$$

in terms of microscopic parameters only.

We now consider instead a dilute, isothermal solution, in which a concentration gradient has been established. Where solute concentration is higher, there will be more phonon-solute collisions per unit of time, and the opposite occurs where the concentration is lower. If dC/dz is the concentration gradient, the excess of collisions per unit of time, in the unit of volume within two layers normal to z, spaced $\langle \Lambda_p \rangle$ one from the other, shall be given by the change in the number density of particles along z over a distance $\langle \Lambda_p \rangle$, i.e., $(dn/dz)\langle \Lambda_p \rangle$, multiplied by $\langle \nu_p \rangle /6$, the frequency of phonon-particle collisions. Diffusive flow J_p^D results from the excess of collisions in the sense of dC/dz. The extra number of these collisions per second and per unit of volume is $(\langle \nu_p \rangle /6)(dn/dz)\langle \Lambda_p \rangle$. From this quantity the average rate of solute motion may be easily obtained. Indeed, since $nm_p = C$, from the usual definition of the diffusion coefficient D_p one has

$$J_p^D = D_p \frac{dC}{dz} \equiv D_p m_p \frac{dn}{dz} = \frac{\langle \Lambda_p \rangle^2 \langle \nu_p \rangle}{6} m_p \frac{dn}{dz} \ , \tag{9}$$

which gives D_p in terms of $\langle \Lambda_p \rangle$ and $\langle \nu_p \rangle$ as $D_p = \langle \Lambda_p \rangle^2 \langle \nu_p \rangle /6$.

On the other hand, in very dilute solutions the density of the gas of phonons and its dynamics should be the same as those of the pure solvent at the same temperature. Therefore the value of $\langle \delta T/\delta z \rangle$ to be introduced in Eq. (8) can be approximated by the expression derived for the pure solvent [14]:

$$\left\langle \frac{\delta T}{\delta z} \right\rangle = \left\{ \frac{m u_l^g}{6K_l \rho_l (C_p)_l \langle \Lambda_l \rangle} \right\}^{1/2} \int_0^{\Theta/T} \rho_l (C_V)_l \, dT \ , \tag{10}$$

where the suffix (l) stands for solvent. Values of the phonon mean free paths, given as $m\langle \Lambda_l \rangle$, and of the local temperature gradients, as $\langle \delta T/\delta z \rangle /m^*$, in some pure liquids, are plotted against temperature in Figs. 2 and 3. In water, m and m^* may be evaluated with sufficient approximation (see Appendix of Ref. [14]) and we get $\langle \Lambda_l \rangle \cong 16 \times 10^{-8}$ cm at room temperature. In the liquids included in Figs. 2 and 3, neither m nor m^* should be very different from those relative to water, and so $\langle \Lambda_l \rangle$ in each case is going to be of the order of 10^{-7} cm. Of course, much shorter mean free paths would be difficult to reconcile with the very concept of a phonon, while much longer paths would imply very infrequent phonon-particle collisions and therefore negligible consequences of the exchanges of energy and momentum.

The local temperature gradients may seem surprisingly high. However, the products $(m/m^*)\langle \Lambda_l \rangle \langle \delta T/\delta z \rangle = (m/m^*)\langle \Delta T \rangle$ are of the order of 300 K, as can be easily verified, and increase linearly with absolute temperature. Therefore, in the explored temperature range, and for the various cases, the percent temperature variation turns out to be in the range $0.3 \leq (\Delta T/T) \leq 0.5$; this means that the local temperature fluctuations amount to one-half or one-third of the absolute temperature, as expected.

It is now possible to proceed further with the determination of the values of the microscopic parameters of the phonon theory of liquids. Equations (8) and (9), indeed, give D_p^{th} and D_p as functions of $\langle \Lambda_p \rangle$, $\langle \nu_p \rangle$, and $\langle \delta T/\delta z \rangle$. Assuming for this last quantity in dilute solutions a value practically coincident with the one of the pure solvent, and when suitable experimental values are available for both D_p^{th} and D_p, it is possible to calculate the respective $\langle \Lambda_p \rangle$ and $\langle \nu_p \rangle$.

There is, however, a difficulty concerning Eq. (8), since in its derivation the effects of thermal radiation pressure on the dispersing phase have not been accounted for. The collisions with the solvent of phonons drifting down the temperature gradient lead to transfer of energy and momentum also to the dispersing phase, so that thermal radiation forces will act (in the same sense) on solute and on solvent. Depending on the condition $[(K/u)_l - (K/u)_p] \gtrless 0$ the solute shall be observed to migrate in the sense of heat flux or against it. This has been experimentally demonstrated to occur both with macroscopic and with microscopic objects suspended in a nonisothermal liquid [13]. Cases where in concentrated solutions thermal diffusion vanishes have also been experimentally studied [27,28]. We attributed this behavior to modifications induced by the solute in the dispersing phase that lead to the condition $(K/u)_l \equiv (K/u)_p$. Equation (8) is unable to justify a vanishingly small coefficient of thermal diffusion, owing to the fact that the effect of drifting phonons on the solvent has not been included in its derivation. The consequence is that the experimental values of D_p^{th} introduced in Eq. (8) will give $\langle \Lambda_p \rangle$'s and $\langle \nu_p \rangle$'s smaller than the true ones, except at extreme dilution. In dilute solutions the error is probably small, and the right order of magnitude may be obtained for either $\langle \nu_p \rangle$ or $\langle \Lambda_p \rangle$. The problem of the radiation pressure developed by phonons on the dispersing phase will be treated elsewhere. Some values of $\langle \nu_p \rangle$ and of $\langle \Lambda_p \rangle$ are given in Table I, calculated from Eqs. (8) and (9) and from some of the best experimental values of D_p^{th} and D_p found in the literature for dilute ionic solutions. Reliable measurements of thermodiffusive coefficients in very dilute solutions are quite scarce. Even less common are cases in which groups of values of D_p^{th} and D_p are avail-

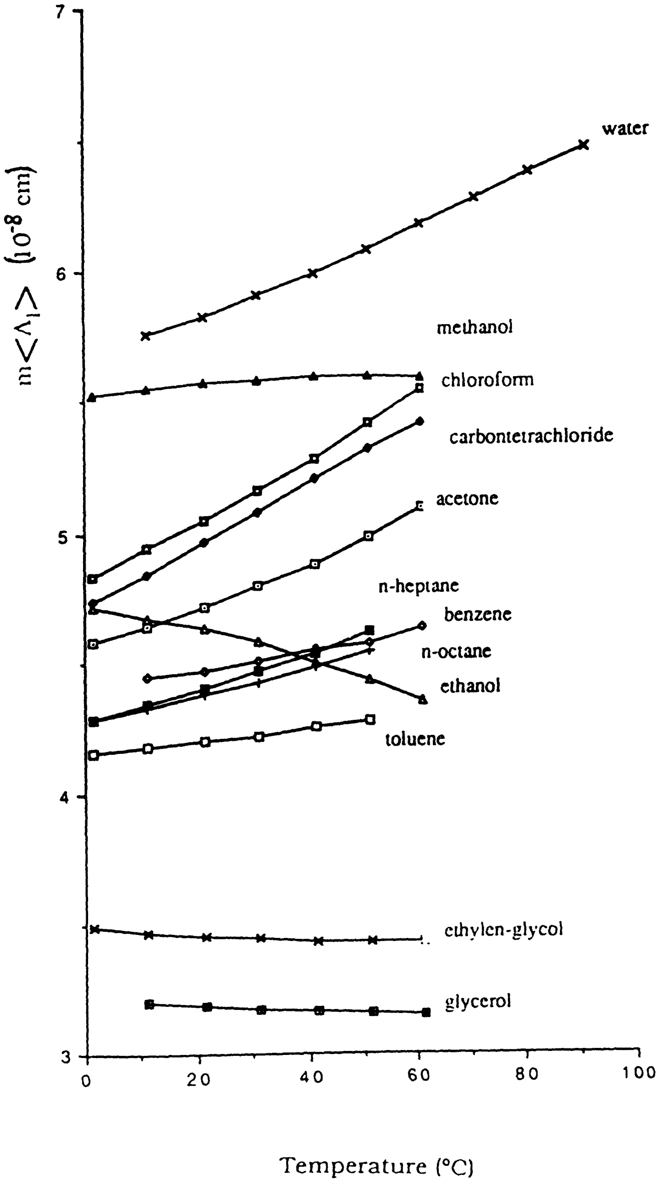

FIG. 2. Plot of the product $m\langle\Lambda_l\rangle$ against temperature for some liquids, calculated from the expression $m\langle\Lambda_l\rangle = 6K_l/\rho_l(C_p)_l u_l^2$, discussed in Ref. [14]. In water, the ratio m of translational to total number of degrees of freedom may be evaluated, decreasing from 0.42 to 0.37 in the range 4–90 °C. Accordingly, for H_2O $\langle\Lambda_l\rangle$ turns out to be about 16×10^{-8} cm at room temperature.

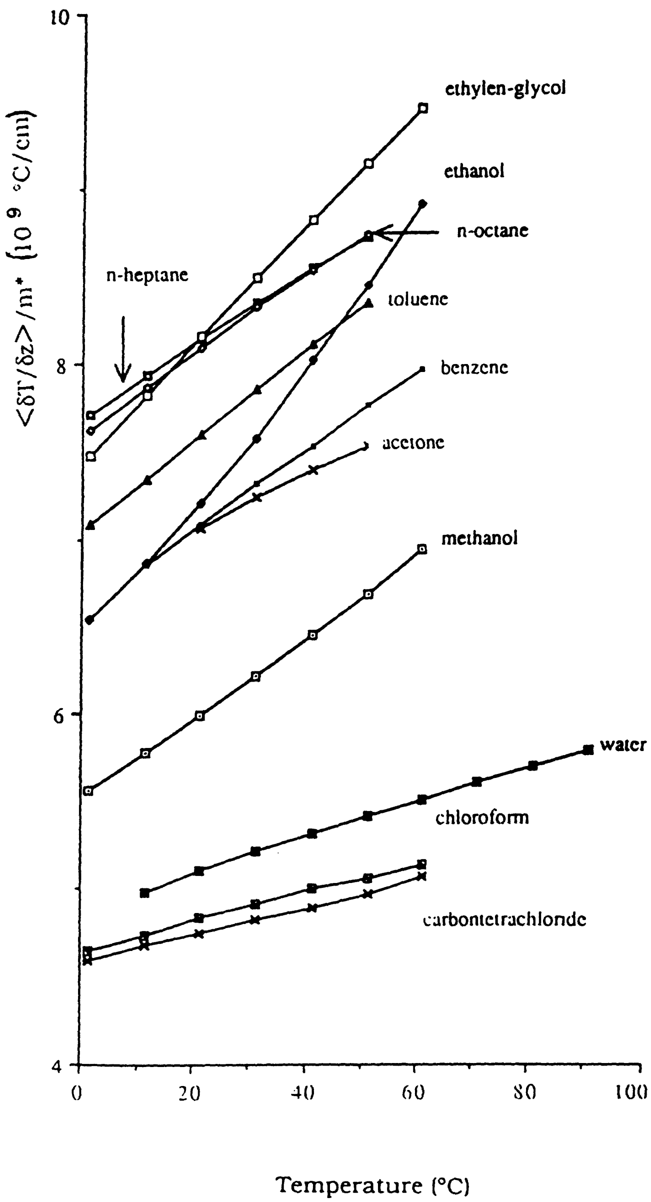

FIG. 3. Plot of the values of the local temperature gradients, divided by m^*, calculated from Eq. (10) for the same liquids of Fig. 2 (with the exception of glycerol, owing to the lack of some data). In the case of water, where m^* may be independently calculated, one gets $\langle \delta T/dz\rangle \cong 9.3\times10^8$ °C/cm at room temperature.

TABLE I. Values of $\langle \Lambda_p \rangle$ and $\langle \nu_p \rangle$ at 25 °C in some electrolytic 0.01*M* aqueous solutions, calculated by means of Eqs. (8) and (9), from literature data for D_p and D_p^{th} [29–31].

Solute	$10^5 D_p$ ($\text{cm}^2\,\text{s}^{-1}$)	$10^8 D_p^{\text{th}}$ ($\text{cm}^2\,\text{s}^{-1}\,{}^\circ\text{C}^{-1}$)	$10^7 \langle \Lambda_p \rangle$ (cm)	$10^{-7} \langle \nu_p \rangle$ (s^{-1})
NaF	1.345	5.044	5.73	25.00
NaCl	1.545	2.518	13.19	5.30
NaBr	1.562	2.734	12.29	6.20
NaI	1.552	0.714	46.74	0.43
NaCl	1.545	2.518	13.19	5.30
KCl	1.914	2.182	18.86	3.20
RbCl	1.971	4.119	10.29	11.00
CsCl	1.954	4.514	9.31	14.00
LiF	1.164	1.804	13.87	3.60
NaF	1.345	5.044	5.73	25.00
KF	1.614	5.246	6.62	22.00
$AgNO_3$	1.69	5.577	6.52	24.00
$CdSO_4$	0.62	4.594	2.90	44.00
K_2SO_4[a]	1.35	7.601	3.82	55.00

[a] $C = 0.045M$.

able for the same solutions.

In Table I some data relative to dilute aqueous solutions of electrolytes were used [29–31]. Unfortunately these solutions cannot be considered sufficiently dilute for our purposes since it is known that diffusion coefficients are concentration dependent between 0.01*M* and 0.001*M* and also thermodiffusive coefficients generally evidence concentration dependence. In the frame of the phonon theory this shows that in electrolytic solutions the local instantaneous temperature gradients cannot be assumed to be the same as those of the pure solvent, even in centimolal mixtures. Accordingly, our tabulated values of $\langle \nu_p \rangle$ and $\langle \Lambda_p \rangle$ are indicative only of the respective orders of magnitude. In Table II $\langle \nu_p \rangle$ and $\langle \Lambda_p \rangle$ have been calculated for very dilute aqueous solutions of polyvinylpyrrolidone of various molecular weights [32]. It may be seen that in these solutions the mean free paths decrease and the number of phonon-particle collisions increase with molecular mass, as is to be expected.

III. ENERGY BALANCE AND HEAT OF TRANSPORT IN A SYSTEM OF INTERACTING PHONONS AND PARTICLES

We want now to investigate more closely the amount of energy exchanged on the average by an impinging phonon, in dependence on both the characteristics of the gas of thermal excitations and of the properties of the obstacle. During an interaction work will be done by thermal radiation forces. The resulting energy exchange, from the point of view of the phonon, is a frequency shift given by

$$\langle \Delta\varepsilon^{\text{ph}} \rangle = h \langle \nu_i - \nu_f \rangle = \kappa h \nu_D = \kappa \frac{h}{2} \frac{u_1^\phi}{a_l} , \tag{11}$$

where ν_D, u_l^ϕ, and a_l are, respectively, the limit Debye frequency, the phase propagation velocity of high-frequency elastic waves in the liquid, and nearest-neighbor distance in the solvent, and κ is a number smaller than 1 (in a Debye spectrum $\kappa = 2^{-1/3}$).

We consider a surface σ lying in the (x,y) plane in a homogeneous liquid medium, subject to a temperature gradient dT/dz applied along z. In this condition, during Δt seconds an amount ΔQ^{ph} of thermal energy carried by phonons is transported across σ. We distinguish between the total heat transport and the fraction carried by phonons, since some propagation of molecular rotations and intramolecular vibrations from one molecule directly to the next also occurs without transformation in translational modes.

The phonons are involved in elastic and anelastic collisions with the lattice that occur wherever the intermolecular harmonic potential is disturbed. Therefore it

TABLE II. Values of $\langle \Lambda_p \rangle$ and $\langle \nu_p \rangle$ for various molecular "cuts" of polyvinylpyrrolidone in aqueous solutions, calculated as in Table I, employing data for D_p and D_p^{th} from Ref. [32].

Polyvinylpyrrolidone molecular weight (amu)	Concentration (molal)	D_p ($\text{cm}^2\,\text{s}^{-1}$)	D_p^{th} (10^{-9} $\text{cm}^2\,\text{s}^{-1}\,{}^\circ\text{C}^{-1}$)	$10^7 \langle \Lambda_p \rangle$ (cm)	$10^{-7} \langle \nu_p \rangle$ (s^{-1})
10 000	3.00×10^{-6}	1.26×10^{-6}	5.13	5.28	2.7
24 000	1.25×10^{-6}	9.40×10^{-7}	4.87	4.15	3.3
40 000	7.50×10^{-7}	7.70×10^{-7}	5.76	2.87	5.6
80 000	3.75×10^{-7}	6.10×10^{-7}	6.08	2.16	7.8
360 000	8.33×10^{-8}	3.05×10^{-7}	6.05	1.08	16.0

is appropriate to deal with the motion of these thermal excitations through σ on the basis of a diffusive model, both in the absence and in the presence of a temperature gradient. We shall no longer consider σ as a purely geometrical entity, but will materialize it in the form of an obstacle, mobile or motionless along z, capable of absorbing or reflecting the impinging phonons. In this way it will be possible to evaluate the energy transformations occurring when thermal excitations collide with the surface. If σ is an integral absorber, the amount $\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$ of thermal energy given by Eq. (11) will be lost by the gas of phonons that shall be "cooled" in proportion. A force must be applied to keep σ immobile, to balance the thermal radiation force exerted by the impinging phonons. When the surface σ is perfectly reflecting and in a state of motion in the sense of dT/dz, i.e., opposite to that of heat flux, the impinging phonons will be reflected back, shifted to higher frequencies, at the expense of work done by the advancing surface on the thermal excitations, through the intermediation of thermal radiation forces. The phonon gas therefore is "heated" during this process, the individual phonons involved being brought to higher-energy states.

We now apply these concepts to diffusion and thermal diffusion of a solute, to derive the energy balance of phonon-particle collisions occurring when either the particles drift down a concentration gradient, or the phonons drift down a temperature gradient externally applied to the liquid. In both cases heat will be transferred from the thermal excitations to the particles. In either process the phonon gas loses amounts of heat equivalent to the mechanical work done on the solute. We assume here that thermal energy exchanged in this way per gram (or per mole) of solute transported, constitutes the "heat of transport" Q^* of the corresponding process. Within the frame of thermodynamics the heat of transport represents the amount of thermal energy that must be supplied at the point from which the moving solute particle is removed, if the temperature at this point has to be kept constant. The thermodynamic theory does not suggest any functional relationship of this quantity with other molecular characteristics of the system, even if a connection with evaporation jumps to the eye.

Various kinetic theories of the heat of transport have been suggested, all based on special assumptions concerning the physical mechanism of the transport process [33,34]. The most fruitful approaches are the ones stemming from adaptations of the view that diffusive processes proceed by a series of activated transitions [35]. No use was made in any of these approaches of the concept of phonon-particle interaction or of the existence of thermal radiation forces. At present, with this notion in our hands, it is evident that the energy $\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$ lost by an impinging phonon in a process of type 1(a) may supply the "Hemmungsenergie" required by the solute particle to break loose from the attraction of the surrounding molecules. Similarly, the "Lochbildungsenergie," i.e., the energy spent to form the hole into which the diffusing particle must be accommodated, would be supplied in the course of a process of type 1(b), the hole being formed in the initial phase of (forward) oscillation of the new excitation generated by this event.

Our hypothesis on the heat of transport is not in contrast with either thermodynamic or kinetic theories; it merely specifies, in an unconventional way, the mechanism responsible for solute transport. If this hypothesis is soundly based, it should be possible to derive from the phonon theory of liquids expressions analogous to the classical thermodynamical ones for Q^*. On these grounds it is easy to obtain simple analytical expressions for the heats of transport. In thermal diffusion the flux of solute particles due to collisions with the drifting phonons is

$$J_p^{\mathrm{th}} = C D_p^{\mathrm{th}} \frac{dT}{dz} = n m_p D_p^{\mathrm{th}} \frac{dT}{dz} = \frac{n m_p}{3} \frac{\langle \Lambda_p \rangle \langle \nu_p \rangle}{\langle \delta T/\delta z \rangle} \frac{dT}{dz} , \tag{12}$$

after introducing expression (8) for D_p^{th}.

A fraction of the flux of phonons across σ is substituted by the flux of particles produced by collisions of type 1(a) that give rise to thermodiffusive flux J_p^{th}. If we call J_q^{th} the fraction of heat flux that disappears during the process of generation of solute drift, we have

$$\begin{aligned} J_q^{\mathrm{th}} &= -2 \langle d\nu_p \rangle n \langle \Delta\varepsilon^{\mathrm{ph}} \rangle \langle \Lambda_l \rangle \\ &= -\frac{1}{3} n \langle \Delta\varepsilon^{\mathrm{ph}} \rangle \langle \nu_p \rangle \frac{dT/dz}{\langle \delta T/\delta z \rangle} \langle \Lambda_l \rangle . \end{aligned} \tag{13}$$

From Eqs. (12) and (13) the amount of heat transferred from the gas of thermal excitations to the solute particles per unit mass of solute transported turns out to be given by the ratio

$$\frac{J_q^{\mathrm{th}}}{J_p^{\mathrm{th}}} = -\frac{\langle \Delta\varepsilon^{\mathrm{ph}} \rangle \langle \Lambda_l \rangle}{m_p \langle \Lambda_p \rangle} \equiv (Q^*)^{\mathrm{th}} . \tag{14}$$

This expression therefore is the analytical form of our definition of the heat of transport in thermal diffusion. Drifting phonons that collide with a solute particle transfer to it a fraction $\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$ of their energy through the intermediation of thermal radiation forces. This energy disappears from the heat flux and at the same time induces a forward jump of average length $\langle \Lambda_p \rangle$ of a particle of mass m_p. Thus we may say that, for each elementary heat current $\langle j_q^{\mathrm{ph}} \rangle$ that is suppressed, an energetically equivalent elementary process of mass transport appears; $\langle d\nu_p \rangle$ collisional events of this kind lead to the disappearance of a heat flux J_q^{th} and to the appearance in its place of a solute flux J_p^{th}. The ratio of these two quantities then represents the amount of heat spent to transport one gram of solute.

If we now proceed to consider the case of an isothermal solution in which there is a concentration gradient, it is easy to see that more phonon-particle collisions per unit of volume and of time will occur in the more concentrated region. Thus the power extracted from the gas of phonons and transmitted to the solute per unit of volume is higher in the concentrated than in the dilute solution. Thermal energy is transformed, through the intermediation of thermal radiation forces, in the displacements of solute particles down the concentration gradient; i.e., thermal energy of the phonon gas is spent to produce diffusive solute flux.

The case of isothermal diffusion may be treated therefore in a way closely analogous to that of thermal diffusion; diffusive solute flux J_p^D is given by Eq. (9). The excess phonon-particle collisions, occurring in the sense from high to low concentration per unit section and per second, give rise to J_p^D. These are equivalent to a "lost" heat flux $-J_q^D$, directed in the opposite sense, amounting to

$$J_q^D = -\frac{\langle v_p \rangle}{6} \frac{dn}{dz} \langle \Lambda_p \rangle \langle \Delta\varepsilon^{\mathrm{ph}} \rangle \langle \Lambda_l \rangle \ , \qquad (15)$$

$(\langle v_p \rangle / 6)(dn/dz)\langle \Lambda_p \rangle$ being the excess of collisions per cubic centimeter and per second, over the distance $\langle \Lambda_p \rangle$.

From Eqs. (9) and (15) one has

$$\frac{J_q^D}{J_p^D} = -2\frac{\langle \Delta\varepsilon^{\mathrm{ph}} \rangle \langle \Lambda_l \rangle}{m_p \langle \Lambda_p \rangle} \equiv (Q^*)^D \ . \qquad (16)$$

Nonequilibrium thermodynamics associates solute transport to a heat of transport. For instance, in isothermal diffusion, the diffusion current density J_p^D of the solute is associated to a heat flux J_q^D given by

$$J_q^D = (Q^*)^D J_p^D \ , \qquad (17)$$

where the quantity $(Q^*)^D$ is thermal energy "transported" per unit of solute mass in isothermal diffusion. Analogous considerations apply to $(Q^*)^{\mathrm{th}}$ of Eq. (14). Dimensionally these heats of transport are a kinetic energy per unit of mass, either in our treatment or in the usual thermodynamic approach.

We thus see that, at least within the linear range of force-flux relationships, the breaking of the system's symmetry by means of a temperature or of a concentration gradient produces quite comparable effects. The anisotropy introduced in the gas of thermal excitations by the temperature gradient produces the radiation pressure that causes thermodiffusive matter flux, resulting in anisotropy of solute distribution. An imposed anisotropic solute distribution in an isothermal solution, on the other hand, also results in an excess of collisions between thermal excitations and particles along the concentration gradient, causing diffusive matter flux and inducing by reaction an anisotropy in the phonon gas. In view of the symmetry of these two processes, it is natural enough that the ratio of heat to particle fluxes in the two cases should turn out to be analogous.

IV. HEAT OF TRANSPORT AND SORET EQUILIBRIUM

We want to calculate now the rate of energy exchange among phonons and solute particles in the nonisothermal steady-state situation known as Soret equilibrium. This corresponds to an exact balance of thermodiffusive solute flux and diffusive backflow. Within the frame of the phonon theory of liquids, outlined above, this calculation may be easily carried out.

We have seen that a phonon of energy $\langle \varepsilon^{\mathrm{ph}} \rangle$, colliding with a solute particle, loses on the average an amount $\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$ of vibrational (thermal) energy, and is frequency shifted from ν_i to ν_f. This amount of energy is transferred to the particle, through work done by thermal radiation force f_p^{th}, dependent on the relevant constitutive properties of solute and solvent. During the interaction the particle is displaced by an amount $\langle \Lambda'_p \rangle$, the duration of the event being $\langle \tau'_p \rangle$. The rate at which the phonon loses its energy then is

$$\langle w^{\mathrm{ph}} \rangle = -\frac{\langle \Delta\varepsilon^{\mathrm{ph}} \rangle}{\langle \tau'_p \rangle} \ . \qquad (18)$$

The rate of working of thermal radiation force f_p^{th} during $\langle \tau'_p \rangle$ in turn will be given by

$$\langle w_p \rangle = -\langle w^{\mathrm{ph}} \rangle$$

$$= \pi r_p^2 H^* \left[\left| \frac{K}{u} \right|_l - \left| \frac{K}{u} \right|_p \right] \left(\frac{\delta T}{\delta z} \right) \frac{\langle \Lambda'_p \rangle}{\langle \tau'_p \rangle} \ . \qquad (19)$$

When a temperature gradient dT/dz is applied to a (dilute) solution, a solute particle experiences, on the average, $2\langle d\nu_p \rangle$ collisions per second in excess along z that push it in the sense of heat propagation. Therefore the average net power spent by the gas of phonons on each solute particle, pushing it along z, is $2\langle d\nu_p \rangle \langle w_p \rangle$. From Eqs. (18) and (19), upon multiplication by $2\langle d\nu_p \rangle$ and introducing the expression (6) for $\langle d\nu_p \rangle$, we get

$$\pi r_p^2 H^* \left[\left| \frac{K}{u} \right|_l - \left| \frac{K}{u} \right|_p \right] = \frac{\langle \Delta\varepsilon^{\mathrm{ph}} \rangle}{\langle \Lambda'_p \rangle \langle \delta T / \delta z \rangle} \ , \qquad (20)$$

both members being now energies per degree Kelvin. Multiplying both sides of Eq. (20) by the (average) Kelvin temperature in the Soret cell, we obtain the energy balance per thermodiffusing solute particle. With reference to one gram of the solute, i.e., to a number of particles N/m_p (N being Avogadro's number and m_p molecular mass of solvated solute particle) we finally have

$$\frac{NT_{\mathrm{av}}}{m_p} \pi r_p^2 H^* \left[\left| \frac{K}{u} \right|_l - \left| \frac{K}{u} \right|_p \right]$$

$$= \frac{N}{m_p} \langle \Delta\varepsilon^{\mathrm{ph}} \rangle \left[\frac{T_{\mathrm{av}}}{\langle \Lambda'_p \rangle \langle \delta T / \delta z \rangle} \right] \ , \qquad (21)$$

where the quantity in square brackets on the right-hand side is dimensionless.

Both members of Eq. (21) are equidimensional with $(Q^*)^{\mathrm{th}}$ and $(Q^*)^D$, as is to be expected, since the process concerned is one of simultaneous thermal and isothermal diffusion balancing each other. The differences of the two expressions figuring in the left- and right-hand sides of Eq. (21) will now be discussed.

Soret equilibrium is determined by the balance of the opposite matter fluxes due to thermal and ordinary diffusion. Equations (14) and (16) show that the latter requires twice as much transfer of energy from phonons to particles to get equal fluxes, as required to keep constant the concentration distribution at Soret equilibrium. Accordingly the total amount of heat lost by the phonon gas per second in the course of collisions of type 1(a) with one gram of solute particles is three times greater than expressed by the right-hand side of Eq. (21). Also the rate of working of thermal radiation forces on one gram of solute is three times that expressed by the left-hand side of the same equation.

Let us concisely discuss this result starting from the left-hand side of Eq. (21), which defines the heat of transport for Soret equilibrium $(Q^*)^s$ as

$$(Q^*)^s = -\frac{3NT_{\mathrm{av}}}{m_p}\pi r_p^2 H^* \left[\left[\frac{K}{u}\right]_l - \left[\frac{K}{u}\right]_p \right] . \qquad (22)$$

Equation (22) represents solute heat of transport in terms of thermal radiation forces developed in the course of phonon-particle collisions.

Soret heat of transport is also calculated through the classical expression [29]

$$(Q^*)^s = -\frac{RT_{\mathrm{av}}^2}{m_p} s_p \left[1 + \frac{\partial \ln\gamma_p}{\partial \ln m_p} \right] , \qquad (23)$$

where s_p is the Soret coefficient, m_p is the (solvated) molecular mass of solute, γ_p and m_p are, respectively, the activity coefficient and the molality of the solution, and R is the gas constant. Equation (23) applies best to nonisothermal binary solutions and is obtained on the basis of the assumption of the validity of Onsager's reciprocal relations [26].

We proceed now to consider the right-hand side of Eq. (21), which will be written as

$$(Q^*)^s = -\frac{3NT_{\mathrm{av}}}{m_p}\kappa h\nu_D \left[\frac{1}{\langle \Lambda'_p \rangle \langle \delta T/\delta z \rangle} \right] , \qquad (24)$$

after introducing the value of $\langle \Delta\varepsilon^{\mathrm{ph}} \rangle$ given by Eq. (11). The relation between $h\nu_D$ and the average kinetic energy of a particle is expressed in terms of the Debye temperature Θ of the solution $\Theta = h\nu_D/K_B$, where K_B is Boltzmann's constant. Therefore we may rewrite Eq. (24) as

$$(Q^*)^s = -\frac{RT_{\mathrm{av}}^2}{m_p} s_p \left[\frac{3}{2}\kappa \frac{\langle \Lambda_p \rangle}{\langle \Lambda'_p \rangle} \frac{\Theta}{T_{\mathrm{av}}} \right] , \qquad (25)$$

having introduced the value of the Soret coefficient:

$$s_p = \frac{2}{\langle \Lambda_p \rangle \langle \delta T/\delta z \rangle} \qquad (26)$$

derived with some slight remanipulation from Eqs. (8) and (9).

At this point two observations are in order.

(1) From Eq. (26) the Soret coefficient may be calculated using the $\langle \delta T/\delta z \rangle / m^*$ of Fig. 2 and the $\langle \Lambda_p \rangle$'s of Tables I and II. Interestingly, calculated and experimental values are proportional, their constant ratio being 0.18, i.e., just what may be expected for m^* in H_2O.

(2) Equation (25) is very similar to the classical expression (23); to become identical, the two numerical quantities in square brackets in the right-hand sides should be equal. These points will be further discussed elsewhere.

V. DISCUSSION AND CONCLUSIONS

We now discuss how the analysis of the energy balance developed above is part of the project to construct a theory of liquids based on the notion of energy and momentum exchange among material particles and phonons mediated by thermal radiation forces. In a previous article [14] we dealt with the problem of the exchange of momentum; here, instead, we concentrated on the complementary aspect of the exchange of energy between the two subsystems, phonons and particles, constituting the liquid.

The points that we shall discuss concern the values found for $\langle \Lambda_p \rangle$ and $\langle \nu_p \rangle$ and the derivation of the expressions for the heats of transport of isothermal and nonisothermal diffusion and of Soret equilibrium. One surprising aspect emerging from the examination of Tables I and II consists in the relatively small value of the frequency of phonon-particle collisions in comparison with the much higher number estimated by the conventional kinetic approach for particle-particle collisions. This fact opens the interesting perspective of fruitfully revising the hitherto intractable problems of transport in liquids. The derivation of the heats of transport in turn has to do with the fundamental issue of the operative equivalence of Onsager's assumption of time reversibility with the reversibility of the processes of phonon-particle interactions.

The values obtained for the mean free path $\langle \Lambda_p \rangle$ of ionic and molecular solutes in dilute solutions correlate well with those deduced in the same cases from the classical kinetic theory of liquids. This is not surprising since the average length of the path traveled by a particle after receiving a given amount of translational energy is independent from the nature of the energy source. Thus it is immaterial for the result whether the collisional event that caused the input of energy occurred with a phonon or with a material particle.

As for the number of collisions with phonons per solute particle and per second, $\langle \nu_p \rangle$, it is much lower than the frequency of collisions among molecules of the solvent that would be expected on the grounds of the kinetic theory of liquids. On the other hand, it is also substantially inferior to what could be expected for phonon-particle interactions in view of the density of the phonon gas in ordinary liquids [14]. Let us try to calculate directly the expected values of $\langle \nu_p \rangle$ in a dilute solution for a solvent in which the number N^{ph} of phonons is known. For simplicity of calculation the phonon population is considered, as already done above, to be constituted by wave packets all of the same energy $\kappa h\nu_D$. Further, phonon density in a dilute solution is assumed to be practically the same as in the pure solvent. If we call σ_p^{ph} the phonon-particle cross section this quantity represents the probability that a phonon, sweeping through the space occupied by a solute particle, exchanges with the latter energy and momentum. The "effective volume" swept by a phonon per second therefore is $\sigma_p^{\mathrm{ph}} u_l^g$, since u_l^g is the velocity at which the section advances. If n_p is the number of solute particles per unit of volume the frequency of collisions $\langle \nu^{\mathrm{ph}} \rangle$ experienced by the phonon will be

$$\langle \nu^{\mathrm{ph}} \rangle = \sigma_p^{\mathrm{ph}} n_p u_l^g \ . \tag{27}$$

Let us consider now N_l^{ph} phonons contained in a box of unit volume filled with the solution; they will collide with the n_p particles of solute $\mathcal{N}_p^{\mathrm{ph}}$ times per second,

$$\mathcal{N}_p^{\mathrm{ph}} = N_l^{\mathrm{ph}} \langle \nu^{\mathrm{ph}} \rangle \ . \tag{28}$$

Each solute particle accordingly experiences on the average $\langle \nu_p \rangle$ collisions per second, where

$$\langle \nu_p \rangle = \frac{N_l^{\mathrm{ph}} \langle \nu^{\mathrm{ph}} \rangle}{n_p} = \sigma_p^{\mathrm{ph}} N_l^{\mathrm{ph}} u_l^g \ . \tag{29}$$

Substituting the values of $\langle \nu_p \rangle$ calculated from diffusive data in dilute solutions and the values of N_l^{ph} and u_l^g relative to the pure solvent, one gets "effective" cross sections σ_p^{ph} some 10^5 times smaller than the geometrical cross sections of the respective solutes.

A solvated ion or a small molecule (such as glucose, fructose, or an amino acid) clearly constitutes a fairly small "obstacle" when it interacts with a phonon. Accordingly, in the large majority of cases the hyperacoustic waves sweeping past solute particles will travel on unaffected and there will be no net transfer of energy and momentum to the solute. At the same time the phonons shall not be frequency shifted either. This is a familiar situation in the propagation of waves, elastic or electromagnetic, past obstacles having cross sections smaller than the wavelength of the impinging perturbation. So the low value of the frequency of collisions $\langle \nu_p \rangle$ leading to exchange of energy and momentum among phonons and solute molecules or ions is not surprising.

There is, however, a very important consequence of such a low value of $\langle \nu_p \rangle$ that should not be overlooked. A solute particle "collides" with phonons less than one time per nanosecond. On the other hand, the average duration of the interaction with a phonon, moving at the speed of sound, is of the order of the picosecond. The same also applies to the case of particle-phonon collisions [event of type 1(b)] where energy is transferred from a solute particle to the gas of phonons. This means that the probability of multiple simultaneous interactions is so low in either case that only single phonon-particle collisions need to be considered. The great simplification for the treatment of all problems of nonequilibrium statistical mechanics of the two-fluid system (gas of phonons and population of particles) that follows from the exclusion of multiple events is evident.

The response of dense fluids to external forces is generally studied by means of the Boltzmann transport equation, relating the derivatives of the one-particle velocity distribution with the collision operator. The collisions themselves are described in this equation as events localized at a point in space and instantaneous in time. This picture, valid in dilute gases, is no longer valid whenever the ratio of the duration of the collision and that of the relaxation period for the approach to equilibrium is strongly affected by the concentration of the colliding objects. The case of multiple simultaneous events is particularly far from the basic assumptions of Boltzmann's approach. In a dense fluid of material particles colliding among themselves, as assumed by the classic kinetic theory of liquids, such multiparticle simultaneous collisions necessarily are quite common. It is very significant that in the phonon-particle two-fluid system the mutual interactions are sufficiently rare so that statistically one only needs to consider single events, localized in space and time.

Equally interesting is the circumstance that an external force field (such as a temperature or a concentration gradient) does not affect the amount of energy and momentum transferred either way in phonon-particle collisions, nor the duration of the event. In Boltzmann's equation the external force field is accounted for only in the free flow term, and does not figure in the collision operator. This may be plausible only as long as the time interval between collisions is much longer than the duration of the collision itself. This condition, that certainly would not be fulfilled by a population of colliding material particles in a dense fluid, is fulfilled instead, as we have seen, by the collisions among phonons and particles.

It seems reasonable therefore that the application of the methods of nonequilibrium statistical mechanics to the two-fluid model of liquids we proposed may make the treatment of transport processes in liquids feasible. Particularly interesting in this context will be the evaluation of the exchanges of energy and momentum among phonons and particles of a pure liquid, rather than with the solute. When that is done, the means of quantitatively dealing with the interactions of heat flow with the medium, apart from component separation, will be in our hands. This is needed to introduce a mechanical resistance to heat flow and accordingly modify the Fourier equation. The above discussion gives reason to hope that the problem may be treated on the basis of Boltzmann's equation, if it is also found that the interactions of phonons with the pure solvent do not give rise to multiple events.

We shall proceed now to discuss the derivation of the expressions for the heats of transport of diffusive and thermodiffusive processes as well as of the one of Soret equilibrium. The connection of the transfer of energy between phonons and particles with the heats of transport is quite straightforward. The underlying logic constitutes the second argument of this discussion.

We have considered phonons as local, instantaneous heat fluxes [Eq. (5)] that disappear as such, wholly or in part, in the course of a collision of type 1(a). Conversely, a material particle may interact with a phonon doing work on it at the expense of its own kinetic energy [case 1(b)]. In either case one of the two subsystems constituting the liquid—the population of material particles—acquires or loses mechanical energy; the other subsystem—the gas of phonons—in correspondence loses or acquires heat, in the form of frequency shifts of the individual wave packets. Thus any thermomechanical or mechanothermal effect involves transport of heat from or to the gas of phonons.

The expressions we derived on the basis of the elementary phonon-particle interactions are coincident with the classical ones derived by the usual thermodynamic methods that assume, as a necessary condition, the validity of Onsager's reciprocal relations [26].

These relations require the existence of universal linear laws for molecular fluctuations, i.e., that the regression of fluctuations obeys the corresponding macroscopic transport equations.

We did not use Onsager's reciprocity principle in our treatment. Since strictly analogous conclusions and coincident formal expressions for the heats of transport are reached by classical nonequilibrium thermodynamics and by nonequilibrium statistics of phonon-particle interactions, we must conclude that the latter method contains, at a deeper level, the exact equivalent of Onsager's relations. This equivalence obviously resides in the symmetry of the elementary interactions of types 1(a) and 1(b), that commute each into the opposite by the operation of time reversal.

If this interpretation is sound, it is reasonable to assume phonon-particle interactions as a basis for a reformulation of nonequilibrium thermodynamics. The nonequilibrium statistical treatment of these elementary events could allow a coherent general treatment of transport processes in dense fluids.

Experiments designed to validate the proposed theory are possible and desirable. A quantitative study of the action of phonon pressure on liquid droplets suspended in an immiscible nonisothermal fluid is now in an advanced phase of preparation. Gravitational forces are easily compensated by density matching, but thermocapillary forces and differential thermal expansion complicate the measurements. The second effect is dominant in Earth-based laboratories, so that our test will be performed in conditions of weightlessness, in future European Space Agency experiments (Spacelab).

A different kind of test may consist in the investigation of thermal diffusion in solutions differing only in solute molecular mass. As is well known, thermal diffusion and Soret equilibrium are very sensitive to molecular mass of the dispersed phase. According to the phonon theory of liquids, such an investigation carried out with spherical molecules of diameters ranging from 3×10^{-8} to 3×10^{-6} cm should yield valuable information on phonon-particle interactions and on the phonon spectrum of liquids. Molecules having the required prerequisites may be prepared from Poly A−, Poly T−, Poly C−, and Poly G−single strand DNA and a good Soret apparatus should have sufficient resolving power.

APPENDIX

We shall discuss here the process of phonon-molecule interaction to deduce some important relations among the quantities $\langle\Lambda_p\rangle$, $\langle\Lambda_p'\rangle$, $\langle\tau_p\rangle$, $\langle\tau_p'\rangle$, and the energy of the impinging phonon. Since we are concerned only with forces and displacements in the direction of the gradients (of temperature or of concentration), our treatment of the problem shall be unidirectional.

We define a probability per unit of time $\mathcal{P}_r$ for the phonon energy to excite the translational degrees of freedom of the solute molecule. So the average translational energy transferred to the molecule during the time of interaction $\langle\tau_p'\rangle$ will be

$$\langle E_t\rangle=\int_0^{\langle\tau_p'\rangle}\mathcal{P}_r\langle\Delta\varepsilon^{\mathrm{ph}}\rangle dt\ . \tag{A1}$$

If we suppose the whole process of energy exchange to be ergodic, $\langle E_t\rangle$ may be considered as the average translational energy of the solute molecule and the above definition may also be used to implicitly define the average interaction time $\langle\tau_p'\rangle$. The momentum transferred to the molecule during $\langle\tau_p'\rangle$ will be

$$\langle\Delta p^{\mathrm{ph}}\rangle=f_p^{\mathrm{th}}\langle\tau_p'\rangle\ , \tag{A2}$$

f_p^{th} being the thermal radiation force acting on the molecule. Having defined $\langle E_t\rangle$ as the average kinetic energy transferred by the phonon to the molecule, it results that

$$\langle\Delta p^{\mathrm{th}}\rangle=\sqrt{2m_p\langle E_t\rangle}\ . \tag{A3}$$

From (A2) and (A3) we deduce

$$\langle\tau_p'\rangle=\frac{\sqrt{2m_p\langle E_t\rangle}}{f_p^{\mathrm{th}}}\ . \tag{A4}$$

This expression puts in correspondence the interaction time $\langle\tau_p'\rangle$ with $\langle\Delta\varepsilon^{\mathrm{ph}}\rangle$ and f_p^{th}. We now apply the kinetic energy theorem to evaluate $\langle\Lambda_p\rangle$. Since the molecule along the path $\langle\Lambda_p\rangle$ spends all the kinetic translational energy received from the phonon, the total work done on the molecule will be equal to zero, so we can write

$$f_p^{\mathrm{th}}\langle\Lambda_p'\rangle+f_p^{v}\langle\Lambda_p\rangle=0\ , \tag{A5}$$

where f_p^v is a coefficient, with the dimensions of a force, related to the average "viscous" dissipation of the molecule by process of type 1(b). The work done on the molecule by the thermal radiation force is $f_p^{\mathrm{th}}\langle\Lambda_p'\rangle=\langle E_t\rangle$, so from Eq. (A5) we finally obtain

$$\langle\Lambda_p\rangle=-\frac{\langle E_t\rangle}{f_p^{v}}\ . \tag{A6}$$

Having thus calculated $\langle\Lambda_p\rangle$ we can now derive an expression for $\langle\Lambda_p'\rangle$. The average momentum variation of the molecule during $\langle\tau_p'\rangle$ will be

$$\langle\Delta p_p\rangle=\langle\tau_p'\rangle(f_p^{\mathrm{th}}+f_p^{v})\ . \tag{A7}$$

From the above expression it also follows that the velocity change is

$$\langle\Delta v_p\rangle=\langle v_p^f-v_p^i\rangle=\frac{\langle\tau_p'\rangle}{m_p}(f_p^{\mathrm{th}}+f_p^{v})\ . \tag{A8}$$

The average translational velocity v_p of the particle during the interaction time is given by

$$\begin{aligned} v_p&=\frac{\langle v_p^f\rangle+\langle v_p^i\rangle}{2}=\langle v_p^i\rangle+\frac{\langle\Delta v_p\rangle}{2}\\ &=\langle v_p^i\rangle+\frac{1}{2}\frac{\langle\tau_p'\rangle}{m_p}(f_p^{\mathrm{th}}+f_p^{v})\ , \end{aligned} \tag{A9}$$

where $\langle v_p^i\rangle$ is the average equilibrium velocity of a particle at temperature T: $\langle v_p^i\rangle=\sqrt{3K_BT/m_p}$. We finally have

$$v_p=\left[3\frac{K_B T}{m_p}\right]^{1/2}+\frac{1}{2}\frac{\langle \tau'_p\rangle}{m_p}(f_p^{\rm th}+f_p^{v}) \ . \tag{A10}$$

It is now possible to calculate $\langle \Lambda'_p \rangle$:

$$\langle \Lambda'_p\rangle=\langle \tau'_p\rangle v_p=\langle \tau'_p\rangle\left[\left[3\frac{K_B T}{m_p}\right]^{1/2}+\frac{1}{2}\frac{\langle \tau'_p\rangle}{m_p}(f_p^{\rm th}+f_p^{v})\right] \ . \tag{A11}$$

After the interaction time $\langle \tau'_p \rangle$, there is a relaxation period in which the molecule loses its excess energy, the momentum of the molecule undergoing a change $-\langle \Delta p_p \rangle$. The average time spent by the molecule in this process of dissipation of the energy received by the impinging phonon is

$$\langle \tau^*_p\rangle=\langle \tau_p\rangle-\langle \tau'_p\rangle=-\frac{\langle \Delta p_p\rangle}{f_p^{v}}=-\langle \tau'_p\rangle\frac{(f_p^{\rm th}+f_p^{v})}{f_p^{v}} \ . \tag{A12}$$

So we can finally deduce the expression for $\langle \tau_p \rangle$:

$$\langle \tau_p\rangle=\langle \tau'_p\rangle+\langle \tau^*_p\rangle=\langle \tau'_p\rangle\left[1-\frac{(f_p^{\rm th}+f_p^{v})}{f_p^{v}}\right]=-\langle \tau'_p\rangle\frac{f_p^{\rm th}}{f_p^{v}} \ . \tag{A13}$$

In a different approach to the problem it could be assumed that the acceleration of the particle and its subsequent viscous deceleration are phenomena distinct in time; i.e., the deceleration of the molecule starts only after the time interval $\langle \tau'_p \rangle$. Equation (A5) should accordingly be rewritten as follows:

$$f_p^{\rm th}\langle \Lambda'_p\rangle+f_p^{v}(\langle \Lambda_p\rangle-\langle \Lambda'_p\rangle)=0 \ . \tag{A14}$$

If we define $\langle \Lambda^*_p \rangle=\langle \Lambda_p \rangle-\langle \Lambda'_p \rangle$, it results that

$$\frac{\langle \Lambda'_p\rangle}{\langle \Lambda^*_p\rangle}=-\frac{f_p^{v}}{f_p^{\rm th}} \ , \tag{A15}$$

which gives us a relation between the distances covered by the molecule during the time $\langle \tau'_p \rangle$ and $\langle \tau^*_p \rangle$ and the intensities of the thermal radiation force and the "viscous" one.

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