Theory of transport processes in a nonequilibrium gas-solid system

V. D. Borman, S. Yu. Krylov, A. V. Prosyanov, and A. M. Kharitonov

Engineering Physics Institute, Moscow

(Submitted 29 July 1985)
Zh. Eksp. Teor. Fiz. **90**, 76–99 (January 1986)

A new class of nonequilibrium effects in a gas-solid system, in which transport processes arise in one medium when a thermodynamic force is set up in the other, is analyzed. Effects of this sort are shown to be important for nonisothermal gas flow in narrow channels (~ 100 Å; the diameter is comparable to the phonon mean free path) or in fine-pore media, where it is necessary to consider the drag exerted on gas molecules by the phonon flux of the nonequilibrium solid as the molecules are scattered by the surface. A thermodynamic analysis is carried out for a unified nonequilibrium system with an interface. A kinetic theory is derived for nonequilibrium interfacial effects by solving the kinetic equations for molecules and phonons together with boundary conditions reflecting the nonequilibrium nature of the medium in contact with the given medium. Under conditions such that the phonon drag of the molecules dominates, the free molecular flux of the gas is proportional to d^2, the square of the channel diameter is independent of the mass m of the gas molecules, and depends strongly on the average temperature (e.g., T^{-2} in the low-temperature limit) and the properties of the solid. In particular, this gas flux is proportional to the fourth power of the sound velocity. All of these dependences are fundamentally different from those established previously for channels of ordinary size, where the (isothermal) gas flux is proportional to $(T/m)^{1/2}d^3$ and weakly dependent on the material of the channel wall. This new theory is generalized to the case of a mixture of gases. The possibility that this effect may have been seen in some previously unexplained experimental data on gas mixtures is discussed.

1. INTRODUCTION

Transport processes in gases in narrow channels and porous media are attracting increasing interest[1,2] because of the extensive potential technological applications of fine-pore media and also because of the appearance of ideal systems for such research, nuclear filters[3] with smooth channels 20–1000 Å in diameter. On the other hand, systems of this type have a fundamental feature which has apparently not been noted previously: In sufficiently thin channels, the kinetic length scales of the gas and the solid (the channel width d if the mean free path of the molecules satisfies $\lambda_M \gtrsim d$, or the phonon mean free path λ_{ph} for a dielectric crystal) may be comparable. In such a case, the assumption of a local equilibrium for the gas in contact with the solid—a reasonable assumption for gaseous systems of ordinary geometric scale (with $d, \lambda_M \gg \lambda_{ph}$)—may be incorrect. Our preliminary calculations[4] for nonisothermal gas flow in channels with $d \sim 100$ Å show that a new component of the gas flux becomes important. This new component is proportional to the temperature gradient in the wall and arises from the drag exerted on the gas molecules by the phonon flux of the nonequilibrium solid. We are seeing here a new type of nonequilibrium phenomenon at an interface, in which transport processes in one medium depend on a nonequilibrium state in another. Effects of this type have not previously been identified in a gas-solid system or, apparently, in other systems with an interface. As a result, the methods of kinetic theory which have so far been developed are "single-phase" methods (the kinetic theory of gases, plasmas, metals, etc.). In the present paper we construct a theory of "interfacial" kinetic phenomena for the example of a system of a low-density gas and a crystal in which mass and heat are transported tangent to the surface.

To some extent, the phonon drag of gas molecules is analogous to the well-known drag effects in the electron-phonon system in a metal, but there is also a fundamental distinction: In this case we are dealing with a drag which involves particles (or quasiparticles) in different media, and the drag process itself is played out at an interface. In order to take this effect into account, we need to treat the gas-solid system as a single, unified nonequilibrium system. Although this representation has not previously been used in the literature, it is in fact necessary if we wish to reach an understanding of several well-known phenomena from the macroscopic point of view. An example is the nonequilibrium polarization in the direction of the angular momentum[5] of polyatomic molecules which are reflected from a surface. This polarization arises when the gas temperature differs from the temperature of the solid[6] or as a gas flows along a surface.[7] Another example is the nonequilibrium desorption of particles (nonequilibrium in terms of the energy of the particles and the direction in which they are moving) from a chemically[8] or physically[9] adsorbed film on a solid surface. These effects, however, can be described even in a (locally) equilibrium approximation with respect to the state of the solid. In contrast, the nonequilibrium phenomena with which we are concerned in the present paper are fundamentally nonlocal phenomena. A macroscopic consequence of the interaction of the gas molecules and the phonons (the drag) at the surface of a solid is a correlation between the heat and mass fluxes in the gas and the heat flux in the solid. As a result, the

0038-5646/86/010043-14$04.00

macroscopic fluxes in one medium exhibit a nonlocal dependence on a thermodynamic force which is set up in the other medium.

It is an extremely complicated problem to describe nonlocal kinetic effects. The methods of nonequilibrium statistical physics which are developed from "first principles"—from the equations for a multiparticle distribution function—are available only for systems with an external mechanical agent,[10] in which case the agent can be incorporated directly in the Hamiltonian of the system. For systems with a thermal agent, fundamental methods have been developed systematically only for a description at the hydrodynamic level.[10] In the present paper we restrict the analysis of nonlocal kinetic effects at an interface to the system consisting of a low-density gas and a crystal. In the "quasigas" system of molecules and phonons we can use kinetic equations of the Boltzmann type for single-particle distribution functions.[11,12] It is found that nonlocal interfacial effects can be described in such a system by incorporating the interaction between the nonequilibrium subsystems of molecules and phonons in the boundary conditions on the distribution functions of these particles at the interface. Boundary conditions of this type are constructed below, in Section 3, from a microscopic picture of the scattering of molecules and phonons by a surface. We also show that boundary conditions of this sort have definite symmetry properties, which reflect the principle of detailed balance (the time reversibility of the microscopic equations of motion) in the case of the interaction of nonequilibrium subsystems.

In Section 4 we solve the problem of the nonisothermal flow of a collisionless gas in a channel with a nonequilibrium wall. We examine the simultaneous solution of the kinetic equations for molecules and phonons with boundary conditions written in the one-phonon approximation.[13] In this approximation, we prove Onsager relations for interfacial cross effects. Calculations based on the continuum model of a solid with a boundary[14,15] show that under conditions such that the phonon drag of the molecules becomes the dominant factor the gas flux through a channel does not depend on the mass m of the gas molecules, does depend on the temperature (strongly; it is proportional to T^{-2} in the low-temperature limit), is proportional to the square of the channel diameter (d^2), and depends strongly on the material of the channel wall, in particular, on the fourth power of the sound velocity. Each aspect of this behavior differs fundamentally from that which has been established for wide channels, where the (isothermal) gas flux is proportional to $(T/m)^{1/2}d^3$ and depends only slightly on the wall material.

In Section 5 we generalize this theory to the case of a mixture of gases. It is found that when we take into account the phonon drag of the molecules the spatial separation of the mixture in a nonisothermal flow through a channel (or porous solid) may be greatly enhanced. We discuss a possible manifestation of this effect in existing experimental data.

Before we take up the derivation of a kinetic theory for these effects, it is useful to look at them from the standpoint of the thermodynamics of irreversible processes (Section 2). The thermodynamic analysis of nonequilibrium phenomena is based on an analysis of entropy production,[16] which makes it possible to identify generalized forces and fluxes in the system and to determine the nature of the (linear) relations between them. As we will show below, in a nonequilibrium system with an interface the entropy production in one medium generally depends on the nonequilibrium state of the other medium. It is this dependence, which implies a nonlocal coupling between the fluxes and forces in different media, which expresses the thermodynamic meaning of this class of nonequilibrium effects. An expression for the entropy production is derived (Subsection 2a) from simple macroscopic considerations which amount to a generalization of the thermodynamics of discontinuous systems[16] to a system with an interface. This expression is also derived by a kinetic theory (Subsection 2b). It is shown here that the matrix of kinetic coefficients includes quantities of two types. First, there are the ordinary kinetic coefficients which are used in a single-phase analysis of transport processes and which determine the macroscopic fluxes (the average fluxes over a cross section of the subsystem) in this case under the influence of the thermodynamic forces which are set up in the same medium. Second, there are new kinetic coefficients, which determine macroscopic fluxes (again, averages over the cross section of the subsystem) in the given medium under the influence of forces applied to the other medium. The derivation of these kinetic coefficients is the basic content of Sections 3–5 of this paper.

2. THERMODYNAMICS OF IRREVERSIBLE PROCESSES IN A UNIFIED NONEQUILIBRIUM GAS-SOLID SYSTEM

a) Macroscopic approach. We consider a weakly nonequilibrium system (Fig. 1) including a gas between solid surfaces with tangential gradients of the gas pressure (∇p); of the gas temperature (∇T_g), and of the temperature of the solid (∇T_S). We assume that the system is homogeneous in the longitudinal direction, that its longitudinal dimension satisfies $b \gg \lambda_M$, λ_{ph}, d; and that there is no heat or mass transport normal to the interfaces.[1)] These conditions are met in the nonisothermal glow of a gas in a capillary or plane gap. Despite the condition $\nabla T_g = \nabla T_s$, it is convenient to treat the temperature gradients ∇T_g and ∇T_s as independent thermodynamic forces which are applied externally to the gas and the solid, respectively. In this approach, the matrix of kinetic coefficients of the system will contain known quantities (pertaining to the gas or the solid) and new coefficients corresponding to interfacial effects.

In accordance with ideas from the thermodynamics of nonequilibrium systems,[16] it can be assumed that a nonequilibrium state of this system is maintained as the result of an exchange of energy and particles between two other systems (A and B) which are in contact with our system (Fig. 1). Under the assumption that systems A and B are quite large, we may assume that they are in equilibrium. Writing the equilibrium thermodynamic relations[17] between the differentials of the energy, the entropy, and the number of particles for systems A and B, and assuming that the total energy and the number of particles are conserved, we can easily derive an expression for $\dot{s}_{AB}$, the change per unit time in the

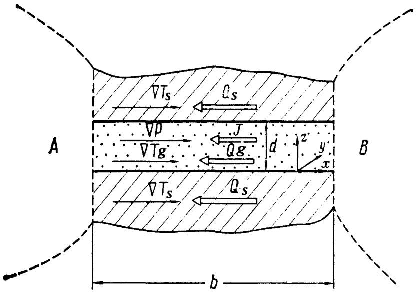

FIG. 1.

net entropy of systems A and B. The quantity $\dot{s}_{AB}$ must be equal (in a steady state) to the entropy production by virtue of dissipative processes in our nonequilibrium system. Ignoring edge effects at the boundaries with systems A and B, we find the following expression for the production of entropy S per unit length of the system:

$$S=\frac{\dot{s}_{AB}}{b}=-J\frac{\nabla p}{p}-Q_g\frac{\nabla T_g}{T^2}-Q_s\frac{\nabla T_s}{T^2}, \tag{2.1}$$

where J, Q_g, and Q_S are the total fluxes (over the cross section of the gas and the solid) of the number of molecules and of the heat in the gas and in the solid. Below, we will also derive expression (2.1) for the entropy production from microscopic (kinetic) considerations.

In the ordinary single-phase construction of the thermodynamics of irreversible processes,[16] an expression for the production of entropy of the gas is found as a sum of the first two terms on the right side of (2.1). The production of entropy of the solid is equal to the third term in (2.1). When there is an interfacial interaction, however, the entropy production in the gas and that in the solid cannot be considered independently, since the dissipation which stems from the collisions of particles (or quasiparticles) of a given medium in the surface region may depend on the nonequilibrium state of the other medium. Consequently, there may in general be a linear relationship between all the thermodynamic forces and fluxes in (2.1), in particular, between quantities pertaining to different media:

$$\begin{vmatrix} J \\ Q_g \\ Q_s \end{vmatrix} = -\begin{vmatrix} L_{11}L_{12}L_{13} \\ L_{21}L_{22}L_{23} \\ L_{31}L_{32}L_{33} \end{vmatrix}\begin{vmatrix} \nabla p/p \\ \nabla T_g/T^2 \\ \nabla T_s/T^2 \end{vmatrix}. \tag{2.2}$$

The matrix $\{L_{ij}\}$ of kinetic coefficients incorporates cross coefficients L_{i3}, L_{3i}, $i=1, 2$, in addition to the ordinary coefficient L_{ii}, $i=1, 2, 3$, and the familiar cross coefficients $L_{12}=L_{21}$, which describe thermotranspiration and mechanocaloric effects.[16] These cross coefficients describe a new physical phenomenon: the onset of transport processes in one medium when a thermodynamic force is set up in another medium. As will be shown below by direct calculation (Section 4), for these new kinetic coefficients, as for the classical coefficients, Onsager relations hold: $L_{ij}=L_{ji}$, i, $j=1, 2, 3$. The nonlocal, nonequilibrium effects which are described by the kinetic coefficients L_{i3} and L_{3i} $(i=1, 2)$ may be interpreted as effects of a drag imposed on the gas molecules by the phonons and of a drag imposed on the phonons by the molecules, respectively. In this sense, these coefficients are analogous to the well-known drag effects in the electron-phonon system in a metal, but in the present case there is the fundamental distinction that the drag process takes place at an interface.

How large are these new kinetic coefficients? Under what conditions would they be important? We assume for definiteness that we are dealing with a gas in a long plane channel with transverse dimensions d and a $(a \gg d)$. We first consider L_{13}. Clearly, the component $-L_{13}\nabla T_s/T^2$ of the gas flux density in the channel—a component which stems from the phonon drag of the molecules—must be proportional to the characteristic gas flux density $n_g\bar{v}$ [n_g is the number density of gas particles and $\bar{v}\sim(T/m)^{1/2}$ is the average velocity of the molecules], to the cross-sectional area $(\lambda_M a)$ of the Knudsen layer near the surface, which the molecules cross without undergoing collisions, and to the dimensionless parameter $\lambda_{ph}\nabla T_s/T$, which is a measure of the deviation of the solid from equilibrium. This component of the gas flux density must furthermore contain a parameter which reflects the efficiency of the "transfer of deviation from equilibrium" from the phonons to the gas molecules. We assume that nearly every impact of a molecule on the surface is accompanied by the creation (or annihilation) of one phonon. Noting that the average momentum of a molecule is comparable to the quasimomentum of a thermal phonon, we may then consider this parameter to be of order unity. We find $L_{13}\sim n_g\bar{v}T\lambda_M\lambda_{ph}a$. Similar arguments lead to the same result for L_{31}:

$$L_{31}\sim n_s cT\lambda_M\lambda_{ph}a\frac{n_g\bar{v}}{n_s c},$$

where n_S is the number density of the solid, and c is the velocity of sound. Here we have taken into account the fact that when a phonon is scattered by the surface the probability for the absorption of this phonon by a gas molecule is small and can be estimated to be the ratio $n_g\bar{v}/n_s c$ of the flux densities of molecules and phonons toward the surface. It is also a simple matter to find L_{23}, $L_{32}\sim TL_{13}$. Working in a similar way for the ordinary kinetic coefficients, we find the familiar results

$$L_{12},\ L_{21}\sim n_g\bar{v}\ T\lambda_M^2 a,\qquad L_{11}\sim n_g\bar{v}\,\lambda_M da,$$
$$L_{22}\sim n_g\bar{v}\ T^2\lambda_M da,\quad L_{33}\sim n_s cT^2\lambda_{ph}Da,$$

where D is the transverse dimension of the solid. The ratios of the "gaseous" off-diagonal kinetic coefficients to the corresponding diagonal coefficients L_{12}/L_{11}, L_{13}/L_{11}, L_{21}/L_{22}, L_{23}/L_{22} are proportional to the Knudsen number $\mathrm{Kn}=\lambda_M/d$. The reason is that the interfacial cross effects, like the known effects of thermotranspiration and the mechanocaloric effect, develop in a Knudsen layer (of thickness $\sim\lambda_M$) near the surface. In the limit of a high gas pressure, these effects disappear. For the ratio of the interfacial and intrafacial cross kinetic coefficients we find $L_{13}/L_{12}\sim\lambda_{ph}/\lambda_M$, $L_{23}/L_{21}\sim T\lambda_{ph}/\lambda_M$. The effects of the phonon drag of the molecules are thus comparable to the thermotranspiration effect and the mechanocaloric effect if

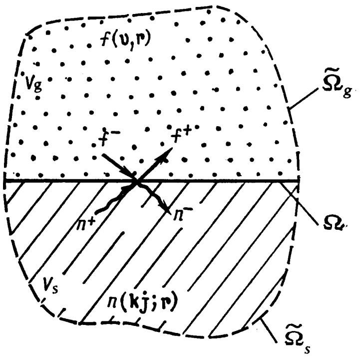

FIG. 2.

$\lambda_M \sim \lambda_{\rm ph}$. At room temperature, however, we would have $\lambda_{\rm ph} \sim 100$ Å, and for most gases λ_M reaches such values at pressures ~ 10 atm. In systems of ordinary geometric scale, the boundary effects in the gas at such pressures are usually negligible.[2)] On the other hand, in collisionless flow ($\mathrm{Kn} \gg 1$), for arbitrary gas pressures, the role of the mean free path of the molecules is played by the channel width d. Replacing λ_M by d in the estimates, we find

$$L_{13}/L_{12} \sim L_{13}/TL_{11} \sim \lambda_\Phi/d, \quad L_{23}/L_{21} \sim TL_{23}/L_{22} \sim T\lambda_{\rm ph}/d\,.$$

In thin channels, of width $d \sim \lambda_{\rm ph}$, it is thus of fundamental importance to take these nonequilibrium effects, L_{13} and L_{23}, into account.

The effect of the deviation of the gas from equilibrium on the heat flux in the solid is small ($L_{31}/T, L_{32} \ll L_{33}$), as is intuitively obvious. According to our calculations, this effect is small because the parameters $\lambda_{\rm ph}/D$ and n_g/n_S are small.

b) Microscopic derivation of an expression for the entropy production. Let us derive an entropy balance equation in a characteristic element of a nonequilibrium heterogeneous system including an interface with small adjacent regions of the media which are in contact (Fig. 2). For this purpose we generalize the formal procedure[11,12] which is used in the kinetic theories of single-phase systems. Using the expressions for the entropy of gases of molecules and phonons,[17,12] we find the following expression for the total entropy of this characteristic element:

$$S=S_{\text{г}}+S_{\text{т}}, \tag{2.3}$$

$$S_{\text{г}}=\int\limits_{V_{\text{г}}} d\mathbf{r} \int d\mathbf{v}\, f \ln\frac{e}{f}, \tag{2.4}$$

$$S_{\text{т}}=\int\limits_{V_{\text{т}}} d\mathbf{r} \sum_{\mathbf{k}j} [\,(n+1)\ln(n+1)-n\ln n\,], \tag{2.5}$$

where $f=f(\mathbf{v}, \mathbf{r}, t)$ and $n=n(\mathbf{k}, j, \mathbf{r}, t)$ are the distribution functions of the gas molecules and the phonons, $\mathbf{v}$ is the velocity of a molecule, $\mathbf{k}$ and j are the wave vector and polarization of the phonon, $\mathbf{r}$ is the spatial coordinate, and the gas is assumed to be monatomic. The integration over $\mathbf{r}$ in (2.4) and (2.5) is carried out over the entire volume of the gas (V_g) and of the solid (V_S) in this characteristic element. We make use of the kinetic equations for the gas molecules and the phonons:

$$\frac{\partial f}{\partial t}+\mathbf{v}\frac{\partial f}{\partial \mathbf{r}}=I_M\{f\}, \tag{2.6}$$

$$\frac{\partial n}{\partial t}+\mathbf{c}\frac{\partial n}{\partial \mathbf{r}}=I_g\{n\}, \tag{2.7}$$

where I_M and $I_{\rm ph}$ are the collision integrals of the molecules and the phonons, respectively, and $\mathbf{c}(\mathbf{k}, j)$ is the phonon group velocity. Differentiating relations (2.3)–(2.5) with respect to the time, replacing the derivatives $\partial f/\partial t$ and $\partial n/\partial t$ with the help of Eqs. (2.6) and (2.7), and then transforming from a volume integral to a surface integral in the terms containing $\partial/\partial\mathbf{r}$, we find

$$\frac{dS}{dt}=-\int\limits_{\Omega_g} \mathbf{J}_g^{(S)}\zeta_g d^2r-\int\limits_{\Omega_s} \mathbf{J}_s^{(S)}\zeta_s\, d^2r+S_g+S_s\,. \tag{2.8}$$

Here

$$\mathbf{J}_g^{(S)}=\int d\mathbf{v}\, \mathbf{v} f\ln\frac{e}{f}, \tag{2.9}$$

$$\mathbf{J}_s^{(S)}=\sum_{\mathbf{k}j}\mathbf{c}[\,(n+1)\ln(n+1)-n\ln n\,], \tag{2.10}$$

$$\dot S_g=-\int\limits_{V_g} d\mathbf{r}\int d\mathbf{v} I_M\{f\}\ln f, \tag{2.11}$$

$$S_s=-\int\limits_{V_s} d\mathbf{r}\sum_{\mathbf{k}j} I_{\rm ph}\{n\}[\,(n+1)\ln(n+1)-n\ln n\,]. \tag{2.12}$$

The integration in the first two terms on the right side of (2.8) is carried out over the complete surface bounding the gas (Ω_g) and the complete surface bounding the solid (Ω_S), respectively, in our characteristic element; ξ_g and ξ_S are the outward normals to these surfaces. Assuming $dS/dt=0$ in a nonequilibrium steady state, and separating the integration over the interface boundary (Ω) from the integration over the outer surfaces of our characteristic element ($\tilde\Omega_g$ and $\tilde\Omega_S$) on the right side of (2.8), we can rewrite Eq. (2.8) as

$$\int\limits_{\tilde\Omega_g} \mathbf{J}_g^{(S)}\zeta_g d^2r+\int\limits_{\tilde\Omega_s} \mathbf{J}_s^{(S)}\zeta_s\, d^2r=\dot S, \tag{2.13}$$

where

$$S=S_g+S_s+S_{\rm srf}, \qquad S_{\rm srf}=-\int\limits_{\Omega} \mathbf{J}_g^{(S)}\zeta_g d^2r+\int\limits_{\Omega} \mathbf{J}_s^{(S)}\zeta_s\, d^2r. \tag{2.14}$$

Expression (2.13) is the entropy balance equation in the steady state. On the left side of this equation we have the total entropy flux across the boundary of our system (Fig. 2), while on the right side we have the internal production of entropy in the nonequilibrium system. The quantities $\dot S_g$ and $\dot S_S$ given by (2.11) and (2.12) describe[11,12] dissipations which result from molecule-molecule and phonon-phonon collisions in the gas volume and in the solid, respectively. The surface production of entropy, $\dot S_{\rm srf}$, in (2.14) is the jump in the total entropy flux at the interface. (The concept of a surface entropy production was originally introduced by Waldmann,[20] in an attempt to derive by a thermodynamic method boundary conditions on the moment equations of the kinetics of low-density gases.) To determine the explicit dependence of $\dot{S}_{\rm srf}$ on the microscopic scattering laws for the molecules and phonons at the interface, we need to use boundary conditions on the distribution functions of the molecules and phonons (we have not previously considered these boundary conditions). In general, boundary conditions of this sort take the form of a functional dependence of the distributions of the (quasi) particles which are reflected from the surface (f^+ and n^-) on the distributions of the (quasi) particles incident on the surface (f^-, n^+):

$$f^+(\mathbf{r})=F\{f^-(\mathbf{r}),\, n^+(\mathbf{r})\},\quad \mathbf{r}\in\Omega, \tag{2.15}$$

$$n^-(\mathbf{r})=\Phi\{f^-(\mathbf{r}),\, n^+(\mathbf{r})\},\quad \mathbf{r}\in\Omega \tag{2.16}$$

When equations like (2.15) and (2.16) are taken into account, expressions (2.9) and (2.10) lead to an expression for $\dot{S}_{\rm srf}$ which is analogous in meaning to expressions (2.11) and (2.12). It relates $\dot{S}_{\rm srf}$ with f^-, n^+, and the microscopic parameters of the interaction (through F and Φ).

The scattering of molecules and phonons by an interface reduces to elastic scattering by the corresponding surface potentials and inelastic scattering associated with the exchange of energy and momentum between molecules and phonons. The latter also gives rise to a dependence of f^+ on n^+ and of n^- on f^- in (2.15) and (2.16). A fundamental point in this paper is the incorporation of the dependence of f^+ on the nonequilibrium distribution n^+ and the dependence of n^- on the nonequilibrium distribution f^-. Boundary conditions of this type will be found below (Section 3) on the basis of microscopic considerations. At this point, we turn to the thermodynamic consequences of the "coupling" of the nonequilibrium distributions f and n at the interface. Regrouping terms in (2.14), we can rewrite the expression for the total entropy production in the heterogeneous system as follows:

$$S=S_{gp}+S_{Sp}, \tag{2.17}$$

$$S_{gp}=S_g-\int\limits_{\Omega}\mathbf{J}_g^{(S)}\zeta_g\,d^2r, \tag{2.18}$$

$$S_{Sp}=S_s-\int\limits_{\Omega}\mathbf{J}_s^{(S)}\zeta_s\,d^2r. \tag{2.19}$$

Since $\dot{S}_g$ and $\mathbf{J}_g^{(S)}$ [see (2.9) and (2.11)] depend directly on only the gas distribution function, the quantity $\dot{S}_{gp}$ in (2.17) may be interpreted as the entropy production of the gas when both molecule-molecule and molecule-surface collisions are taken into account; $\dot{S}_{Sp}$ is the corresponding quantity for the solid. In this sense [cf. (2.14)] the entropy production in (2.17) is additive, as is the entropy itself in (2.3). However, by virtue of the dependence of f^+ on n^+ in (2.15), it follows from (2.18), (2.9), and (2.11) that the entropy production of the gas depends on the nonequilibrium state of the solid. Analogously, the entropy production of the solid generally depends on the nonequilibrium state of the gas. As a result, in a unified nonequilibrium system the transport processes in one medium cannot in general be examined without reference to the transport processes in the other medium.

When we ignore the coupling of the nonequilibrium distribution functions f and n at the interface, we can treat Eq. (2.13), with (2.17), as the formal sum of two independent equations pertaining to different media. We are then led to a single-phase formulation of the thermodynamics of irreversible processes.[16] [For example, an expression like (2.18) was used in Ref. 21 in deriving a kinetic basis for the applicability of the methods of the thermodynamics of nonsteady systems to the dynamics of low-density gases.] The single-phase approximation in a description of a nonequilibrium heterogeneous system corresponds to two possible representations. The first is that in which the interaction the particles of the given medium with elements of other media can be replaced by an interaction with a given potential barrier. An example is the resistance of a channel in isothermal (Poiseuille) flow of a gas, which is found in the zeroth approximation by considering only the elastic scattering by the surface potential, which leads to an accommodation of the tangential momentum of the molecules. The second case is that in which the nonequilibrium medium in contact with the medium under consideration can be assumed to be locally in equilibrium. This assumption implies $n^+=n_0$ in (2.15) and $f^-=f_0$ in (2.16), where n_0 and f_0 are corresponding locally equilibrium distributions. This approximation is used in most problems of the kinetics of low-density gases (heat transfer between a gas and a surface, thermotranspiration, etc.). As for the kinetics of a solid, the presence of a gas above its surface can usually be completely ignored. Perhaps the only exceptional case would be the dependence of the attentuation of surface sound on the pressure of the gas.[22]

Let us return to the complete nonequilibrium system in Fig. 1. The entropy balance in an element of the system of unit length (along the x axis) will evidently again be of the form in (2.13). Here $\dot{S}$ is the total entropy production in the element presently under consideration, and the integral on the left side of (2.13) is evaluated over the external surfaces, i.e., over the two vertical planes, Ω' and Ω'', described by the equations $x=x'$ and $x=x''$, which bound the element. We make use of the fact that in a weakly nonequilibrium system the distribution functions differ only slightly from locally equilibrium functions:

$$f(\mathbf{v},\mathbf{r})=f_0(v,x)\,[1+\varphi(\mathbf{v},\mathbf{r})],$$

$$f_0=\exp\left(\frac{\mu_g(x)}{T_{\rm r}(x)}-\frac{mv^2}{2T_g(x)}\right),\quad |\varphi|\ll 1; \tag{2.20a}$$

$$n(\mathbf{k}j,\mathbf{r})=n_0(\omega,x)\,[1+\psi(\mathbf{k}j,\mathbf{r})],$$

$$n_0=\left[\exp\left(\frac{\hbar\omega}{T_s(x)}\right)-1\right]^{-1},\quad |\psi|\ll 1. \tag{2.20b}$$

Here μ_g is the chemical potential of the gas, which, like the temperature, depends on the coordinate x, and $\hbar\omega(\mathbf{k}j)$ is the energy of a phonon. Using (2.9) and (2.20a), we find the following expression for the total entropy flux across Ω_g' that part of the plane Ω' which intersects the gas:

$$\int\limits_{\Omega_g'} \mathbf{J}_g^{(S)} \zeta_g \, d^2 r \approx \frac{1}{T_g(x')} \widetilde{Q}_g - \frac{\mu_g(x')}{T_g(x')} J, \tag{2.21}$$

where $\widetilde{Q}_g$ is the total energy flux through the gas. The energy flux $\widetilde{Q}_g$ and the particle number flux J in (2.21) are integrals of the functions $v_x \frac{mv^2}{2} f_0 \varphi$ and $v_x f_0 \varphi$ over the surface and over the phase volume of the molecules, respectively. On the right side of (2.21) we have omitted some analogous terms, which appear raised to a power higher than the first in the integrand in the expression for the function φ. Analogously, using (2.20b), we find the following expression for the total entropy flux across Ω_S', that part of the plane Ω' which intersects the solid:

$$\int\limits_{\Omega_s'} \mathbf{J}_s^{(S)} \zeta_s \, d^2 r \approx \frac{1}{T_s(x')} Q_s \ . \tag{2.22}$$

We also write relations for the entropy fluxes across the Ω' plane, and we substitute them along with (2.21) and (2.22) into Eq. (2.13). Transforming from the total energy flux through the gas, $\widetilde{Q}_g$, to the heat flux Q_g, and making use of the linear dependence of μ and T on x, we immediately find Eq. (2.1).

Comparing the macroscopic derivation of Eq. (2.1) (Section 2a) with the kinetic derivation of this equation, we note that the former is based on three postulates: 1) entropy balance, $\dot{S} = \dot{S}_{AB}/b$; 2) the hypothesis of a local equilibrium, which in this case means the use of equilibrium thermodynamic relations for systems A and B (Fig. 1); and 3) the treatment of the nonequilibrium system with an interface as a unified whole. According to the kinetic theory, postulate 1) is simply a consequence of the kinetic equations; expressions (2.20a) and (2.20b) are equivalent to postulate 2); and coupled boundary conditions like (2.15) and (2.16) correspond to postulate 3).

There is another point to be noted. In the expression (2.1) found for the entropy production and in the expressions (2.2) found from it for the kinetic coefficients, the total heat and mass fluxes (over the cross section of the system) are used. In this form, the expressions are completely consistent with experiment, where it is always total fluxes which are measured. It can be shown, however, that an analysis of nonlocal phenomena (which these interfacial cross effects obviously are) should be carried out in terms of local values of the thermodynamic forces and fluxes, coupled with each other by integral relations with nonlocal kernels. In principle, relations of this sort could easily be derived by analogy with the derivation above [it is sufficient to return to a volume integral on the left side of (2.13), noting that there are no entropy fluxes across the interface in approximation (2.21), (2.22), and then working with local fluxes]. In the case at hand, however, of gradients ∇T and ∇p which are independent of $\mathbf{r}$, the relations of this sort degenerate[10] and reduce to (2.1), (2.2).

3. BOUNDARY CONDITIONS ON THE DISTRIBUTION FUNCTIONS OF THE MOLECULES AND PHONONS

In the kinetic theory of gases, the Boltzmann equation is used. If an interaction of molecules with a solid surface must be taken into account, the Boltzmann equation is supplemented with boundary conditions which relate the distribution functions of the molecules incident on the surface with those of the molecules reflected from it.[11,23]. Boundary conditions of this type can be constructed without a rigorous derivation, on the basis of physical considerations. Strictly speaking, we also lack a formal derivation of the possibility of applying to a system with an interface a kinetic equation for a single-particle distribution function which is derived from an equation for a multiparticle distribution function in an unbounded gas.[24] From the physical standpoint, however, the validity of this formulation of the boundary-value problems would hardly raise any doubt. In the present paper, where we are also offering only a "physical" derivation of the basic equations, we are extending this approach to the unified nonequilibrium system consisting of a gas and a solid. Our purpose in this section of the paper is to derive boundary conditions for the distribution functions of the molecules and the phonons, taking into account the nonequilibrium state of the solid and the gas, respectively. We assume that the surface is formed by a cleaved face of a single crystal and has no chemisorbed layer. As we will show below, under certain restrictions on the gas density, the temperature, and the purity of the crystal such boundary conditions can be obtained by applying the relations of formal scattering theory to the interaction of the molecules and the phonons with the surface.

In general, the distribution function of the incident gas molecules, f^-, and that of the molecules reflected from the surface, f^+, are related by an equation of the type[11,23]

$$|\mathbf{v}\boldsymbol{\xi}|\, f^+(\mathbf{v}) = \int\limits_{\mathbf{v}'\boldsymbol{\xi}<0} d\mathbf{v}' \, |\mathbf{v}'\boldsymbol{\xi}| \, W(\mathbf{v}' \to \mathbf{v}) \, f^-(\mathbf{v}'), \tag{3.1}$$

where $\boldsymbol{\xi}$ is the unit normal to the surface, directed from the solid into the gas. If the (physical) adsorption of molecules on the solid surface can be ignored,the kernel W of integral transformation (3.1) does not depend on f^- and represents the probability density for a transition of the molecule from a state with velocity $\mathbf{v}'$ to a state with velocity $\mathbf{v}$ in the course of scattering by the clean surface. We assume that the average time t_a spent by a molecule in the effective range of the surface forces is much shorter than the time t_d for the decay of the vibrational state of the solid. (For the case of scattering of molecules by a surface without capture we would have $t_a \sim r_0/\tilde{v} \sim 10^{-12}$ s, where r_0 is a scale length of the effective range of the surface forces, and t_d is equal in order of magnitude to the average lifetime of the phonons, having a value $t_d \sim 10^{11}$ s both in the interior and near the surface of sufficiently pure crystals at room temperatures.[27,12]) The scattering of molecules by a surface can be treated by dynamic scattering theory. The probability W can then be written[25,13]

$$W(\mathbf{v}' \to \mathbf{v}) = \sum_{ss'} \rho(s') \, W_D(\mathbf{v}'s' \to \mathbf{v}s) \ . \tag{3.2}$$

Here s' and s are sets of quantities characterizing the state of the solid respectively before and after the collision of the molecule, W_D is the probability density for a dynamic transition in the molecule-solid system, and ρ is the distribution function over the states of the solid. In the approaches which have been taken previously,[25,13] the solid has been assumed to be at equilibrium; correspondingly, the assumption $\rho(s') \propto \exp(-E_{s'}/T)$ was used, where E'_s is the energy of the solid. The basic feature of the theory which we are deriving here is the incorporation in (3.2) of a nonequilibrium state of the solid. It turns out that when we use a special representation for the states s', s we can —without calculating ρ—express the kernel $W(\mathbf{v}'\to\mathbf{v})$ in terms of the distribution function of the phonons incident on the surface. In speaking of the states s we mean a set of occupation numbers $\{N_i\}$ of vibrational normal modes of a semi-infinite harmonic crystal. Included in this category are[28] the collective vibrations which involve either a finite number of atomic layers near the solid surface (surface modes) or the entire crystal (internal modes). For simplicity, we will ignore surface modes, which make an additive contribution to the nonequilibrium interfacial effects under consideration here in the single-phonon approximation, which we use below. The internal modes are determined by specifying their asymptotic behavior in the interior of the crystal. They can be chosen in such a way[15,29] that each mode corresponds to a wave which is incident on the surface with a wave vector $\mathbf{k}$, a polarization j, a frequency $\omega(\mathbf{k},j)$, and a component of the group velocity $\mathbf{c}(\mathbf{k},j)$ which is normal to the surface $\zeta = \partial\omega/\partial\,\mathbf{k}\zeta > 0$; and a corresponding set of reflected waves. This behavior of the vibrational normal modes of a solid, determined unambiguously by the values of $\mathbf{k}$ and j of the wave incident on the surface, corresponds to the representation of diverging waves in formal scattering theory.[29] Formal scattering theory relates the transition probability W_D with $s = \{N_{\mathbf{k}j}\}$ and $s' = \{N'_{\mathbf{k}j}\}$ to the matrix elements of the $\hat{T}$ scattering operator:

$$W_D(\mathbf{v}', \{N_{\mathbf{k}j}'\}\to\mathbf{v}, \{N_{\mathbf{k}j}\})$$

$$=\frac{2\pi}{\hbar|\mathbf{v}'\zeta|}\left(\frac{m}{2\pi\hbar}\right)^3 |\mathbf{v}, \{N_{\mathbf{k}j}\}\,|\,\hat{T}\,|\,\mathbf{v}', \{N_{\mathbf{k}j}'\})\,|^2\delta(\varepsilon-\varepsilon'), \quad (3.3)$$

$$\varepsilon = \frac{mv^2}{2} + \sum_{\mathbf{k}j} \hbar\omega N_{\mathbf{k}j}. \quad (3.4)$$

When the probability W_D, which depends on the set of initial occupation numbers $\{N'_{\mathbf{k}j}\}$, according to (3.3), is averaged with the distribution function ρ in expression (3.2), the probability W becomes a function of the average occupation numbers $\bar{N}'_{\mathbf{k}j}$ of each mode $(\mathbf{k}, j)$ before the collision:

$$\bar{N}'_{\mathbf{k}j} = \sum_{\{N'_{\mathbf{k}j}\}} N'_{\mathbf{k}j}\rho(\{N'_{\mathbf{k}j}\}). \quad (3.5)$$

In a determination of the vibrational normal modes by this method, the average occupation number $\dot{\bar{N}}'_{\mathbf{k}j}$ represents the distribution function of the phonons which are incident on the surface. That function was denoted $n^+(\mathbf{k}, j)$ above, and it must obey the kinetic equation (2.7). We thus have $W = W(\mathbf{v}'\to\mathbf{v};\, n^+(\mathbf{k}, j))$ for the kernel of the integral transformation (3.1). When we take into account the dependence of the probability W on the phonon distribution function, expression (3.1) is an unknown boundary condition on the distribution function of the molecules which are scattered from the surface of a nonequilibrium solid. The explicit functional dependence of W on $n^+(\mathbf{k}, j)$ can be written only for processes involving the scattering of molecules by a surface which involve the creation (or annihilation) of a certain number of phonons. We will go through this procedure below (in the Appendix) in the single-phonon approximation for W_D.

We now take up the construction of a boundary condition for phonons. We first consider the case in which a crystal is bordered by a vacuum. We assume that the phonon mean free path ($\lambda_{\text{ph}} \sim 10^{-6}$ cm at $T \sim 300$ K; Ref. 12) is considerably larger than the dimension of the surface region (a few atomic layers[28]), where the surface has a significant effect on the vibrations of atoms. We also note that the anharmonicity of the surface atoms is not much greater than that of an atom in the interior of a solid, according to experiments.[27] We can thus ignore the collisions of phonons near the surface. In constructing the boundary condition on the phonon distribution function we can therefore deal with the scattering of phonons by a surface potential associated with the rupture of some of the bonds of the atoms in the surface layer[28] and taken into account in the harmonic approximation. At the interface of a crystal with vacuum, the distribution functions of the phonons incident on the surface (n^+) and of the phonons reflected from the surface (n^-) can thus be related by

$$|\mathbf{c}\zeta|\,n^-(\mathbf{k}j) = \sum_{\mathbf{k}_1 j_1\,(\mathbf{c}_1\zeta>0)} |\mathbf{c}_1\zeta|\,V(\mathbf{k}_1 j_1 \to \mathbf{k}j;\,\omega)\,n^+(\mathbf{k}_1 j_1), \quad (3.6)$$

where V is the probability for the transition of a phonon with $\hbar\omega$ from the state (mode) $(\mathbf{k}_1 j_1)$ to the state $(\mathbf{k}j)$. Methods for calculating V are given in Ref. 28. A relation similar in structure to (3.6) also holds[30] for the case of an interface between two solids.

A gas above the surface also leads to the absorption or creation of phonons in collisions of molecules with the surface. Using transition probability (3.3), we can write the change per unit time in the average number of phonons in some mode $\mathbf{k}_1 j_1$ as

$$\dot{\bar{N}}_{\mathbf{k}_1 j_1} = \int_{\mathbf{v}\zeta>0} d\mathbf{v} \int_{\mathbf{v}'\zeta<0} d\mathbf{v}'\,|\mathbf{v}'\zeta|\,f^-(\mathbf{v}') \sum_{\{N'\}\{N\}} \rho(\{N'_{\mathbf{k}j}\})\,(N_{\mathbf{k}_1 j_1} - N'_{\mathbf{k}_1 j_1})$$

$$\times W_D(\mathbf{v}', \{N'_{\mathbf{k}j}\} \to \mathbf{v}, \{N_{\mathbf{k}j}\}). \quad (3.7)$$

As in the case of W, the quantity $\dot{\bar{N}}_{\mathbf{k}_1 j_1}$ depends on the distribution function of the phonons incident on the surface, by virtue of (3.5), and also on the distribution function of the molecules: $\dot{\bar{N}}_{\mathbf{k}_1 j_1} = \dot{\bar{N}}_{\mathbf{k}_1 j_1}\{f^-, n^+\}$. In describing the vibrations of a semi-infinite solid by the method described above, the quantity $\dot{\bar{N}}_{\mathbf{k}_1 j_1}$ represents that change in the flux density of $(\mathbf{k}_1 j_1)$ phonons incident on the surface which is caused by the creation or annihilation of these phonons through the interaction of gas molecules with the surface. Consequently, the boundary condition on the phonon distribution function at the solid-gas interface can be written

$$|\mathbf{c}\zeta|\,n^-(\mathbf{k}j) = \sum_{\mathbf{k}_1 j_1\,(\mathbf{c}_1\zeta>0)} [|\mathbf{c}_1\zeta|\,n^+(\mathbf{k}_1 j_1) + \dot{N}_{\mathbf{k}_1 j_1}]\,V(\mathbf{k}_1 j_1 \to \mathbf{k}j;\ \omega). \quad (3.8)$$

The boundary condition on the phonons could be written in a different (equivalent) way. For example, in a calculation of W_D in (3.3) on the basis of scattering theory, we could use a converging-wave representation[29] for s', s. This approach would correspond to introducing normal vibrational modes of a semi-infinite crystal, whose asymptotic form is a set of waves incident on the surface and a single reflected wave. In this case, $\dot{N}_{\mathbf{k}j}$ would depend on the distribution function of the phonons reflected from the surface and would not appear inside the summation on the right side of (3.8); instead, it would appear additively on the left side of (3.8). However, this way of writing the boundary condition is less convenient for use in a kinetic theory.

It is not difficult to show that the generalized boundary conditions on the molecules and phonons satisfy some general requirements which we would expect from the macroscopic standpoint. For example, by virtue of the normalization of the functions W_D and ρ in (3.2), the probability W is normalized in the sense $\int W d\mathbf{v} = 1$, so that the flux densities of molecules incident on and reflected from the surface are equal in (3.1) (there is no accumulation of molecules at the wall). In contrast, despite the normalization of the probability V in (3.8), in the scattering of phonons by a solid-gas interface in a nonequilibrium system the flux densities of incident and reflected phonons (i.e., the energy fluxes) are not equal, because of the condition $\dot{N} \neq 0$. If $f^- = f_0$ and $n^+ = n_0$, where f_0 and n_0 are equilibrium distributions with an identical temperature, we have $\dot{N}_{\mathbf{k}_1 j_1}\{f_0, n_0\} = 0$. In this case, relations (3.1) and (3.8) lead to $f^+ = f_0$ and $n^- = n_0$, as they should in an equilibrium system.

To pursue the calculations and also to determine the physical meaning of the coupling of the nonequilibrium distribution functions of the molecules and the phonons at an interface in a weakly nonequilibrium system, we find it convenient to rewrite boundary conditions (3.1) and (3.8) in a linearized form, making use of (2.20a) and (2.20b):

$$|\mathbf{v}\zeta|\,f_0\varphi^+(\mathbf{v}) = \int_{\mathbf{v}'\zeta<0} d\mathbf{v}'\,|\mathbf{v}'\zeta|\,W_0(\mathbf{v}' \to \mathbf{v})\,f_0(\mathbf{v}')\,\varphi^-(\mathbf{v}') + \sum_{\mathbf{k}_1 j_1\,(\mathbf{c}_1\zeta>0)} P(\mathbf{k}_1 j_1 \to \mathbf{v})\,\psi^+(\mathbf{k}_1 j_1), \quad (3.9)$$

$$|\mathbf{c}\zeta|\,n_0\psi^-(\mathbf{k}j) = \int_{\mathbf{v}'\zeta<0} d\mathbf{v}'\,G(\mathbf{v}' \to \mathbf{k}j)\,\varphi^-(\mathbf{v}') + \sum_{\mathbf{k}_1 j_1\,(\mathbf{c}_1\zeta>0)} V(\mathbf{k}_1 j_1 \to \mathbf{k}j;\ \omega)\,[|\mathbf{c}_1\zeta| + R_{\mathbf{k}_1 j_1}]\,n_0\psi^+(\mathbf{k}_1 j_1). \quad (3.10)$$

Here

$$W_0 = W|_{n^+=n_0}, \quad R_{\mathbf{k}j} = \left.\frac{d\dot{N}_{\mathbf{k}j}}{dn}\right|_{n^+=n_0},$$

and the kernels W_0, P, G, and R of integral transformations (3.9) and (3.10) depend only on the locally equilibrium distributions f_0 and n_0 and also on the parameters which determine the dynamics of the scattering of the molecules and phonons. We also note that the temperature varies only in the direction tangent to the surface. In the Appendix we give expressions for the kernels W_0, P, G, and R which are found in the single-phonon approximation for W_D, which is justified[13] for the scattering of light molecules by a surface. We also give the explicit expressions for the kernels for the continuum model of a solid with a boundary and with a repulsive exponential potential for the molecule-surface interaction.

In the case $\psi = 0$, Eq. (3.9) reduces to a boundary condition which is used in the kinetic theory of gases, in the case in which the vessel wall can be assumed at equilibrium. The new term (the second term) on the right side of (3.9), which corresponds to the scattering of the molecules of an equilibrium gas by the surface of a nonequilibrium solid, causes the distribution function of the reflected molecules to depend on the phonon distribution function. Analogously, the second term on the right side of (3.10) corresponds to the scattering of the phonons of a nonequilibrium solid by a boundary with an equilibrium gas. The first term reflects the additional creation (or annihilation) of phonons at the surface due to the nonequilibrium nature of the gas. The kernels P and G describe the mutual drag of molecules and phonons and are responsible for nonequilibrium interfacial effects, as we will see in Section 4.

How is the principle of detailed balance manifested in a nonequilibrium gas-solid system? By virtue of the time reversibility of the microscopic equations of motion, the dynamic probabilities for the transitions, W_D and V, have the property

$$W_D(\mathbf{v}',\ s' \to \mathbf{v},\ s) = W_D(-\mathbf{v},\ s^T \to -\mathbf{v}',\ s'^T), \quad (3.11a)$$

$$V(\mathbf{k}_1 j_1 \to \mathbf{k}j;\ \omega) = V(-\mathbf{k}j \to -\mathbf{k}_1 j_1;\ \omega), \quad (3.11b)$$

where the T means time reversal. As a result of (3.11a), the kernels of integral relations (3.9) and (3.10) also have definite symmetry properties. The probability W_0 for the scattering of a molecule by an equilibrium wall satisfies the well-known reciprocity relation[25,31]

$$|\mathbf{v}'\zeta|\exp\left(-\frac{mv'^2}{2T}\right) W_0(\mathbf{v}' \to \mathbf{v}) = |\mathbf{v}\zeta|\exp\left(-\frac{mv^2}{2T}\right) W_0(-\mathbf{v} \to -\mathbf{v}'). \quad (3.12)$$

This relation follows directly from (3.2), since in an equilibrium solid $\rho(s')$ is a Gibbs distribution. Using (3.11a) and (3.11b), we easily find the following results for the kernels R, P, and G from expressions (A.7), (A.8), and (A.9) in the single-phonon approximation:

$$R_{\mathbf{k}j} = -R_{-\mathbf{k}j}, \quad (3.13)$$

$$[n_0(\mathbf{k}j) + 1]\,P(\mathbf{k}j \to \mathbf{v}) = G(-\mathbf{v} \to -\mathbf{k}j). \quad (3.14)$$

These relations are analogs of reciprocity relation (3.12) for, respectively, the scattering of phonons by an interface with an equilibrium gas and for the interaction between nonequilibrium subsystems of molecules and phonons. Relation (3.14) leads to Onsager relations for the interfacial cross kinetic coefficients [$L_{3i} = L_{i3}$, $i = 1, 2$ in (2.2)], as we will show below.

Although the new reciprocity relations in (3.13) and (3.14) were derived here in the single-phonon approximation, we made no additional assumptions, other than properties (3.11a) and (3.11b), in their derivation. Accordingly, analogous relations apparently hold in the general case.

4. TRANSPORT PROCESSES IN A NONEQUILIBRIUM GAS-SOLID SYSTEM

To calculate the kinetic coefficients L_{ij}, $i, j = 1, 2, 3$ [see (2.2)], of a nonequilibrium gas-solid system (Fig. 1), we need to jointly solve kinetic equations for molecules and phonons. We restrict the discussion below to the case of a collisionless gas ($\mathrm{Kn} = \lambda_m/d \gg 1$), in which transport processes are determined entirely by the interaction of molecules with the surface, so that the interfacial cross effects should be manifested to the greatest extent (Section 2). A generalization to arbitrary values of Kn would require the additional use of methods[23,32] of the kinetic theory of gases, and this generalization is not of fundamental interest. We will therefore ignore the collision integral in Boltzmann equation (2.6) (unless otherwise stipulated). To avoid complicating the calculations with points which are not of fundamental importance, we use the phonon collision integral in (2.7) in the τ approximation:

$$I_{\mathrm{ph}} = -[n(\mathbf{k}j) - n_0(\mathbf{k}j)]\,\tau_{\text{т}}^{-1}.$$

Choosing the coordinate system in such a way (Fig. 1) that the xy plane coincides with the lower surface, while the upper surface is described by the equation $z = d$, and using (2.10a) and (2.20b), we can rewrite kinetic equations (2.6) and (2.7) in linearized form:

$$v_x K_1 + v_z \frac{\partial \varphi}{\partial z} = 0, \qquad 0<z<d, \tag{4.1}$$

$$c_x K_2 + c_z \frac{\partial \psi}{\partial z} = -\psi \tau_{\text{т}}^{-1}, \qquad z<0, \qquad z>d. \tag{4.2}$$

Here

$$K_1 = \frac{\nabla n_g}{n_g} + \left(\frac{mv^2}{2T} - \frac{3}{2}\right)\frac{\nabla T_{\text{г}}}{T_{\text{г}}}, \qquad K_2 = (n_0+1)\hbar\omega \frac{\nabla T_{\text{т}}}{T_{\text{т}}^2}.$$

As boundary conditions on the distribution functions of the molecules and the phonons at the surface $z = 0$, we use relations (3.9) and (3.10), derived above. For simplicity, we assume that the reflection of molecules and phonons from the $z = d$ surface is diffuse:

$$\varphi^-|_{z=d} = 0, \qquad \psi^+|_{z=d} = 0. \tag{4.3}$$

Here and below, the plus and minus signs specify the distribution functions of the molecules and phonons which are moving respectively upward ($v_z > 0$, $c_z > 0$) and downward ($v_z < 0$, $c_z < 0$). The boundary conditions in (4.3) correspond to, for example, reflection from a very rough wall and are used in calculations by most authors.[32,30] In the present paper, this formulation of the problem makes it possible (on the one hand) to incorporate nonequilibrium interfacial effects [between the gas and the lower ($z < 0$) solid] and (on the other) to solve the problem analytically, by reducing the system of integral equations on (3.9), (3.10) to algebraic equations. The solution of system of equations (4.1)–(4.3), (3.9), (3.10) leads to the following expressions for the distribution functions of the gas molecules and of the phonons of the lower solid ($z < 0$):

$$\begin{aligned}\varphi^+(\mathbf{v}, z) &= -\frac{v_x}{v_z} z K_1 + \int\limits_{v_z'<0} d\mathbf{v}' \left|\frac{v_z'}{v_z}\right| \frac{f_0(v')}{f_0(v)} \varphi^-(\mathbf{v}', 0)\, W_0(\mathbf{v}' \to \mathbf{v}) \\ &\quad + \frac{1}{|v_z| f_0} \sum_{\mathbf{k}_1 j_1 (c_{1z}>0)} P(\mathbf{k}_1 j_1 \to \mathbf{v})\, \psi^+(\mathbf{k}_1 j_1, 0),\end{aligned} \tag{4.4}$$

$$\varphi^-(\mathbf{v}, z) = \frac{v_x}{v_z}(d-z) K_1, \qquad 0<z<d; \tag{4.5}$$

$$\begin{aligned}\psi^-(\mathbf{k}j, z) &= -c_x \tau_s K_2 \left(1 - \exp\left[-\frac{z}{c_z \tau_s}\right]\right) + \frac{1}{|c_z| n_0} \exp\left(-\frac{z}{c_z \tau_s}\right) \\ &\times \Bigg[\sum_{\mathbf{k}_1 j_1 (c_{1z}>0)} (|c_{1z}| + R_{\mathbf{k}_1 j_1})\, n_0(\mathbf{k}_1 j_1)\, \psi^+(\mathbf{k}_1 j_1, 0)\, V(\mathbf{k}_1 j_1 \to \mathbf{k}j; \omega) \\ &\quad + \int\limits_{v_z'<0} d\mathbf{v}'\, G(\mathbf{v}' \to \mathbf{k}j)\, \varphi^-(\mathbf{v}', 0)\Bigg],\end{aligned} \tag{4.6}$$

$$\psi^+(\mathbf{k}j, z) = -c_x \tau_s K_2, \quad z<0. \tag{4.7}$$

Using distribution functions (4.4)–(4.7) to calculate the flux densities of the number of particles and of the heat in the gas and the solid, and transforming to the total fluxes over the cross section of the system, we find expressions for the kinetic coefficients L_{ij} in (2.2). Below we give expressions for all the coefficients except L_{33}; in the case $\lambda_{\mathrm{ph}} \ll D$, that coefficient reduces to the product of the volume thermal conductivity of the solid and its thickness D, and is of no interest. The interfacial kinetic coefficients are

$$L_{i3} = -da \int\limits_{v_z>0} d\mathbf{v} A_i \frac{v_x}{v_z} \sum_{\mathbf{k}_1 j_1 (c_{1z}>0)} P(\mathbf{k}_1 j_1 \to \mathbf{v})\, c_{1x} \tau_s [n_0(\mathbf{k}_1 j_1) + 1]\, \hbar\omega(\mathbf{k}_1 j_1), \tag{4.8}$$

$$L_{3i} = -da \sum_{\mathbf{k}j (c_z<0)} \hbar\omega c_x \tau_s \int\limits_{v_z'<0} d\mathbf{v}'\, G(\mathbf{v}' \to \mathbf{k}j) \frac{v_x'}{v_z'} A_i(v'), \quad i=1,2 \tag{4.9}$$

$$A_1 = 1, \qquad A_2 = mv^2/2 - 5\,T/2.$$

replacing the kernel P by the kernel G in (4.8) in accordance with reciprocity relation (3.14), and changing the notation of the integration variables, we see that Onsager relations hold for the new kinetic coefficients: $L_{i3} = L_{3i}$, $i = 1,2$.

Let us compare the interfacial kinetic coefficients L_{i3}, $i = 1, 2$, which are related to the drag exerted on molecules by phonons, with the coefficients L_{ij}, $i, j = 1, 2$, found in the (single-phase) kinetic theory of gases. The latter coefficients have been calculated in many places[16,32,33] through the use of simple boundary conditions of the type (4.3). To the best of our knowledge, there has been no previous analysis of the microscopic dynamics of the scattering in this connection. Calculations using (4.4) and (4.5) lead to

$$L_{ij}=-d^2a\int\limits_{v_z>0}d\mathbf{v}\frac{v_x^2}{v_z}f_0A_iA_j-d^2a\int\limits_{v_z>0}d\mathbf{v}\frac{v_x}{v_z}A_i$$

$$\times\int\limits_{v_z'<0}d\mathbf{v}'v_x'f_0(v')A_j(v')W_0(\mathbf{v}'\to\mathbf{v});\qquad i,j=1,2\qquad(4.10)$$

Using the reciprocity relation (3.12) for W_0, we can easily verify that the single-phase kinetic coefficients in (4.10) satisfy the familiar[16] Onsager relations $L_{12}=L_{21}$. The first term in (4.10) is the solution of the problem for the case of diffuse reflection of molecules from both walls, as is easily shown. The second term incorporates the microscopic scattering dynamics at the lower wall under the assumption that this wall is in equilibrium. The integral in the first term diverges. This fact, which has been established previously for the problem of gas flow in a plane gap, is a consequence of the circumstance that molecules having a sufficiently small normal velocity component v_z travel arbitrarily large distances through the gap without undergoing collisions. In order to find finite values of L_{ij}, $i,j=1,2$, we must either (a) take into account the finite length or finite width of the channel,[34] if one or the other is smaller than λ_M, or (b) take into account the collision integral[33] in (4.1), if we are interested in an infinite channel at large but finite Knudsen numbers. We will not reproduce the calculations, which have been reported elsewhere; we simply note that in the latter case the first term in (4.10) is proportional to $(\gamma_1\ln\mathrm{Kn}+\gamma_2)$, where γ_1 and γ_2 are coefficients whose values depend on the particular model chosen for the collision integral. The second term in (4.10) may also diverge if the scattering by the surface described by the probability W_0 incorporates, in addition to other processes, specular reflection of the molecules, which does not lead to slowing of the gas flow. Calculations carried out with the help of expression (A.6) for W_0 show that in our single-phonon approximation the divergent part of the second term in (4.10) agrees to within a constant factor with the first term in (4.10). As a result, the coefficients γ_1 and γ_2 are redefined and no further problems arise in the calculations of L_{ij}, $i,j=1,2$. The interfacial effects L_{i3} and L_{3i}, $i=1,2$, stem only from the inelastic interaction of the molecules with the surface, so that the integrals in (4.8) and (4.9) do not diverge.

A calculation of the kinetic coefficients in (4.8)–(4.10) with the help of expressions (A.6)–(A.8) leads to the following results:

$$L_{11}=n_{\text{г}}\bar{v}d^2a[\gamma_1\ln\mathrm{Kn}+\gamma_2+B_1],\qquad(4.11)$$

$$L_{12}=L_{21}=-n_g\bar{v}d^2aT\left[\frac{\gamma_1}{2}\ln\mathrm{Kn}+\gamma_3+B_2\right],\qquad(4.12)$$

$$L_{13}=L_{31}=n_g\bar{v}daTc_t\tau_sB_3,\qquad(4.13)$$

where γ_1, γ_2, and γ_3 are constants of order unity, and c_t is the transverse sound velocity in the solid. The kinetic coefficients L_{22}, L_{23}, and L_{32}, which are associated with heat transfer in the gas, are similar in form to (4.11)–(4.13), differing by an unimportant redefinition of the constants. The quantities B_i in (4.11)–(4.13) are

$$B_i=\frac{m\omega_D^3}{\rho_sc_t^3}b_i,\qquad i=1,2;\qquad(4.14)$$

$$B_3=\frac{(mT)^{1/2}\omega_D^3}{\rho_sc_t^4}b_3,\qquad(4.15)$$

where ρ_S is the density of the solid, and ω_D is the Debye frequency. The quantities b_i are defined by

$$b_1=\frac{T^3}{4\pi^{9/2}(\hbar\omega_D)^3}\int\limits_{u_z>0}d\mathbf{u}u_xu_ze^{-u^2}\int\limits_0^{\eta_D}d\eta\eta\int\limits_0^{2\pi}d\varphi\int\limits_0^{\pi/2}d\vartheta\sin\vartheta$$

$$\times\sum_{j=t,l}\left(\frac{c_t}{c_j}\right)^4|\beta_j(\vartheta)|^2p_j\left\{\frac{\mathrm{Re}\,b_j^{(+)}}{b_j^{(+)}}(n_0+1)H_j^{(+)}\right.$$

$$\left.+\frac{\mathrm{Re}\,b_j^{(-)}}{b_j^{(-)}}n_0H_j^{(-)}\right\}\qquad(4.16)$$

$$b_3=\frac{T^3}{4\sqrt{2}\pi^{9/2}(\hbar\omega_2)^3}\int\limits_{u_z>0}d\mathbf{u}u_z^2e^{-u^2}\int\limits_0^{\eta_D}d\eta\eta^2n_0(n_0+1)$$

$$\int\limits_0^{2\pi}d\varphi\cos\varphi\int\limits_0^{\pi/2}d\vartheta\sin^2\vartheta$$

$$\times\sum_{j=t,l}\left(\frac{c_t}{c_j}\right)^3|\beta_j(\vartheta)|^2\left\{\frac{\mathrm{Re}\,b_j^{(+)}}{b_j^{(+)}}H_j^{(+)}+\frac{\mathrm{Re}\,b_j^{(-)}}{b_j^{(-)}}H_j^{(-)}\right\}.\qquad(4.17)$$

Here

$$b_j^{(\pm)}=\left\{1\mp\frac{\eta}{u_z^2}[1-2p_j\sin\vartheta(u_x\cos\varphi+u_y\sin\varphi)\right.$$

$$\left.\pm\eta p_j^2\sin^2\vartheta]\right\}^{1/2},$$

$$H_j^{(\pm)}=\frac{u_x}{p_j}(1-b_j^{(\pm)})\mp\eta\sin\vartheta\cos\varphi,\qquad\mathbf{u}=\left(\frac{m}{2T}\right)^{1/2}\mathbf{v},$$

$$p_j=\frac{1}{c_j}\left(\frac{T}{2m}\right)^{1/2},\qquad\eta=\frac{\hbar\omega}{T},\qquad\eta_D=\frac{\hbar\omega_D}{T},$$

c_l is the longitudinal sound velocity, and ϑ and φ are the spherical angles specifying the orientation of the phonon quasimomentum vector **k**. The expression for b_2 differs from (4.16) through multiplication of the integrand by $(u^2-5/2)$. The quantities b_i in (4.16) and (4.17) are functions of the parameters c_t/c_l and $\eta_D=\hbar\omega\epsilon_D/T$. It can be shown that under the condition $\eta_D\gg1$ we have $b_i\sim\eta_D^{-3}$, $i=1,2,3$, while at $\eta_D\lesssim1$ the quantities b_i depend only weakly on η_D (no more strongly than $\eta_D^{1/2}$). Calculations from (4.16) and (4.17) with $c_t/c_l=0.6$ and $\eta_D=1$ yield $b_1=2.4\cdot10^{-3}$, $b_2=0.8\cdot10^{-3}$, and $b_3=3.6\cdot10^{-3}$.

The quantities B_i, $i=1,2,3$, in (4.11)–(4.13) incorporate the single-phonon scattering of molecules by the $z=0$ surface. In the case $B_1=B_2=0$, expressions (4.11) and (4.12) correspond to the flow of a gas through a channel one of whose walls reflects molecules diffusely, while the other does so in specular manner. In the limit $\mathrm{Kn}\to\infty$, we have $L_{11}/L_{12}=2/T$, which is the same as the result published previously, obtained through the use of a specular-diffuse model for boundary conditions for the gas distribution function. Deviations from this relation have been observed in several experiments[35]: these deviations depend on the particular gas and the particular solid. It follows from (4.11) and

(4.12) that such deviations could be associated with quantities of the type B_1 and B_2, which incorporate the dynamics of the molecule-surface interaction at a microscopic level. At present it is difficult to make a detailed comparison of expressions (4.11) and (4.12) with experiment, primarily because experiments generally use rough surfaces covered with some uncontrolled chemisorbed layer, while the calculations were carried out for scattering by a clean crystal surface.

Expression (4.13), which we have derived for the interfacial cross coefficient L_{13}, corresponds to what we would expect on the basis of physical considerations (Section 2), since we have $c_t\tau_S \sim \lambda_{\text{ph}}$. The quantity B_3 in (4.13) represents a coefficient for the "transfer of a deviation from equilibrium" from the solid to the gas or a coefficient for the drag exerted on molecules by phonons. Substitution of the corresponding quantities into (4.15), for gaseous He and a quartz surface at room temperature, for example, yields $B_3 \approx 0.1$; for bismuth or tin surfaces we find $B_3 \approx 0.2$; and for titanium and aluminum surfaces we find $B_3 \approx 0.03$. The result $B_3 \ll 1$ is a predictable consequence of the use of the single-phonon approximation, which will always (within its range of applicability) lead to approximately specular scattering.[13] For heavier gas molecules, for which multiphonon processes are important, and the probability for inelastic scattering of the molecules by the surface is higher, we would expect $B_3 \sim 1$.

Formally extending expression (4.14) to amorphous solids, we find $B_3 \sim 1$ for He and for polymer materials with a low density and a low sound velocity. Consequently, the effects of the phonon drag on the molecules are seen most clearly in the porous polymer filters which are widely used for gas separation and also in polymer nuclear filters.[3]

The logarithmic term in (4.11) and (4.12) is a consequence of the plane geometry of the problem. In the case of a cylindrical channel (a porous object) this term should be omitted, while otherwise these expressions would retain their form with slightly redefined coefficients. It follows from a comparison on (4.11), (4.12), and (4.13) that in thin channels of size $d \sim \lambda_{\text{ph}}$ the phonon drag on the molecules ($\sim L_{13}$) is comparable to thermotranspiration ($\sim L_{12}$) and also (under the condition $\nabla T/T \sim \nabla p/p$) to the isothermal conductivity of the channel ($\sim L_{11}$).

The new kinetic coefficient L_{13} has a temperature dependence different from L_{11}, L_{12}, determined primarily by the T dependence of λ_{ph}. We know[12] that we have $\lambda_{\text{ph}} \propto T^{-1}$ at $T \gg \hbar\omega_D$ and $\lambda_{\text{ph}} \propto T^{-5}$ at $T \ll \hbar\omega_D$. Using (4.13), (4.15), (4.17), and (2.2), we find that the gas flux in the channel associated with the phonon drag on the molecules is proportional to T^{-1} at $T \gg \hbar\epsilon_D$ or to T^{-2} at $T \ll \hbar\omega_D$. The temperature dependence of the isothermal flux ($\sim L_{11}$) and that of the thermocreep flux ($\sim L_{12}$) are approximately $T^{1/2}$ and $T^{-1/2}$. Consequently, at fixed gradients of the pressure and the temperature, the effect of the deviation of the wall from equilibrium on the gas flux in a channel should increase with decreasing average temperature.

We also note that L_{13} is independent of the mass of the molecules (in contrast with L_{11} and L_{12}, with a mass dependence of approximately $m^{-1/2}$). This result, derived here in the single-phonon approximation, is apparently more general, since it follows from physically transparent arguments. For a given change in the momentum of a molecule, associated with the creation (or annihilation) of phonons, the magnitude of the change in the velocity of the molecule is inversely proportional to m, and the probability for an inelastic collision of a molecule with a solid is proportional to m.

Among other important results we note that L_{13} is proportional to the gap width d (or to the square of the diameter, in the case of a cylindrical channel, and it depends very strongly on the material of the solid, in particular, on c_t^4 [see (4.13) and (4.15)]. The known kinetic coefficients L_{11} and L_{12} are proportional to d^2 (or to the cube of the diameter) and depend only weakly on the material of the channel wall.

5. PROPERTIES OF THE FLOW OF A GAS MIXTURE IN A NARROW CHANNEL

As we will show below, the fact that the phonon drag of the molecules, L_{13}, is independent of the mass of the gas molecules substantially changes the process by which a gas mixture is separated as it flows through a narrow channel, although this result appears at first glance to be paradoxical.

The separation factor α for a two-component gas mixture is defined by[36]

$$\alpha = \frac{\tilde{\xi}^{(1)}}{\tilde{\xi}^{(2)}} \Big/ \frac{\xi^{(1)}}{\xi^{(2)}}, \tag{5.1}$$

where $\xi^{(1)}$ and $\xi^{(2)}$ are the concentrations of component i in the flow entering the channel and in the flow leaving the channel, respectively. If the pressure of the mixture at the exit can be ignored[36] (emergence into vacuum), expression (5.1) reduces to the ratio of the flow velocities $u^{(1)}$ and $u^{(2)}$ of the components in the channel: $\alpha = u^{(1)}/u^{(2)}$.

It is an elementary matter to generalize the theory derived above to the case of a mixture of gases, since the motion of each of the components of the mixture in the channel is independent in the collisionless case, determined exclusively by collisions of molecules of the given type with the surface. For the flow velocity of component i we can write

$$\mathbf{u}^{(i)} = \mathbf{u}_0^{(i)} + \mathbf{u}_1^{(i)}, \tag{5.2}$$

$$\mathbf{u}_0^{(i)} = -\frac{1}{n^{(i)}ad}\left(L_{11}^{(i)}\frac{\nabla p^{(i)}}{p^{(i)}} + L_{12}^{(i)}\frac{\nabla T_g}{T^2}\right), \tag{5.3}$$

$$\mathbf{u}_1^{(i)} = -\frac{1}{n^{(i)}ad} L_{13}^{(i)} \frac{\nabla T_s}{T^2}. \tag{5.4}$$

Here $p^{(i)}$ and $n^{(i)}$ are the partial pressure and the density of mixture component i, and the kinetic coefficients $L^{(i)}$ are determined from expressions (4.11)–(4.13) with $m = m^{(1)}$ and $n_g = n^{(i)}$. [Expressions (5.2)–(5.4) are written in vector form solely for convenience below; we will not take up here the tensor properties which the kinetic coefficients could in general exhibit.] Since $L_{13}^{(i)}$ is independent of $m^{(i)}$ we can omit the index i from $\mathbf{u}_1^{(i)}$ in (5.4). Using (5.2)–(5.4), we can write the separation factor as

$$\alpha = \alpha_0\left[1 - \frac{\mathbf{u}_1\mathbf{u}_0^{(2)}}{(\mathbf{u}_0^{(2)} + \mathbf{u}_1)\mathbf{u}_0^{(2)}}\left(1 - \frac{1}{\alpha_0}\right)\right], \tag{5.5}$$

where $\alpha_0 = u_0^{(1)}/u_0^{(2)}$. In deriving (5.5) we assumed for definiteness $u_1 \leqslant u_0^{(2)}$ and $m^{(2)} > m^{(1)}$. If we set $L_{11}^{(i)}$, $L_{12}^{(i)} \propto [m^{(i)}]^{-1/2}$, as is usually assumed in the literature,[36] we can reduce the expression for α_0 to the usual expression for the ideal separation factor: $\alpha_0 = (m^{(2)}/m^{(1)})^{1/2}$.

For isothermal flow of a mixture ($\nabla T = 0$) we $u_1 = 0$ [see (5.4)], and the separation factor in (5.5) is equal to α_0. Expression (5.5) again leads to the result $\alpha = \alpha_0$ in the case of nonisothermal flow in a large-diameter channel (but under the condition $\mathrm{Kn} \gg 1$), in which case the phonon drag on the molecules can be ignored. In a narrow channel with $d \sim \lambda_{\mathrm{ph}}$ ($\lambda_{\mathrm{ph}} \sim 100$ Å at $T \sim 300$ K), however, the separation process is quite different under isothermal and nonisothermal conditions. If the values of $\nabla p^{(2)}$ and ∇T are such that we have $u_1 \sim u_0^{(2)}$, the separation factor α is quite different from α_0. It follows from (5.5) that we have $\alpha > \alpha_0$ if the temperature gradient is directed opposite the pressure gradient. In this case, however, the flow velocity of the mixture [see (5.2)] will be lower than in the isothermal case. If, on the other hand, ∇T and $\nabla p^{(2)}$ are in the same direction, the flow rate of the mixture in the channel will increase, and we will have $\alpha < \alpha_0$. The reason for this behavior of the mixture is that the phonon drag on the molecules, which is independent of the nature of the gas, leads to an identical decrease (or increase) in the flow rate for the two components and thus an increase (or, respectively, decrease) in the ratio of the flux densities of the light and heavy components.

In this case of flow in a channel, the separation factor could in principle be increased without bound in this manner. If the flow of the heavy component is cut off entirely, and we have $\mathbf{u}_0^{(2)} = -\mathbf{u}_1$, $\mathbf{u}^{(2)} = 0$, we find $\alpha = \infty$. An important point is that although the flux density of the light component does decrease, it remains nonvanishing: $\mathbf{u}^{(1)} = \mathbf{u}_0^{(1)}(\alpha_0 - 1)/\alpha_0$. In a real porous medium, α will of course always be finite because of the distribution in pore diameters.

To the best of our knowledge, there has been no previous special study of the nonisothermal flow of gases in narrow channels. The literature does, on the other hand, reveal data which suggest that the effect predicted here has already been observed experimentally. Haul[37] has reported observing a separation of an isotopic mixture of oxygen, $\mathrm{O^{16}O^{18}}$-$\mathrm{O_2^{16}}$, with an anomalously high separation factor, $\alpha \approx 1.2$ at $T \sim 77$ K, in contrast with the normal value $\alpha \approx 1.024$ at $T \sim 300$K [cf. $(m^{(2)}/m^{(1)})^{1/2} = 1.03$]. Haul studied the effect of surface diffusion on the separation. Subsequent theoretical and experimental studies[36,38] showed that for this particular mixture surface diffusion does not give rise to a significant increase in α in comparison with the value in ordinary gas diffusion, and the unique results of Ref. 37 have gone unexplained.[38]

Estimates of the average pore diameter (d_{av} of the filter used in Ref. 37 yield $d_{\mathrm{av}} \sim 100$ Å (this estimate is based on the specific surface area, the porosity, and the size of the sample, which were reported there). The presence of a significant temperature drop across the filter, a poor heat conductor of thickness ~ 1 cm, during its cooling by liquid nitrogen would be extremely likely, since Haul[37] reported no special measures to stabilize the temperature of the system. The anomalously large value found for the separation coefficient in Ref. 37 might therefore be a consequence of the phonon drag on molecules which we have been discussing in this paper.

We wish to thank V. M. Zhdanov, L. A. Maksimov, and B. I. Nikolaev for a discussion of these results and for useful advice.

APPENDIX

To find explicit expressions for the kernels W_0, P, G, and R in boundary conditions (3.9) and (3.10) on the distribution functions of the molecules and the phonons at the interface, we need to calculate the probability W_D for a transition in the molecule-surface system. This probability is determined by expression (3.3). We restrict the discussion here to the single-phonon approximation (the first Born approximation of the distorted-wave method[29]), which is justified in the case of the scattering of light molecules. We modify the methods of Ref. 13 to suit the problem at hand.

The molecule-surface interaction potential can be written

$$V = V_0 + V_1,$$

$$V_1 = \sum_{\xi \neq 0} e^{i\xi\mathbf{r}} V_1'(\xi) + \sum_{\mathbf{k}j\,(c_z>0)} [e^{i\mathbf{k}_\tau\mathbf{r}} V_1''(\mathbf{k}j)\, a_{\mathbf{k}j} + e^{-i\mathbf{k}_\tau\mathbf{r}} V_1''^{*}(\mathbf{k}j)\, a_{\mathbf{k}j}^{+}]. \qquad (\mathrm{A.1})$$

Here a^+ and a are the creation and annihilation operators for phonons in the divergent-wave representation, discussed in Section 3, ξ is the reciprocal-lattice vector of the semi-infinite crystal which is tangent to the surface, $\mathbf{k}_\tau$ is the tangential component of the phonon quasimomentum vector, $\mathbf{r}$ is the coordinate of the gas molecule, and the quantities V_0, V_1', and V_1'' depend only on the distance from the molecule to the surface. The first term in V_1 describes, along with V_0, the interaction of molecules with the frozen lattice, all of whose atoms are in their equilibrium positions; the second term in V_1 incorporates the thermal vibrations of the solid in the linear approximation in the small displacement of an atom from its equilibrium position. Using (A.1), we can calculate W_D from (3.3) in the first Born approximation of the distorted-wave method:

$$W_D(\mathbf{v}', \{N_{\mathbf{k}j}'\} \to \mathbf{v}, \{N_{\mathbf{k}j}\}) = W_{el}\ (\mathbf{v}' \to \mathbf{v}) \prod_{\mathbf{k}j(c_z>0)} \delta(N_{\mathbf{k}j}' - N_{\mathbf{k}j})$$
$$+ \sum_{\mathbf{k}j(c_z>0)} [(N_{\mathbf{k}j}'+1) W_{\mathbf{k}j}^{(+)}\ (\mathbf{v}' \to \mathbf{v})\, \delta(N_{\mathbf{k}j} - 1 - N_{\mathbf{k}j}')$$
$$+ N_{\mathbf{k}j}' W_{\mathbf{k}j}^{(-)}\ (\mathbf{v}' \to \mathbf{v})\, \delta(N_{\mathbf{k}j} + 1 - N_{\mathbf{k}j}')] \cdot \prod_{\mathbf{k}_1 j_1 \neq \mathbf{k}j} \delta(N_{\mathbf{k}_1 j_1} - N_{\mathbf{k}_1 j_1}'), \qquad (\mathrm{A.2})$$

where

$$W_{el} = \frac{2\pi}{\hbar} \left(\frac{m}{2\pi\hbar}\right)^3 \frac{1}{|v_z'|}\, \delta\left(\frac{mv^2}{2} - \frac{mv'^2}{2}\right)$$
$$\left|\left(M \middle| \sum_{\xi \neq 0} e^{i\xi\mathbf{r}} V_1'(\xi) \middle| M'\right)\right|^2, \qquad (\mathrm{A.3})$$

$$W_{\mathbf{k}j}^{(\pm)}=\frac{2\pi}{\hbar}\left(\frac{m}{2\pi\hbar}\right)^3\frac{1}{|v_z'|}\delta\left(\frac{mv^2}{2}\pm\hbar\omega-\frac{mv'^2}{2}\right)$$

$$|(M|h^{(\pm)}|M')|^2. \qquad (A.4)$$

Here $h^{(-)}=\exp(i\mathbf{k}_\tau\mathbf{r})V_1''(\mathbf{k}j)$, $h^{(+)}=h^{(-)*}$, and the functions $|M)$ determine the motion of a molecule in the potential V_0 and constitute the solution of the corresponding Schrödinger equation. In writing (A.3) and (A.4), we have taken into account the circumstance that, for the particular way in which we have partitioned the potential in (A.1), the functions $|M)$ differ by only a phase factor in the representations of convergent and divergent waves.[13] The quantity W_{el} in (A.2) describes the elastic nonspecular reflection of a molecule from the surface (without any energy transfer), and the quantities $W_{kj}^{(\pm)}$ have the meaning of probabilities for the creation (or annihilation) of a single phonon.

The probability for specular reflection, which is not calculated directly in the single-phonon approximation for the partitioning of the potential in (A.1), can be found from the normalization condition corresponding to a unit total probability for the scattering:

$$\mathbf{v}_3=\mathbf{v}-2\boldsymbol{\zeta}(\mathbf{v}\boldsymbol{\zeta}),$$

$$W_D(\mathbf{v}',s'\to\mathbf{v}_3',s')=1-\sum_{\{N\}}\int_{v_z>0}d\mathbf{v}W_D(\mathbf{v}',\{N_{\mathbf{k}j}'\}\to\mathbf{v},\{N_{\mathbf{k}j}\}). \qquad (A.5)$$

Expression (A.5) can be used as a measure of the reasonableness of the single-phonon approximation which we are using, since the probability for specular reflection which is calculated from (A.5) must be nonnegative. Using (A.11), we can show that this condition does hold for light gases (He and Ne) for molecules with energies up to ~1000 K.

Using expression (A.2) for the transition probability, along with (3.2), (3.4), (3.5), and (2.20), we find expressions for the integral kernels in boundary conditions (3.9) and (3.10) in the single-phonon approximation:

$$W_0(\mathbf{v}'\to\mathbf{v})=W_{el}+\sum_{\mathbf{k}j(c_z>0)}[n_0W_{\mathbf{k}j}^{(-)}+(n_0+1)W_{\mathbf{k}j}^{(+)}]$$
$$+\delta(\mathbf{v}-\mathbf{v}_3')$$
$$\left\{1-\int_{v_z>0}d\mathbf{v}\left[W_{el}+\sum_{\mathbf{k}j(c_z>0)}(n_0W_{\mathbf{k}j}^{(-)}+(n_0+1)W_{\mathbf{k}j}^{(+)})\right]\right\}, \qquad (A.6)$$

$$P(\mathbf{k}_1j_1\to\mathbf{v})=n_0\int_{v_z'<0}d\mathbf{v}'|v_z'|f_0(v')\Big[W_{\mathbf{k}_1j_1}^{(-)}+W_{\mathbf{k}_1j_1}^{(+)}$$
$$-\delta(\mathbf{v}-\mathbf{v}_3')\int_{v_z>0}d\mathbf{v}(W_{\mathbf{k}_1j_1}^{(-)}+W_{\mathbf{k}_1j_1}^{(+)})\Big], \qquad (A.7)$$

$$G(\mathbf{v}'\to\mathbf{k}j)=|v_z'|f_0(v')\sum_{\mathbf{k}_1j_1(c_{1z}>0)}V(\mathbf{k}_1j_1\to\mathbf{k}j;\omega)$$
$$\int_{v_z>0}d\mathbf{v}[(n_0+1)W_{\mathbf{k}_1j_1}^{(+)}-n_0W_{\mathbf{k}_1j_1}^{(-)}], \qquad (A.8)$$

$$R_{\mathbf{k}_1j_1}=\int_{v_z>0}d\mathbf{v}\int_{v_z'<0}d\mathbf{v}'|v_z'|f_0(v')[W_{\mathbf{k}_1j_1}^{(+)}-W_{\mathbf{k}_1j_1}^{(-)}]. \qquad (A.9)$$

For specific calculations in Section 4 we need explicit expressions for the kernels in (A.6)–(A.9) for the model of the solid and for the potential of the molecule-surface interaction, V. For the solid we use a model of a continuum with a free boundary[14]; the vibrational spectrum of the model is quantized as in Ref. 15. We choose the potential V to be

$$V=p\exp\{-2q[z-u_z(x,y)]\}, \qquad (A.10)$$

where $\mathbf{u}(x,y)$ is the displacement of a surface element of the continuum with equilibrium coordinates $(x,y,0)$ as a result of thermal vibrations. When we take the limit $q\to\infty$ in the final expressions, we find that (A.10) corresponds to an infinitely high potential barrier. Using these models, we find the following results for the probabilities in (A.3) and (A.4):

$$W_{el}=0,\quad W_{\mathbf{k}j}^{(\pm)}=\frac{m^2|v_zv_z'|}{\hbar_{\rho_s}V_s\omega(\mathbf{k}j)}|\beta_j(\vartheta)|^2\delta\left(\mathbf{v}_\tau'\mp\frac{\hbar\mathbf{k}_\tau}{m}-\mathbf{v}_\tau\right)$$
$$\times\delta\left(|v_z|-\left\{v_z'^2\mp\frac{2\hbar\omega(\mathbf{k}j)}{m}\pm\frac{2\hbar}{m}\mathbf{v}_\tau'\mathbf{k}_\tau-\frac{\hbar^2k_\tau^2}{m^2}\right\}^{1/2}\right) \qquad (A.11)$$

Here $\mathbf{v}_\tau$ is the component of the molecular velocity tangent to the surface, V_S is the volume of the solid, and the quantities β_j, which are functions of the angle (ϑ) between $\mathbf{k}$ and the normal to the surface, are given by expressions (1.7) and (1.12) of Ref. 15. Expressions (3.9) and (3.10), with (A.6)–(A.9) and (A.11), give us the boundary conditions which we need for the distribution functions of the molecules and the phonons for the models which we have used for the solid and for the molecule-surface interaction potential.

[1)] Otherwise, it would be difficult to carry out a thermodynamic analysis, since the temperature and density of the gas would change significantly over a distance on the order of λ_M near the surface.

[2)] In the literature[18,19] we find indications that in several technical applications (high-precision measurements of various quantities) the thermotranspiration effect turns out to be important even at these high pressures. According to the estimates here, interfacial cross effects may also be important in these cases. A resolution of this question requires additional analysis, which we will report separately

[1] N. V. Karlov, I. K. Meshkovskiĭ, R. P. Petrov, Yu. N. Petrov, and A. M. Prokhorov, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 48 (1979) [JETP Lett. **30**, 42 (1979)].

[2] V. D. Akin'shin, B. T. Porodnov, V. D. Seleznev, and V. V. Surguchev, IMTF **1**, 67 (1984).

[3] G. N. Flerov and V. S. Barashenkov, Usp. Fiz. Nauk **114**, 351 (1974) [Sov. Phys. Usp. **17**, 783 (1975)].

[4] V. D. Borman, S. Yu. Krylov, and A. M. Kharutnov, Pis'ma Zh. Tekh. Fiz. **11**, 430 (1985) [Sov. Tech. Phys. Lett. **11**, 179 (1985)].

[5] V. D. Borman, L. A. Maksimov, B. I. Nikolaev, and V. I. Troyan, Dokl. Akad. Nauk SSSR **207**, 1082 (1972) [Sov. Phys. Dokl. **17**, 1170 (1973)].

[6] V. D. Borman, L. A. Maksimov, B. I. Nikolaev, and V. I. Troyan, Zh. Eksp. Teor. Fiz. **64**, 526 (1973) [Sov. Phys. JETP **37**, 269 (1973)].

[7] J. J. G. M. Van derTol, S. Yu. Krylov, L. J. F. Hermans, and J. J. M. Beenakker, Phys. Lett. **99A**, 51 (1983).

[8] G. Comsa, in: Dynamics of Gas-Surface Interaction, Speringer Ser. Chem. Phys., Vol. 21, New York, 1982, p. 117.

[9] K. G. Landa, J. E. Hurst, J. Cowin, L. Wharton, and D. J. Auerbach, Surf. Sci. **130**, 395 (1983).

[10] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Nonequilibrium statistical thermodynamics), Nauka, Moscow, 1971.

[11] E. M. Lifshitz and L. P. Pitaevskiĭ, Fizicheskaya kinetika, Nauka, Moscow, 1979 (E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics, Pergamon, Oxford, 1981).

[12] V. L. Gurevich, Kinetika fononnykh sistem (Kinetics of Phonon Systems), Nauka, Moscow, 1980, Ch. I.

[13] F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering*, Academic, New York, 1976, Ch. 8, 9, 10 (Russ. Transl. Mir, Moscow, 1980).

[14] L. D. Landau and E.M. Lifshitz, Teoriya uprugosti, Nauka, Moscow, 1965, Ch. III (Theory of Elasticity, Addison-Wesley, Reading, Mass., 1970).

[15] I. M. Khalatnikov, Zh. Eksp. Teor. Fiz. **22**, 689 (1952).

[16] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, American Elsevier, New York, 1962 (Russ. Transl. Mir, Moscow, 1967).

[17] L. D. Landau and E. M. Lifshitz, Statistichevkaya fizika, Part I, Nauka, Moscow, 1976, §40 (Statistical Physics, Pergamon, New York).

[18] J. L. Garcia Fierro and A. M. Garcia, Vacuum **31**, 79 (1981).

[19] T. N. Abramenko, Inzh.-Fiz. Zh. **46**, 776 (1984).

[20] L. Waldmann, Z. Naturforsch **22a**, 1269 (1967).

[21] S. P. Bakanov, B. V. Deryagin, and V. I. Roldugin, Usp. Fiz. Nauk **129**, 255 (1979) [Sov. Phys. Usp. **22**, 813 (1979)].

[22] A. A. Oliner (editor), *Acoustic Surface Waves*, Springer-Verlag, New York, 1978 (Russ. Transl. Mir, Moscow, 1981).

[23] M. N. Kogan, Dinamika razrezhennogo raza (Dynamics of Low-Density Gases), Nauka, Moscow, 1967, Ch. II–VI.

[24] N. N. Bogolyubov, Problemy dinamicheskoĭ teorii v statisticheskoĭ fizike, Gostekhizdat, 1946 (Problems of Dynamic Theory in Statistical Physics, in: Studies in Statistical Mechanics, ed. by J. deBoer and G. F. Uhlenbeck, Vol. 1, Wiley, New York, 1961).

[25] I. Kuščer, Surf. Sci. **25**, 225 (1971).

[26] S. R. Morrison (editor), *The Chemical Physics of Surfaces*, Plenum, New York, 1976.

[27] V. G. Khamdamov, V. I. Vettegrin', and I. I. Novak, Fiz. Tverd. Tela (Leningrad) **22**, 3242 (1980) [Sov. Phys. Solid State **22**, 1896 (1980)].

[28] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and N. N. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic, Orlando (1976).

[29] R. G. Newton, *Scattering Theory of Waves and Particles*, McGraw-Hill, New York, 1966.

[30] L. A. Zaitseva and I. B. Levinson, Fiz. Tverd. Tela (Leningrad) **24**, 1286 (1982) [Sov. Phys. Solid State **24**, 731 (1982)].

[31] L. A. Maksimov and A. V. Il'in, Lektsii po fizicheskoĭ kinetike (Lectures on Physical Kinetics), MFTI, Moscow, 1974, Ch. I, §3.

[32] C. Cercignani, *Theory and Application of the Boltzmann Equation*, American Elsevier, New York, 1976, Ch. 7 (Russ. Transl. Mir, Moscow, 1978).

[33] H. F. P. Knapp and I. Kuscer, Physica **104A**, 95 (1980).

[34] V. D. Borman, S. Yu. Krylov, B. I. Nikolaev, V. A. Ryabov, and V. I. Troyan, Zh. Eksp. Teor. Fiz. **79**, 1787 (1980) [Sov. Phys. JETP **52**, 904 (1980)].

[35] J. P. Hobson, Vac. Sci. Technol. **7**, 351 (1970); **8**, 290 (1971).

[36] S. M. Villani (editor), Obogashchenie urana (Enrichment of Uranium), Energoatomizdat, Moscow, 1983, Ch. 3.

[37] R. A. W. Haul, Naturwissenschaften **41**, 255 (1954).

[38] W. G. Trawick and A. S. Berman, J. Chem. Phys. **26**, 709 (1957).

Translated by Dave Parsons