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Phonon-particle interactions and transport processes in liquids

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The theory of thermal radiation forces is extended to the local interactions occurring among phonons and the material particles of a liquid, also in the absence of an external temperature gradient. In a solution, energy and momentum can be transferred by an impinging phonon to a particle, or the latter may perform work on the first, shifting it to a higher frequency. Upon time reversal, each of these elementary interactions commutes into the other. Isothermal diffusion, thermomechanical and mechanothermal effects in solutions can be interpreted within this unifying frame of reference. The density of the "gas" of thermal excitations, and the average of energy exchanged per interaction can be calculated from experimental data for common liquids. Nonequilibrium statistical mechanics and irreversible thermodynamics might be fruitfully revisited on the basis of the notion of phonon-particle interactions, since these are processes that occur at a more elementary level than the regression of fluctuations. Accordingly, the statistical approach proposed here may lead to a microscopic interpretation of Onsager's reciprocity relations.

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I. INTRODUCTION

Systems constituted by liquids, or solids and liquids, crossed by a flux of thermal energy, exhibit a complex phenomenology. A unifying theoretical approach has been proposed, to explain on a common basis various supposedly unrelated effects, characteristic of these nonisothermal systems [1–3]. Such effects include the following: (i) the production of component fluxes coupled to heat flow in liquid solutions (thermal diffusion); (ii) the generation of forces, distinct from those due to changes of buoyancy, on solid slabs suspended in a liquid, when liquid and solid are crossed by a flux of thermal energy; (iii) the production of volume flow and/or the production of a pressure difference in a nonisothermal porous medium permeated by a liquid (thermoosmosis); (iv) the selective transport of solutes—eventually proceeding against gradients of electrochemical potential—across a porous membrane crossed by heat flux (thermodialysis). According to the theory of thermal radiation forces, the common microscopic cause of these macroscopically observable effects consists of the exchange of momentum among the phonons drifting along the temperature gradient and the particles constituting the materials crossed by the heat flow. In general, a pressure difference will be produced across a surface element dS, oriented normal to a temperature gradient dT/dz wherever the medium has different properties in front of and behind dS (see Fig. 1). The pressure will be higher on the side where the quantity H^*K/u is bigger, K and u being thermal conductivity and velocity of propagation of ultrahigh-frequency elastic waves (phonons) and H^* a dimensionless constant, proportional to the reflection coefficient of acoustic waves across dS. As for the surface dS, it may be the limit between two adjacent extended media, or the surface of a solute particle or the solvation layer surrounding such a particle, or just an element of an isothermal surface normal to the temperature gradient in a nonisothermal liquid.

In the case of two adjacent media, it is easy to correlate the observed sense of thermal radiation force also with the values of the respective rates of entropy production σ due to conductive transport of thermal energy in each of the media. As is well known,

$$\sigma = J_q X_q = \frac{K}{T^2}\left[\frac{dT}{dz}\right]^2 , \tag{1}$$

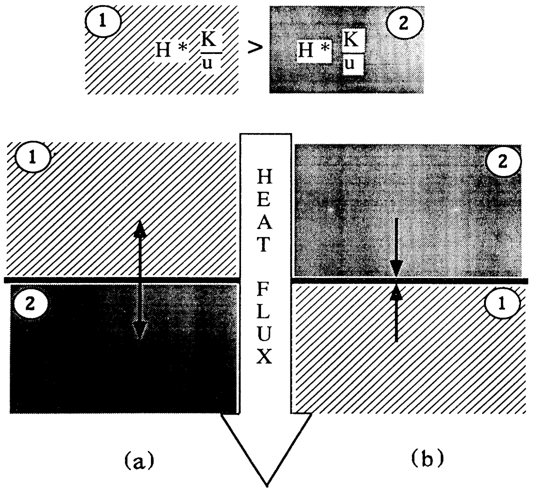


FIG. 1. Thermal energy flowing across the boundary between two adjoining media 1 and 2 produces repulsion of the receiving surface when this one belongs to the medium with the lower $[H^*(K/u)]$ [as in 1(a)]. In the opposite case, represented in 1(b), there is attraction. Thermal radiation pressure on the medium that has the lower $[H^*(K/u)]$ pushes it along with the heat current in either case.

$J_q = -K(dT/dz)$ being the heat flux and $X_q = -(1/T^2)(dT/dz)$ the correlated generalized force, and T the temperature of the medium. Of course, Eq. (1) is valid for the case of pure heat conduction, i.e., when there are no coupled effects of matter transport. If thermal conductivities across a surface S normal to the temperature gradient are K_1 and K_2, the rates of entropy production are σ_1 and σ_2. Indeed, J_q is conserved across S, while the temperature gradient changes as $1/K$.

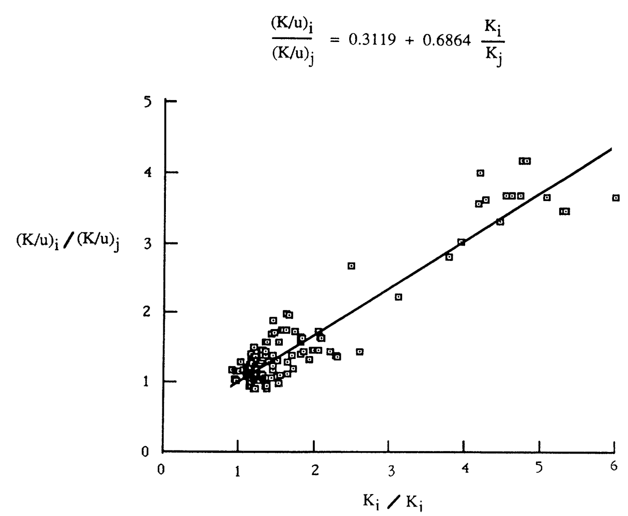


FIG. 2. For most couples of media, the ratios of the momentum conductivities (K/u) are proportional to those of the respective heat conductivities K. The data compiled in the figure are relative to almost 160 couples of substances, mostly liquids, for which experimental data are available. It is probable that the scatter of points on the two sides of the line is due mostly to inaccuracies of the experimental data.

Interestingly, for most couples of media there is a quasilinear correlation among the ratios of the momentum conductivities K/u and those of the corresponding thermal conductivities K (see Fig. 2). Thus the medium with the smaller K/u value is the medium in which the heat flux generates higher rates of entropy production. As seen above, this is also the medium that is pushed in the sense of the heat current. It has been shown [1–3] that the concept of thermal radiation pressure can be employed to quantitatively describe all the phenomena mentioned above, under (i)–(iv), due to the action of externally applied temperature gradients. The stringent connection among thermal radiation effects and the rate of entropy production owing to the flow of heat suggests that some fundamental relationship between the statistical mechanics of phonons and particles on one hand, and nonequilibrium thermodynamics on the other, should exist.

Before starting to deal with this aspect of the problem, we want to generalize the concept of thermal radiation force, applying it at the molecular level and within liquid or solid-liquid systems that are at thermal equilibrium.

II. THERMAL EXCITATIONS IN LIQUIDS

The generally accepted model of the liquid state is that of a dense gas; i.e., it is assumed that, with sufficient ingenuity, the behavior of a liquid system could be always deduced from a gas-kinetic approach, suitably modified. This opinion is supported by the great successes of kinetic models, for instance, in explaining osmotic pressure, diffusion of solutes and Brownian motion. The opposite approach, which considers liquids as solids lacking long-range order and constituted by particles having a greater freedom of relative motion, is less generally known even if it has had illustrious proponents.

Peter Debye in 1912 extended his theory of the specific heats of solids to the liquid state [4], neglecting in this case transverse waves, owing to the absence of rigidity. Longitudinal high-frequency waves—phonons—were assumed in his study to be very similar to the collective oscillations of solids. Thermal energy in a liquid is considered to be equidistributed among the various internal degrees of freedom of the particles, the rotations of single particles (or also local domains), and the phonons. These propagate in the medium in the same way as they do in solids, since intermolecular forces in liquids have practically the same intensity as in the respective solids. Leon Brillouin accepted Debye's argument, but observed that the lack of the transverse waves would lead to a higher limiting Debye frequency (ν_D) in liquids with respect to solids, a circumstance which seems illogical and cannot be accepted. He suggested [5] that the lacking normal modes could be replaced by rotations of single particles, and also by transverse ring-shaped vortexes endowed only with kinetic energy. This concept was then further developed by Landau in his theory of the specific heat of liquid ^{4}He. A fundamental consequence of Debye's theory is that at very low temperatures the specific heats of substances which can still exist in the liquid state should obey a law of proportionality to the third power of absolute temperature:

$$C_v \approx \frac{12}{5}\pi^4 R \left[\frac{T}{\Theta}\right]^3 , \tag{2}$$

where R is the gas constant and Θ is the "Debye temperature" of the substance.

Many experimental verifications have lent strong support to Debye's theory: besides confirmation of Eq. (2), we shall mention here only the direct experimental evidence obtained by the study of the interaction of phonons with light. In his general theory of the interaction of elastic waves with light, Brillouin [6] had predicted the existence of a detectable Doppler shift in the light waves crossing a liquid into which pressure waves were propagated. The refractive index changes associated with the periodic density variation will scatter light at an angle α to an incident collimated beam of optical frequency ν_0 only for acoustic plane-wave fronts satisfying the Bragg condition for reflection. The Doppler shift $\Delta\nu$ shall be

$$\frac{\Delta\nu}{\nu_0} = \pm 2\frac{u_l}{c_l}\sin(\tfrac{1}{2}\alpha) , \tag{3}$$

where u_l is the propagation velocity of the elastic waves in the liquid, and c_l is the velocity of light of frequency ν_0 in it. The frequency shift $\Delta\nu$ is equal to the frequency of the elastic waves responsible for the scattering. This theory soon found unambiguous experimental verification in acoustically excited liquids.

The detection of spontaneous and randomly oriented ultrahigh-frequency waves sets a much more difficult experimental problem, which could be solved only when laser sources became available and phonons could be detected in a number of liquids at ordinary temperatures [7–12] and Eq. (3) was verified, yielding values of the propagation velocity of phonons u_l and of the corresponding hypersonic frequencies $\nu_{\mathrm{ph}} \equiv \Delta\nu$.

Thus the existence of phonons in liquids is by now a well-established experimental fact; the spectrum of the frequencies of these elastic waves extends to the mode in which neighboring molecules in the liquid vibrate in opposition of phase (Debye limit frequency ν_D). The propagation velocities correspond to those at ultrasonic frequencies, being some 4–10 % higher. Since there is velocity dispersion, phase u_l^ϕ and group u_l^g velocity of phonons shall differ slightly, being related by the usual expression:

$$u_l^g = u_l^\phi - \lambda_l \frac{du_l^\phi}{d\lambda_l} , \tag{4}$$

λ_l being the wavelength in the liquid.

Two circumstances should be mentioned that will be useful in the following. One is that phonons carry energy $h\nu$ and momentum $h\nu/u_l^g$. Compared with photons, the amount of energy carried by a phonon is a few hundred times smaller than that carried by an infrared photon, while u_l^g is over five orders of magnitude smaller than c. Accordingly, the momentum coupled with a certain amount of heat transported by phonons is 100–1000 times larger than that coupled with the same amount of heat transported as infrared radiation. The other has to do with the occurrence of interactions among the gas of thermal excitations and the medium. Owing to the lack of long-range order in liquids, the periodicity of the liquid lattice only extends over very short stretches, so that interactions leading to transfer of energy and momentum occur quite often. In solutions, solute particles play a role equivalent to that of an impurity in the solid lattice, i.e., that of a center of phonon's scatter. Furthermore, in liquids, motions of parts of the medium relative to the rest may occur, so that when, for instance, an advancing solute particle compresses a phonon, the frequency of the latter is Doppler shifted, and its energy and momentum are increased.

III. DIFFUSIVITY OF PHONONS AND THE GENESIS OF LOCAL TEMPERATURE GRADIENTS

The existence of thermal excitations, consisting of high-frequency elastic waves in liquids, has various interesting consequences. Let us consider an isothermal liquid, and in it a plane surface of unit area, arbitrarily oriented. In the absence of an externally imposed temperature gradient, there will be no net heat flux through the surface. A large number of phonons, however, shall cross it at any instant, owing to their random motions. Since the wave vectors of phonons will be isotropically distributed in space, we can treat the problem as if they were ordered along three mutually orthogonal directions. If the z axis is oriented normal to our surface that lays in the (x,y) plane, one sixth of the phonons are assumed to travel at any instant in the $(+z)$ sense, and just as many along $(-z)$. We now want to calculate the intensity of the unidirectional phonon fluxes crossing the surface normal to z.

Thermal energy per unit of volume of the liquid is the integral between absolute zero and T of the product $\rho_l(C_v)_l$ of the density and specific heat at constant volume. A fraction m of this total heat content corresponds to collective oscillatory molecular motions and represents the energy density of the "gas" of phonons, q_l^{ph}, which accordingly may be expressed as

$$q_l^{\mathrm{ph}} = m^* \rho_l (C_v)_l T , \tag{5}$$

where the constant m^* includes m and also accounts for the approximation introduced with the substitution of the product $\rho_l(C_v)_l T$ in place of the integral of $\rho_l(C_v)_l$ over the interval $(0 \leftrightarrow T)$.

Individual phonons propagate energy with the velocity u_l^g and, owing to the lack of long-range order in the liquid, only proceed between successive interactions along an average distance $\langle \Lambda_l \rangle$ that represents the mean free path of the wave packets in the medium. Thus the phonons can be considered as a "gas" of wave packets, exchanging energy and momentum with the material particles of the medium owing to the imperfect periodicity of its lattice. This means (a) that we assume heat conduction in liquids to be due to the diffusivity of phonons, and (b) that diffusivity of phonons may be evaluated by means of the familiar Boltzmann kinetic method. In this way an expression for heat diffusivity D_l^* may be obtained, correlating it with some relevant dynamic characteristics of the gas of phonons. Since we consider transport phenomena in liquids as due to the interaction among phonons and particles, phonon-phonon interactions can be neglected in the evaluation of the coefficient of ordinary diffusion of the system, as such collisions do not alter the total energy or the global distribution of momentum carried by thermal excitations.

These considerations relate the diffusivity coefficient D_l^{ph} of the phonon gas with the thermal diffusivity D_l^* of the liquid system as long as there is no electronic contribution to heat transport. So, in the liquid systems we are considering,

$$D_l^* \equiv m D_l^{\mathrm{ph}} , \tag{6}$$

where m is the same constant defined above. Then we may write

$$\langle \Lambda_l \rangle = \left[\frac{6 D_l^* \langle \tau^0 \rangle}{m} \right]^{1/2} , \tag{7}$$

where $\langle \tau^0 \rangle$ is the mean time interval between two successive collisions. The rationale is that, owing to exchange among the various degrees of freedom, thermal energy may diffuse as rotational and/or vibrational energy of a diffusing molecule, and not only in the form of phonons.

Equation (7) may be now written in a different form, substituting in place of $\langle \tau^0 \rangle$ the ratio $\langle \Lambda_l \rangle / u_l^{\phi}$ and introducing the usual relation [13] between thermal conductivity K_l and heat diffusivity D_l^*, that is, $K_l = D_l^* \rho_l (C_p)_l$. In this way we obtain the expression

$$K_l = \frac{m}{6} \rho_l (C_p)_l \langle \Lambda_l \rangle u_l^{\phi} . \tag{8}$$

With reference to this equation, it should be remembered that in our approach each wave packet is considered as a local heat current j_q^{ph} instantaneously propagating in the medium. At the microscopic level each phonon then may be represented by the expression

$$j_q^{\mathrm{ph}} = \frac{q_l^{\mathrm{ph}}}{6} \frac{\langle \Lambda_l \rangle}{\langle \tau^0 \rangle} = \frac{q_l^{\mathrm{ph}}}{6} \left[\frac{6 D_l^*}{m \langle \tau^0 \rangle} \right]^{1/2} = K_l \left\langle \frac{\delta T}{\delta z} \right\rangle . \tag{9}$$

It should be observed that thermal conductivity K_l in Eq. (9) is obviously a microscopic definition. In agreement with Onsager [14], however, we assume that the kinetic and thermodynamic approaches must exactly agree in the mean. This enables us to use in this and subsequent equations the macroscopic value of K_l also when dealing with local heat fluxes due to propagation of individual phonons between two successive interactions with material particles. The second term of Eq. (9) states the same concept of Eq. (7), i.e., that the phonons may be considered as a classical particle gas, specifically accounting this time for the density q_l^{ph} of the gas of thermal excitations [Eq. (5)]. Substituting in place of $\langle \Lambda_l \rangle$ the second member of Eq. (7), one obtains the third expression in (9); in the last one, the instantaneous heat flux j_q^{ph} has been considered as due to a local, instantaneous temperature gradient $\delta T / \delta z$. Of course, here the more-common relationship of cause to effect of temperature gradient to heat flux is inverted, and it is the flux of thermal energy constituted by the phonon current that generates the temperature gradient. Over any reasonable time interval, or through any macroscopic surface, there will always be two mutually opposite heat fluxes of equal intensity and the net temperature gradient due to random motion of phonons will disappear. For this reason, we call $\delta T / \delta z$ a "virtual temperature gradient" and write it with the δ symbol. Having supposed the medium to be homogeneous and isothermal, we can generalize Eq. (9), saying that everywhere in the liquid, local heat currents j_q^{ph} suddenly arise, proceed along a direction **r** for a time interval $\langle \tau^0 \rangle$, and then disappear.

It should be remembered that attention has been called in the past by many authors to the striking parallelism of the plots representing the temperature dependence of the products $\rho_l (C_p)_l u_l^g$ and the analogous plots of the corresponding thermal conductivities (Fig. 3). A similar analogy has been also observed in the pressure dependence of these quantities. Since the ratio $K_l / \rho_l (C_p)_l u_l^g$ has the dimensions of a length, it is natural, in our approach, to interpret this as the average phonon mean free path $\langle \Lambda_l \rangle$. This suggests that local temperature fluctuations ΔT arise stochastically in the liquid along average distances $\langle \Lambda_l \rangle$. The intensity of the heat currents should be proportional to the density of diffusible thermal energy q_l^{ph}, and accordingly

$$K_l \frac{\langle \Delta T \rangle}{\langle \Lambda_l' \rangle} = \tfrac{1}{6} q_l^{\mathrm{ph}} u_l^g = \frac{m^*}{6} \rho_l (C_v)_l u_l^g T . \tag{10}$$

For the $\langle \Lambda_l' \rangle$ defined in this way to be coincident with the $\langle \Lambda_l \rangle$ of Eq. (8), it must be

$$\frac{\langle \Delta T \rangle}{T} = \frac{m^*}{m} \frac{(C_v)_l}{(C_p)_l} \frac{u_l^g}{u_l^{\phi}} . \tag{11}$$

An expression for the product $\langle \delta T / \delta z \rangle^2 \langle \tau^0 \rangle$ may be derived by combining Eqs. (5)–(9) and the relation between K_l and D_l^*:

$$\left\langle \frac{\delta T}{\delta z} \right\rangle^2 \langle \tau^0 \rangle = n_1 \frac{T^2}{D_l^*} , \tag{12}$$

where $n_1 = (m^*)^2 / 6 m \gamma_1^2$, and γ_1 is the ratio $(C_p / C_v)_1$.

The set of equations derived above can be used to calculate the actual values of q_l^{ph}, $\langle \Lambda_l \rangle$, $\langle \delta T / \delta z \rangle$, and $\langle \tau^0 \rangle$, as well as the number of phonons per unit of volume N_l^{ph} of common liquids (see Table I–IV in the Appendix). In particular, for the calculation of N_l^{ph} (Table II), we only have rough estimates, obtained by equating the mean energy calculated by either a gas-kinetic or by our own "statistical" approach based on phonon interactions. These contrasting approaches may be fruitfully compared only with the aim of getting order-of-magnitude estimates for N_l^{ph}. We shall proceed now to show that our approach can be advantageously

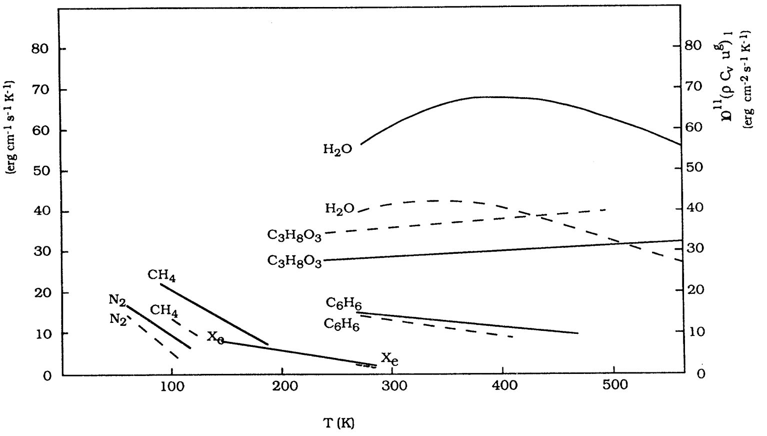


FIG. 3. The products $\rho_l(C_v)_l u_l^g$ and their temperature dependence are compared with the corresponding values of thermal conductivities. On the abscissae are absolute temperature; on the ordinates are the values of the two quantities being compared. Thermal conductivities, solid lines; $\rho_l(C_v)_l u_l^g$ product, dashed lines.

applied to diffusive processes in isothermal and nonisothermal liquids.

IV. PHONON-PARTICLE INTERACTIONS AND THE PROCESSES OF DIFFUSION AND THERMAL DIFFUSION

We shall now investigate the dynamic consequences of the reversible interactions among phonons and particles based on the notion of thermal radiation force [1–3]. The force produced by a temperature gradient on a particle of radius r_p is

$$f_p^{\text{th}} = \pi r_p^2 H^* \left[\left[\frac{K}{u} \right]_l - \left[\frac{K}{u} \right]_p \right] \frac{dT}{dz} , \tag{13}$$

where subscripts l and p indicate solvent and particle, respectively. This expression finds ample support in experiments of thermal diffusion both with electrolytic and nonelectrolytic solutions, as well as in macromolecular solutions [15–26]. The force f_p^{th} of Eq. (13) results from a macroscopic analysis, where the contributions of many phonon-particle collisions are averaged.

The principles of conservation of momentum and energy for a phonon-particle system are

$$(\Delta p)^{\text{ph}} = \frac{1}{u_l}(h\nu_1 - h\nu_2) = f_p^{\text{th}} \langle \tau^{\bullet} \rangle , \tag{14}$$

$$(\Delta \varepsilon)^{\text{ph}} = (h\nu_1 - h\nu_2) = f_p^{\text{th}} \langle \Lambda_p^{\bullet} \rangle , \tag{15}$$

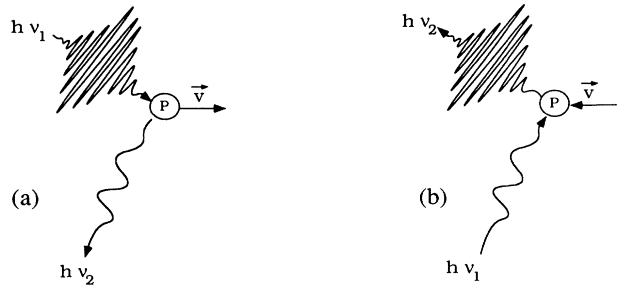
where the superscript ph and the subscript p stand for phonon and particle, respectively. The symbol (●) superimposed to $\langle \tau^{\bullet} \rangle$ and to $\langle \Lambda_p^{\bullet} \rangle$ indicates that these quantities are referred to the solute rather than to the solvent molecules. Equation (13) evidently applies equally well to the case of externally applied temperature gradients as to that of the local gradients connected with phonon's random motion; this justifies the third expressions in Eqs. (14) and (15).

A solute particle in a liquid is an object which may be useful for detecting these forces and for yielding information on the intensity of the local, instantaneous temperature gradients $\langle \delta T/\delta z \rangle$, as well as on the length of the characteristic time $\langle \tau^{\bullet} \rangle$ that represents the average duration of each phonon-molecule interaction, well different from $\langle \tau^0 \rangle$, a quantity referring to phonon dynamics in the dispersing phase. A distinct problem is that of determining the influence of phonon-particle collisions on the dynamic behavior of the solute. The cross section of a solute particle generally is small enough not to be simultaneously crossed, even at thermal equilibrium, by perfectly balanced numbers of phonons propagating in opposite senses during a short time interval such as $\langle \tau^{\bullet} \rangle$. The mass of such a particle is sufficiently small so that its state of motion will be appreciably modified in consequence of an interaction with a single phonon. Thus at the order of magnitude of ionic, molecular, and macromolecular solutes, it can be predicted that in the isothermal medium the particles shall be kept by collisions with phonons in a state of perpetual Brownian motion.

Each phonon-particle collision leads to exchange of momentum and energy between the impinging high-frequency wave packet and the particle, as schematically represented in Fig. 4(a). The inverse process, that of transfer of momentum and energy between a fast moving particle and a phonon, is represented in Fig. 4(b). Within a solution that is isotropic and macroscopically homogeneous, these events do not cause macroscopically observable effects, since they have no preferred direction in space, and are equidistributed within the whole volume occupied by the system. Only in the presence of a symmetry breaking factor will observable phenomena due to phonon-particle interactions appear.

The symmetry of the "gas" of phonons is broken by introducing a temperature gradient, while symmetry of the distribution of particles is broken by establishing a gradient of solute concentration. In either case, the exchanges of energy and momentum among thermal excitations and material particles becomes unbalanced.

The flow of phonons owing to ∇T produces an excess of processes of the type shown in Fig. 4(a), the probability of such events becoming higher in the sense of the heat flux, resulting in net solute flow and in the buildup of a concentration gradient (thermal diffusion). Conversely, a solute flux, whatever its cause, induces a directional un-



$$(\Delta p)^{Ph} = \frac{1}{u_l}(h\nu_1 - h\nu_2) = f^{th}\langle\tau^{\cdot}\rangle$$

$$(\Delta \varepsilon)^{Ph} = (h\nu_1 - h\nu_2) = f^{th}\langle\Lambda_p^{\cdot}\rangle$$

FIG. 4. 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) in which a particle transfers energy and momentum to a phonon. Commuting (t) into $(-t)$, any of the two processes is transformed into the opposite one.

balance in the interactions that transfer energy and momentum from the particles to thermal excitations [processes of the type shown in Fig. 4(b)], resulting in the buildup of a temperature gradient (Dufour effect). (The Dufour effect is more complex than that, being due to the combined action of solute flux and solvent countercurrent on the gas of phonons. It will be discussed by us elsewhere.) On the other hand, diffusive solute flux follows from the decreased probability of phonon-solute interactions in solute-depleted portions of the solution compared with the one in solute-concentrated regions. Therefore, solute jumps down the concentration gradient will occur more frequently than those in the opposite sense, giving rise to matter flow (isothermal diffusion).

The existence of the effects of isothermal diffusion, thermal diffusion and the Dufour effect compels us to consider situations of unbalance between the two fundamental types of phonon-particle interactions described in Fig. 4 during which either the gas of phonons transfers energy and momentum in excess to the particles or vice versa.

Heating on one side and cooling on the other displaces the center of mass of the energy, leading to the production of a flux of thermal energy in the system, a process that tends to bring back the center of mass of the energy to the original position. The occurrence of the interactions of the type shown in Fig. 4(a), however, causes solute drift (thermal diffusion), an event that in turn gradually displaces the center of mass of the particles. For the two centers of mass to move back again to the original position, all the energy introduced into the system must become equidistributed again throughout the solution. A similar analysis may be made of the events which follow the introduction of solute from one side. The symmetry of the two types of interaction, shown in Figs. 4(a) and 4(b), is imposed by the principle of momentum conservation, which also ensures the time reversibility of the process. We shall now proceed to analyze quantitatively the process of phonon-particle interaction. The phonon, impinging on a particle, interacts with it during a time interval $\langle\tau^{\cdot}\rangle$ by means of a thermal radiation force f_p^{th} that drives the particle through the liquid along an average distance $\langle\Lambda_p^{\cdot}\rangle$. In the course of this motion, f_p^{th} will be in dynamic equilibrium with the viscous resistance f_p^{η} and the energy $(\Delta\varepsilon)^{\text{ph}} = (h\nu_1 - h\nu_2)$ lost by the phonon returns to the liquid as frictional heat. The momentum lost by the phonon, $(\Delta p)^{\text{ph}} = (1/u_l)(h\nu_1 - h\nu_2)$, will be similarly transferred to the liquid during the time interval $\langle\tau^{\cdot}\rangle$ taken by the interaction.

The Stokes equation for the motion of a spherical molecule in a medium of viscosity η_1 gives

$$\pi r_p^2 H^* \left[\left[\frac{K}{u}\right]_l - \left[\frac{K}{u}\right]_p \right] \left\langle \frac{\delta T^{\cdot}}{\delta z} \right\rangle = 6\pi r_p \eta_l v_p^d \;. \tag{16}$$

Multiplying both sides by $\langle\tau^{\cdot}\rangle$ and putting $\langle\Lambda_p^{\cdot}\rangle = v_p^d\langle\tau^{\cdot}\rangle$, we have

$$\langle\Lambda_p^{\cdot}\rangle = \frac{r_p}{6\eta_l} H^* \left[\left[\frac{K}{u}\right]_l - \left[\frac{K}{u}\right]_p \right] \left\langle \frac{\delta T^{\cdot}}{\delta z} \right\rangle \langle\tau^{\cdot}\rangle \;. \tag{17}$$

We may now proceed to deal with the case where the symmetry-breaking element is a temperature gradient applied along z. If its intensity is not too high, we can assume that there will be no nonlinear effects and that the (initial) state of the system at the microscopic level locally continues to be similar to the one at uniform temperature, except for the flux of thermal excitations along z. This means that a solute particle at a given place in the solution where the temperature is T experiences the same average number of collisions per second as if the temperature were uniform, the only difference with the isothermal state being that it undergoes collisions with phonons that are originated in two half-spaces along z, one hotter and the other cooler. According to Eq. (5) the density of the phonon gas depends on the temperature of the liquid. If $\langle\nu^{\cdot}\rangle$ was the average total number of phonon-solute collisions per second in the isothermal liquid at $T \equiv T_0$, this number stays constant, but collisions occurring in the direction z no longer consist of $\langle\nu^{\cdot}\rangle/6$ events in each of the two senses, but there will be an excess $\langle d\nu^{\cdot}\rangle$ per second in the sense of heat propagation, and an equal defect $\langle -d\nu^{\cdot}\rangle$ in the opposite one. In the linear range it is to be expected that $\langle d\nu^{\cdot}\rangle$ shall be proportional to the temperature gradient dT/dz applied to the system. Every collision produces a jump of the particle over the distance $\langle\Lambda_p^{\cdot}\rangle$, and thus every second the solute travels a distance $2\langle\Lambda_p^{\cdot}\rangle\langle d\nu^{\cdot}\rangle$ along z. This quantity therefore represents the velocity of thermodiffusive drift of the molecule along z. By the definition of the coefficient of thermal diffusion D_p^{th}, as drift velocity in a temperature gradient of 1 °C/cm, we then have

$$D_p^{\text{th}} \frac{dT}{dz} = 2\langle\Lambda_p^{\cdot}\rangle\langle d\nu^{\cdot}\rangle \;. \tag{18}$$

The situation in the presence of the external temperature gradient dT/dz consists of a heat flux $J_q^z = -K_1(dT/dz)$ superimposed to two equal and opposite local heat fluxes $+(J_q^z)^0 = -K_l\langle \delta T'/\delta z\rangle_+$ and $-(J_q^z)^0 = +K_l\langle \delta T'/\delta z\rangle_-$, proceeding between $z - \langle \Delta z_1^{\text{ph}}\rangle/2$ and $z + \langle \Delta z_1^{\text{ph}}\rangle/2$ in the two senses along z. [Here again, assuming the same thermal conductivity K_l to determine the heat flux J_q and the "local" heat fluxes $\pm(J_q^z)^0$ is equivalent to introducing the Onsager reversibility hypothesis, as already discussed in relation to Eq. (9).] Thus obviously

$$\frac{\langle dv'\rangle}{\langle v'\rangle/6} = \frac{dT/dz}{\langle \delta T'/\delta z\rangle}, \tag{19}$$

and therefore

$$D_p^{\text{th}} = \frac{\langle v'\rangle\langle \Lambda_p'\rangle}{3\langle \delta T'/\delta z\rangle}. \tag{20}$$

We proceed now to consider an isothermal solution of average concentration c_0 in which the solute is not uniformly distributed along z, the concentration gradient being dc/dz. In this system the collisions cause diffusive flux, the coefficient of diffusion of the solute D_p being connected with the average length of the random walks $\langle \Lambda_p'\rangle$ and with the number of jumps per sec and per particle $\langle v'\rangle/6$ by the well-known relation

$$D_p = \frac{\langle \Lambda_p'\rangle^2\langle v'\rangle}{12}, \tag{21}$$

$\langle \Lambda_p'\rangle$ being proportional to $\langle \delta T'/\delta z\rangle$.

From Eqs. (20) and (21) we get the following expression for the Soret coefficient S_p of the solute particles:

$$S_p = \frac{D_p^{\text{th}}}{D_p} = \frac{4}{\langle \Lambda_p'\rangle\left\langle \dfrac{\delta T'}{\delta z}\right\rangle}. \tag{22}$$

We have thus seen how macroscopic anisotropies introduced in the form of gradients of temperature or concentration give origin to observable fluxes of matter through phonon-particle interactions occurring at the microscopic scale. There is equivalence of anisotropies induced in the gas of thermal excitations with the ones induced in the distribution of material particles.

V. DISCUSSION

This attempt to develop a phonon theory of liquids rests on two facts, by now well established. One has been known since the pioneering works of Debye [4] and Brillouin [5,6], and consists of the existence of phonons, ceaselessly propagating within dense fluids. Surprisingly, a general theory of the liquid state has not been constructed on this basis, notwithstanding the experimental verifications of the existence of phonons in ordinary liquids [7–12]. This has been due to the lack of a broad enough understanding of a mechanism that dynamically links the kinetics of the material particles with that of the gas of phonons. This missing link, the thermal radiation force, is now in our hands, and may be used to build a kinetic theory of liquids. It has been shown that a flux of thermal energy crossing a surface of discontinuity between two adjoining media produces a pressure on such surface. Macroscopically, this radiation pressure is measured by the change of the momentum flux J_q/u coupled with the heat flux J_q across the boundary from the first to the second medium. It has been also shown that thermal radiation forces arise in the course of the interaction of heat flux with individual solute molecules and ions [21–26], this interaction being responsible for thermal diffusion in solutions.

These findings call attention to the fact that at the microscopic level, transfer of momentum and energy occurs among single phonons and particles. If that is the case, the existence of a macroscopic temperature gradient applied to the liquid no longer is a necessary condition for the appearance of effects due to thermal radiation forces. Each phonon, randomly propagating within the isothermal fluid, constitutes a local heat current, coupled to a local flux of momentum. When it encounters, along its path, a site where the properties of the medium change, the thermal radiation force that is produced leads to the exchange of energy and momentum. A discontinuity that may cause such an interaction could be a solute particle or any site where the harmonic potential of the lattice is disturbed. It has thus become practicable to extend the theory and methods of thermal radiation forces to the microscopic level and also in isothermal liquid systems. It is encouraging that the orders of magnitude of all the new physical quantities introduced by this approach may be obtained and that they turn out to be both internally consistent and correspondent to what would be expected on general grounds for quantities representing molecular motions in liquids.

Two types of fundamental interactions must be considered, corresponding to the diagrams of Figs. 4(a) and 4(b). An impinging phonon will lose or acquire energy and momentum crossing the boundary between the surrounding liquid and the solvated particle, depending on the relative values of the K/u of the two materials. When a particle has a negligible velocity relative to the medium and $(K/u)_l > (K/u)_p$, an event of the type shown in Fig. 4(a) is produced; if, however, $(K/u)_l < (K/u)_p$, the event may be of the type shown in Fig. 4(b). Another simple case is that of a rapidly moving macromolecule and a phonon impinging at a glancing angle on the advancing boundary. Upon reflection, the phonon will be Doppler shifted to higher frequency: this is an event of the type shown in Fig. 4(b) in which the particle loses energy in the form of work done by compressing the elastic wave that in this way acquires an extra amount of energy $(h\nu_r - h\nu_i)$, and momentum $(1/u_{\text{ph}})(h\nu_r - h\nu_i)$, where the subscript r denotes the "reflected" wave and i the "impinging" wave. It is easy to imagine analogous cases of direct and inverse processes of phonon interaction with the vibrational modes of the macromolecular structure, or with rotations of a nonspherical particle around one of its axes of inertia.

In the conditions of equilibrium—i.e., in an isothermal solution of uniform concentration—the amounts of energy and momentum transferred from the gas of phonons to the particles shall be equal, over any not infinitesimal time interval, to those simultaneously transferred from the population of particles to the phonons. When, however, the symmetry of the system is broken by imposing a gradient of temperature or of concentration, an unbalance is produced. In either case, the collisional events reduce the asymmetry initially induced in the corresponding subsystem (gas of phonons or population of particles). At the same time, however, they induce an asymmetry in the other subsystem, originally undisturbed.

We proceed now to a critical analysis of the connections existing among microscopic events and macroscopic phenomena, to outline the physical principles ruling the reversal of perturbations and the return of the system to the symmetric equilibrium configuration. Let us consider the case of the application of a temperature gradient dT/dz to a uniform solution. This leads to a displacement of the center of mass of the energy (Fig. 5). In the common case, where $(K/u)_{\text{solvent}} > (K/u)_{\text{solute}}$, an excess of processes of the type shown in Fig. 4(a) follows, and the drift of solute causes a displacement of the center of mass of the particles. In the case considered in the figure, the solute particles drift in the sense of J_q. Since the liquid is practically incompressible, the condition $J_v = 0$, i.e., there will be no net volume flux, applies, and a volume of solvent equal to that of the solute that has been transferred downhill will be transported in the opposite sense. The centers of mass of solvent and solute are both displaced; as a consequence, the center of mass of the solution as a whole is also displaced, owing to the different densities of dispersing and disperse phases, ρ_1 and ρ_2.

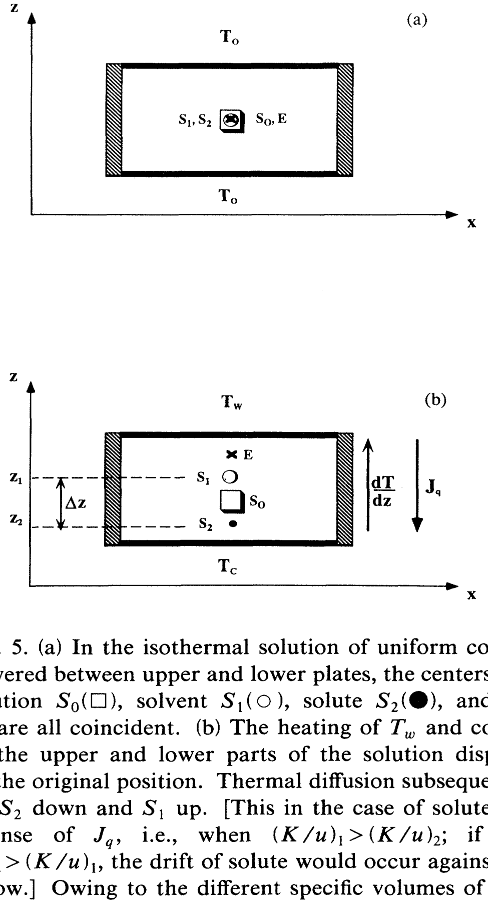


FIG. 5. (a) In the isothermal solution of uniform concentration layered between upper and lower plates, the centers of mass of solution S_0(□), solvent S_1(○), solute S_2(●), and energy $E(\times)$ are all coincident. (b) The heating of T_w and cooling to T_c of the upper and lower parts of the solution displaces E above the original position. Thermal diffusion subsequently displaces S_2 down and S_1 up. [This in the case of solute drift in the sense of J_q, i.e., when $(K/u)_1 > (K/u)_2$; if instead $(K/u)_2 > (K/u)_1$, the drift of solute would occur against that of heat flow.] Owing to the different specific volumes of disperse and dispersing phases, S_0 also drifts along z.

If Δt seconds were needed to reach the situation represented in Fig. 5(b), the net mass flow J_M of the thermodiffusive process was

$$J_M = (\rho_2 - \rho_1)\frac{\Delta z}{\Delta t} A = (\rho_2 - \rho_1) D_2^{\text{th}} \frac{dT}{dz} A \ , \tag{23}$$

A being the horizontal cross section of the cell and D_2^{th} the coefficient of thermal diffusion of the solute. Accordingly, mechanical momentum appeared at the macroscopic level, connected with the mass flow, since the center of mass of the material system was displaced. It is readily seen that

$$\begin{aligned} \frac{d(mv)}{dt} &= J_M \frac{\Delta z}{\Delta t} = (\rho_2 - \rho_1) \left[\frac{\Delta z}{\Delta t} \right]^2 A \\ &= (\rho_2 - \rho_1) \left[D_2^{\text{th}} \frac{dT}{dz} \right]^2 A \ . \end{aligned} \tag{24}$$

This, of course, corresponds to the net rate of transfer of momentum from the gas of phonons to the solute particles in the course of the processes of the type shown in Fig. 4(a) that occurred in the liquid following the establishment of the temperature gradient.

In the case just considered by us, the system is mechanically isolated but receives thermal energy from above and loses heat from below. We want now to consider a system that is mechanically and thermally isolated, constituted by a cell similar to the one of Fig. 5, containing a concentrated solution of density ρ_s on the bottom and the pure solvent, of density $\rho_0 < \rho_s$ layered above. An impermeable septum avoids diffusion, until it is extracted, without disturbing the equilibrium of the system. After a time interval Δt the diffusive process will have displaced the center of mass of the material system, owing to the different densities of disperse and dispersing phases and to the condition $J_v = 0$ that also applies in this case. As was done above, we can calculate here the net mass flow and the $d(mv)/dt$ due to the diffusive process of solute and solvent:

$$\begin{aligned} \frac{d(mv)}{dt} &= J_M \frac{\Delta z}{\Delta t} = (\rho_s - \rho_0) D_s \frac{\Delta z}{\Delta t} \frac{dn}{dz} A \\ &= (\rho_s - \rho_0) \left[\frac{\Delta z}{\Delta t} \right]^2 A \ , \end{aligned} \tag{25}$$

where D_s is the diffusion coefficient of the solute, and dn/dz is the time-averaged value of the concentration gradient during Δt expressed in terms of the change of the number of solute molecules along z.

How was it possible that the momentum of the isolated material system changed? Could we observe from outside the process by, say, suspending the system to a spring and watching for a change of the tension of the latter during diffusion?

The answer, coming from the kinetic theory of the liquid state proposed by us, is straightforward: the gas of phonons that initially was uniformly distributed gave an excess of collisions with solute particles down their concentration gradient, and of course also gave an excess of collisions pushing the molecules of the solvent in the opposite sense. In the conditions of equal and opposite volume fluxes of the disperse and dispersing phases, the phonon gas transfers an excess of energy and momentum to the material medium in the sense of solute diffusion (the opposite would have occurred where $\rho_s < \rho_0$). The momentum lost by the gas of phonons in the course of diffusion is transferred to the material system through processes of the type shown in Fig. 4(a), accelerating the particles down the gradient of concentration. These molecules moving with a higher than average velocity, however, transfer back part of the momentum to the population of thermal excitations through processes of the type shown in Fig. 4(b). The net rate of momentum loss by the population of phonons is equal to the difference of the rates of transfer of momentum by processes shown in Figs. 4(a) and 4(b). This is used by the material system to displace the center of mass of the solution at the observed rate.

The energetics of the collisional processes of the types shown in Figs. 4(a) and 4(b) associated with the processes of thermal diffusion and isothermal diffusion will be discussed by us elsewhere [27]. It is clear, however, that isothermal diffusion cannot be really isothermal, since the ensemble of the processes of the types shown in Figs. 4(a) and 4(b), being unbalanced, produce by reaction an anisotropy in the gas of phonons. Macroscopically, this will be observed in the form of local temperature gradients connected with the diffusive front (the mechanocaloric effect).

VI. CONCLUSIONS

The formulation of a viable kinetic theory of liquids now appears to be feasible, being based on the existence of phonons and on the mechanism of thermal radiation forces. These forces mediate the exchanges of energy and momentum among phonons and particles, both in equilibrium and nonequilibrium conditions. In the latter case, transport phenomena are due to statistical imbalance in the phonon-particle interactions operating at the molecular level. We have dealt here only with the simple cases of isothermal and thermal diffusion, but it is evident that other transport phenomena may also be treated within the same frame of reference. The mechanocaloric effect may be conceived as the result of shifting of phonons by advancing particles that compress the high-frequency thermal waves. In an analogous way, shear within a flowing liquid could result in Doppler shifting of the phonons exchanged between neighboring regions of the fluid in relative motion. A net transfer of momentum from the faster-moving layer to the slower one would then ensue, accounting for a new kind of viscous coupling. The heats of transport represent the net transfer of energy from the gas of phonons to the population of particles (or vice versa) in the course of any process of transport [27]. Finally, it should be observed that a parabolic equation such as Fourier's expression for heat conduction cannot represent transport of thermal energy if this consists in the flux of phonons interacting with matter through thermal radiation forces.

Apart from possible future developments, we should try to understand why an approach based on nonequilibrium statistical mechanics of a two-fluid system (the gas of phonons and the population of particles) succeeds, where the traditional molecular approach to the problem of the response of a dense fluid to external forces via the Boltzmann equation fails. An answer may be found in the compelling analysis made many years ago by Prigogine [28] of the difficulties met by the Boltzmann equation in its application to transport processes in dense fluids. As is well known, this equation relates the derivatives of the one-particle velocity distribution function with the collision operator. Now the collisions are described in Boltzmann's expression as events instantaneous in time, and localized at a point in space. This oversimplification, valid in dilute gases, does not hold true any more in dense media, where the ratio of the duration of a collision and that of the relaxation period for the approach to equilibrium is strongly affected by the concentration of the particles. In the case of phonon-particle collisions, the interaction lasts a length of time $\langle \tau' \rangle$, which is also the time interval taken by the system to approach equilibrium. In his critical discussion of the response of a dense fluid to external generalized forces, Prigogine also pointed out that in Boltzmann's equation the external force field is accounted for only in the free-flow term, while it does not figure in the collision operator. That may be plausible until the time interval between collisions is much longer than the duration of the collision itself. In dense fluids this condition certainly is not fulfilled, and therefore an alternative treatment is needed that may account for the energy transferred by the force field to the particles during the course of the collision. In the thermal radiation force approach, the transfer of energy and momentum among phonon and particle occurs (in either sense) owing to the inhomogeneity introduced by the externally applied gradient that constitutes the force field; this inhomogeneity accounts for the amount of energy and momentum actually transferred from one of the two interacting subsystems to the other.

This last observation brings us to the conundrum of the correlation of our statistical approach with the other science that deals with transport phenomena, i.e., nonequilibrium thermodynamics. Its central dogma is Onsager's assumption of the existence of universal linear laws for molecular fluctuations and on the identification of the laws of the regression of fluctuations with the corresponding macroscopic transport equations.

Our statistical approach indeed gives us the possibility of a microscopic understanding of Onsager reciprocity relations. This understanding has its basis in the theory of fluctuations. In fact, if we study the motion of a statistical ensemble using the microcanonical description, the result is that in the phase space of the system under study we may not only define the probability distribution with which the system fluctuates around an equilibrium position (i.e., around some mean values of representative microscopic parameters describing the system), but we may also attempt the extension to nonequilibrium processes for this probability distribution. This latter extension gives us the possibility to define the probability with which a system at point (r,p) of phase space at time t may occupy the point (r',p') at time t'. This probability distribution, which we shall denote by $\mathcal{P}(r,p,r',p',\tau)$ $(\tau=t-t')$, is endowed of some symmetry requisites directly derived from the microscopic evolution laws governing the system in the phase space. Of particular interest are the properties of time reversal of the microscopic mechanism of evolution; so, if we individuate in the phonon-particle interactions the undefined microscopic evolution mechanism to which Onsager refers in his works, we can use the time-reversal invariance of the phonon-particle scattering to give a more specific and physically defined basis to the symmetries of the already-defined probability density $\mathcal{P}$. Now the Onsager reciprocity coefficients are, in the statistical approach of nonequilibrium thermodynamics, linked directly to the probability density $\mathcal{P}$ as can be found in the quoted work of Onsager, in the sense that the main time-momentum symmetry properties of $\mathcal{P}$ directly give rise to the symmetry of the Onsager coefficients, once stated as the time-reversal invariance of the microscopic scattering processes. This makes it possible to assume the phonon-particle interaction as the right candidate for a truly microscopic foundation of nonequilibrium thermodynamics.

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APPENDIX

The values will be calculated of the various physical quantities that figure in the kinetic theory of liquid proposed by us. Expressions will be derived connecting m^*, n_l, $\langle \Lambda_l \rangle$, $\langle \tau^0 \rangle$, and $\langle \delta T/\delta z \rangle$ with constitutive properties of the fluids; tables of the numerical values of these quantities in some common liquids will also be given. The orders of magnitude found and the dependence of the characteristic parameters of the theory on temperature and the nature of the materials conform to logical expectations.

Our first problem concerns the total number of degrees of freedom that may be attributed to a molecule within a condensed fluid, the difficulty residing here in the enumeration of rotational modes. It is well known how this evaluation depends to some extent upon the structural model adopted. For instance, in liquid water, assuming the "vacant lattice point" structural model [29,30], each H_2O at 0 °C would have approximately one rotational mode per molecule; this number will gradually increase with temperature, following the decrease of the fraction of molecules participating to the local icelike domains. In the "flickering-cluster" model [31–33], cluster members posses one degree of rotational freedom, while nonclustered molecules have three. At room temperature, where about 70% of the molecules at any instant belong to a cluster [34,35], the rotational modes in the average will be about 1.6 per molecule. Somewhat similar conclusions may be reached on the basis of other structural models [36–38].

Accordingly, the total number of degrees of freedom will change in water from a little over seven to about nine, when the temperature rises from melting to the critical point, with a value near to 7.6 at +25 °C; this yields $m_{\mathrm{H_2O}}^{25\,^\circ\mathrm{C}}=0.395$. Similar problems are met with other liquids, the most complex cases being those of associated polar liquids, such as water; conclusions of comparable accuracy can be reached in most occasions. An additional problem, however, arises with organic liquids having complex constituent molecules, where the counting of the numbers of vibrational modes may become difficult. We shall not consider here any of these cases.

We may now use Eq. (8) to derive $\langle \Lambda_l \rangle$:

$$\langle \Lambda_l \rangle = \frac{6K_l}{m\rho_l (C_p)_l u_l^{\phi}} \cong \frac{6K_l}{m\rho_l (C_p)^l u_l^{g}} , \tag{A1}$$

where the last expression represents a good approximation of the exact one. Indeed, group velocity of elastic waves in liquids has been experimentally found not to increase over 14% with frequency over a range of ten decades. Hence $\lambda_l (du_l^{\phi}/d\lambda_l) \cong 0$, and from Eq. (4) $u_l^{\phi} \cong u_l^{g}$.

Values of the phonon mean free path $\langle \Lambda_l \rangle$, calculated by means of Eq. (A1) for water and some common liquids, are listed in Tables I and II; in the first, $\langle \Lambda_l \rangle$ at various temperatures has been calculated for H_2O, and in the second $\langle \Lambda_l \rangle$ are given for fluids representing various classes of liquids. In Table II the orders of magnitude of phonon densities are also indicated.

A brief comment is in order. Since, according to Eq. (5), N_l^{ph} increases with temperature, is it not contradictory that $\langle \Lambda_l \rangle$ also increases (Table I for water)? Since $\langle \Lambda_l \rangle$ has been defined as the mean distance traveled by a phonon between two successive collisions with material particles, it should increase when the liquid expands.

TABLE I. The mean free path of phonons in water has been calculated by means of Eq. (A1) at temperatures between melting and boiling points. The increase of $\langle \Lambda_l \rangle$ with temperature is due both to the dependence of $K_{\mathrm{H_2O}}$, $\rho_{\mathrm{H_2O}}$, $(C_p)_{\mathrm{H_2O}}$, and $u_{\mathrm{H_2O}}$ on T and to the decrease of m owing to the greater rotational freedom assumed on the basis of the flickering cluster model.

T (K)	273	280	300	320	340	360	373
$\langle \Lambda_l \rangle$ (Å)	14.60	14.85	15.56	16.00	16.50	17.10	17.40

TABLE II. Phonon mean free paths in various liquids at $T=293$ K. The calculation of $\langle \Lambda_l \rangle$ has been done by means of Eq. (A1) as in Table I. The order of magnitude of the number of phonons per cm^3 in the five liquids has been deduced from the density of energy of the phonon gas [Eq. (5)], assuming all phonons to have an energy $\langle h\nu \rangle$ equal to two thirds of $h(\nu_l)_D$, where $(\nu_l)_D$ is the Debye limit frequency in the liquid.

Substance	Benzene	Carbon tetrachloride	Glycerol	Methyl alcohol	Water
$\langle \Lambda_l \rangle$ (Å)	17.80	12	15.48	19	15.32
$\langle N \rangle_{\mathrm{ph}}$ (units of 10^{-22})	$\cong 4$	$\cong 10$	$\cong 6$	$\cong 8$	$\cong 14$

Thermal expansion of H_2O is $\alpha_{H_2O} \approx 0.8 \times 10^{-3}$ °C^{-1}, and $(1/\langle \Lambda_{H_2O} \rangle)(d\langle \Lambda_{H_2O} \rangle /dT) \approx 1.8 \times 10^{-3}$ °C^{-1} in the 0–100 °C range. The difference of the two values can be attributed to temperature-dependent modifications of water structure and to the increase of free molecular rotations [changes of $(C_v)_l$ and m^*].

It is now necessary to derive the average lifetime of a phonon $\langle \tau^0 \rangle$ between two successive interactions with the lattice:

$$\langle \tau^0 \rangle = \frac{\langle \Lambda_l \rangle}{u_l^{\phi}} \cong \frac{\langle \Lambda_l \rangle}{u_l^{g}} . \tag{A2}$$

Some typical values of $\langle \tau^0 \rangle$ for common liquids are listed in Table III.

The definitions of $\langle \Lambda_l \rangle$ through Eq. (A1) and of $\langle \tau^0 \rangle$ by means of Eq. (A2) account for interactions of the phonons with every kind of lattice defect or impurity. For instance, in water, the periodicity of the lattice is disturbed not only by impurities—there including OH^- and H^+ ions—but also by flickering clusters, icebergs or any other structure that phonons feel as an alteration of the harmonic potential of the lattice.

The quantity m^* has been defined as

$$m^* = m \frac{\int_0^{\Theta/T} \rho_l (C_v)_l dT}{\rho_l (C_v)_l T} , \tag{A3}$$

Θ having the same meaning as in Eq. (2). This expression can be written as

$$m^* = m f[\Theta/T] , \tag{A4}$$

where the term $f[\Theta/T]$ can be shown to range from $\frac{1}{4}$ at low temperatures ($T \ll \Theta$) to 1 at high temperatures ($T \gg \Theta$). It can be observed, on the other hand, that upon introduction of the definition of Debye temperature [39,40] the ratio Θ/T may be written in the form

$$\frac{\Theta}{T} = \frac{(h\nu_D)_l}{k_B T} = \frac{h u_l^{\phi}}{k_B T (\lambda_D)_l} = \frac{h u_l^{\phi}}{2 k_B T a} , \tag{A5}$$

where $(\nu_D)_l$ is the Debye frequency in the liquid, $(\lambda_D)_l$ the corresponding phonon wavelength, and a the nearest-neighbor distance. This shows that the definition of m^* [(A4)] depends on structural parameters of the liquid, such as m, u_l^{g}, and a, and upon universal constants.

To calculate n_l we shall use the well-known relation between $(C_p)_l$ and $(C_v)_l$:

$$(C_p)_l = (C_v)_l + T \frac{\alpha_l^2}{\beta_l \rho_l} , \tag{A6}$$

where α_l and β_l are the coefficients of volume thermal expansion (isobaric) and isothermal compressibility of the liquid.

One then has

$$n_l = \frac{(m^*)^2}{6 m \gamma_l^2} = \frac{m}{6 \gamma_l^2} \left[\int_0^{\Theta/T} \rho_1 (C_v)_l dT / \rho_l (C_v)_l T \right]^2 , \tag{A7}$$

and Eq. (12) thus becomes

$$\left\langle \frac{\delta T}{\delta z} \right\rangle^2 \langle \tau^0 \rangle = \frac{m}{6 K_l \rho_l (C_p)_l} \left[\int_0^{\Theta/T} \rho_l (C_v)_l dT \right]^2 , \tag{A8}$$

where we have expressed thermal diffusivity by means of the more-accessible, related quantity K_l.

From (A8) and (A2) we finally have

$$\left\langle \frac{\delta T}{\delta z} \right\rangle = \left[\frac{m u_l^{g}}{6 K_l \rho_l (C_p)_l \langle \Lambda_l \rangle} \right]^{1/2} \int_0^{\Theta/T} \rho_l (C_v)_l dT . \tag{A9}$$

Typical values of $\langle \delta T / \delta z \rangle$ calculated by means of Eq. (A9) for some common liquid substances are given in Table IV.

A brief comment on the orders of magnitude of the quantities $\langle \tau^0 \rangle$, $\langle \Lambda_l \rangle$, and $\langle \delta T/\delta z \rangle$ is appropriate here. It is a source of satisfaction that they turn out to corre-

TABLE III. Average phonon lifetimes in various liquids at 293 K calculated by means of Eq. (A2). The velocity u_l^{g} that has been used is the one of ultrasonic waves in the frequency range of some 10^7 Hz.

Substance	Benzene	Carbon tetrachloride	Glycerol	Methyl alcohol	Water
$\langle \tau^0 \rangle (10^{12} s)$	1.37	1.31	0.81	1.75	1.02

TABLE IV. Value of the instantaneous local temperature gradients due to phonon propagation in some liquids. The local temperature gradients listed here have been calculated by means of Eq. (A9). The meanings of the quantities in this equation and their values have been discussed in the text.

Substance	Benzene	Carbon tetrachloride	Glycerol	Methyl alcohol	Water
$\langle \delta T/\delta z \rangle (10^{-8}\,{}^{\circ}\mathrm{C\ cm^{-1}})$	5.49	8.50	8.33	6.44	9.32

spond so well to logical expectations. Much longer phonon mean free paths would decrease drastically the number of interactions of thermal excitations with the material particles. The rates of exchange of momentum and energy would then have practically no influence on transport phenomena. A substantially shorter mean free path, on the other hand, would be incompatible with the existence of a wave packet. Similar considerations also apply to the results of the calculation of $\langle \tau^0 \rangle$.

Of particular interest, then, are the values of $\langle \delta T/\delta z \rangle$ deduced from Eq. (A9). The conspicuous intensity of the local gradients speaks for relatively large local thermal radiation forces. On the other hand, multiplied by the $\langle \Lambda_l \rangle$'s, these gradients reveal temperature fluctuations of 10^1-10^2 °C, i.e., local $d\rho/\rho$ of $10^{-3}-10^{-1}$, in good agreement with optical measurements.

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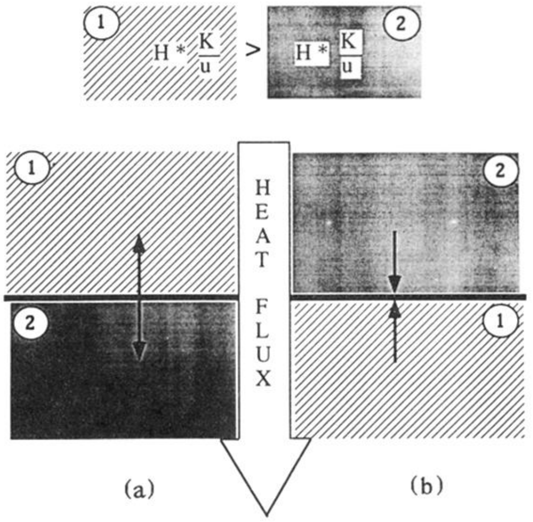

FIG. 1. Thermal energy flowing across the boundary between two adjoining media 1 and 2 produces repulsion of the receiving surface when this one belongs to the medium with the lower $[H^*(K/u)]$ [as in 1(a)]. In the opposite case, represented in 1(b), there is attraction. Thermal radiation pressure on the medium that has the lower $[H^*(K/u)]$ pushes it along with the heat current in either case.