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Molecular Transport in the Nanometer Regime

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Properties of molecular transport in nanometer channels where the molecules move all or most of the time in interaction with the surface are shown to differ significantly from those in macroscopic structures. Apart from strong deviations from ordinary flow in its dependence on channel dimensions and temperature, under nonisothermal conditions a new phenomenon arises by the coupling of the molecular flow to the thermally induced phonon flux in the solid. Special attention is given to the manifestation of these effects in the thermomolecular pressure difference as it is the experimentally most easily accessible quantity.

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In recent times the behavior of molecules confined to narrow pores has been the object of extensive studies; see, for example, [1-4]. So far little attention has been given to the behavior of gas flow under these conditions.

In decreasing the diameter of a channel well into the nanometer region the molecules move always or nearly always in the interaction region with the solid, and one enters into a new regime for gas flow through these channels. We will show how under these conditions the gas flow through narrow channels deviates strongly from that in the traditional Knudsen regime [5]. Moreover, in the presence of a temperature gradient a new interphase phenomenon occurs: The thermal flow of phonons in the solid couples to the gas and gives rise to a drag phenomenon on the molecules.

Two regimes can be distinguished: In the most extreme situation the interaction regions of the walls overlap and the molecules move constantly in interaction with the solid. Before one enters this regime the interaction regions do not overlap. The time the molecules spent in the interaction region, however, is weighted with a Boltzmann factor when compared to the interaction free zone. Hence there is a range of diameters where the molecules still spend most of their time in the interaction zone and where the contribution to transport from the interaction free region can be neglected. We will treat the first case in some detail and give a summary on what is to be expected in the second case.

Consider a system of two reservoirs connected by a set of parallel channels with diameter d, comparable to the characteristic range $L \leq 1.0$ nm of the surface-molecule potential field V_s. The density of the molecules per unit length of the channel n_l is considered to be low enough that molecule-molecule collisions can be neglected with respect to the interaction with phonons and surface defects. We will further assume that the structure of the potential well in the axial direction is uniform. This situation is to a good approximation valid for physical adsorption at not too low temperatures [6]. Under these conditions the motion of the molecules along the channel axis between two consecutive interactions with the phonons or defects is considered to be free and one has effectively a one-dimensional (1D) flow.

Our approach is based on ideas developed earlier where the interaction of molecules with a solid is treated in the framework of kinetic theory as the interaction with a phonon gas [7]. A good description of various surface phenomena was obtained [6-9] in an approximation where only the motion parallel to the surface is treated explicitly, while averaging over the direction normal to the surface. The molecules in the channel are characterized by the (quasiclassical one-particle) distribution function $\rho(v_x,E_y,E_z,x,t)$ where v_x is the velocity of molecular free motion along the axis and E_y,E_z are the energies (kinetic plus potential) of molecular vibrational motion perpendicular to the axis collectively denoted by Γ.

The kinetic equation for the distribution function can be written as

$$\frac{\partial\rho}{\partial t}+v_x\frac{\partial\rho}{\partial x}=I\{\rho\}\,, \tag{1}$$

where $I\{\rho\}$, the analog of the free gas collision integral, describes the relaxation of molecules by phonons and surface defects. It can be written as

$$I\{\rho\}=\int d\Gamma'\rho(\Gamma')\dot{w}(\Gamma'\rightarrow\Gamma)-\rho(\Gamma)\int d\Gamma'\dot{w}(\Gamma\rightarrow\Gamma')\,,$$

where $d\Gamma=(4m^2E_yE_z)^{-1/2}dv_xdE_ydE_z$. The probability of changing the molecular state per unit time $\dot{w}(\Gamma\rightarrow\Gamma')$ is an average over all (vibrational) states of the solid. We want also to take into account the nonequilibrium state of the solid if a temperature gradient along the channel is maintained. When the deviation from equilibrium is sufficiently small, $\dot{w}$ and, consequently, $I\{\rho\}$ can be written as

$$\dot{w}=\dot{w}_0+\delta\dot{w},\quad I\{\rho\}=I_0\{\rho\}+\delta I\{\rho\}\,.$$

We will treat first the single relaxation-time approximation for I_0 and make rough estimates for δI later. Thus, we write

$$I\{\rho\}=-\frac{\rho-\rho_0}{\tau}+\delta I\{\rho\}\,. \tag{2}$$

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The local equilibrium distribution function ρ_0 is given by

$$\rho_0 = n(x)\left[\frac{m}{2\pi kT(x)}\right]^{3/2} \exp\left(-\frac{mv_x^2}{2kT(x)} - \frac{E_y+E_z}{kT(x)}\right);$$

for the relaxation time one has $\tau^{-1} = \int d\Gamma' \dot{w}_0(\Gamma \to \Gamma')$. Some qualitative conclusions about properties of δI in Eq. (2) can be obtained from general arguments without detailed microscopic calculations. Because of phonon-molecule (quasi-)momentum exchange, the phonon flux in the nonequilibrium solid must, by symmetry, produce a vector-type distortion ($\propto v_x/v_0$) of the molecular distribution function. It will be proportional to the dimensionless parameter $l\nabla T/T$ which describes how strongly the phonon distribution deviates from its equilibrium state. For a crystalline solid l is obviously the phonon mean free path, $l = \lambda_{\mathrm{ph}}$. So we can write

$$\frac{\delta I}{\tau^{-1}} = \frac{v_x}{v_0} h(v_x^2, E_y, E_z)\lambda_{\mathrm{ph}} \frac{\nabla T}{T}. \tag{3}$$

The following estimates of macroscopic flows in the system can be obtained without further specification of the explicit form of the function h.

Solving the kinetic equation (1) [using Eqs. (2), (3)] in a linear approximation in the given gradients $\nabla n_l/n_l$, $\nabla T/T$ and calculating the molecular flux, $G = \int d\Gamma v_x \rho$, one obtains the following:

$$G = G_n + G_T + G_{\mathrm{ph}}, \tag{4}$$

$$G_n = -\tfrac{1}{2} n_l \tau v_0^2 \nabla n_l / n_l, \tag{5}$$

$$G_T = -\tfrac{1}{2} n_l \tau v_0^2 \nabla T/T, \tag{6}$$

$$G_{\mathrm{ph}} = -C_{\mathrm{ph}} n_l v_0 \lambda_{\mathrm{ph}} \nabla T/T. \tag{7}$$

Here $v_0 = (2kT/m)^{1/2}$ is the thermal molecular velocity. On the basis of earlier work [10] we expect C_{ph} to be of order 1.

From the experimental point of view it is more convenient to take p and T as the independent variables. These are the only directly accessible quantities through their values in the outside vessels. The gradients in the channel will in the linear regime be directly given by the difference in pressure and temperature between the vessels. To relate n_l to the pressure and temperatures in the vessels we approximate the potential in the channels by a well of constant depth V across the channel. For the ends of the channels we now obtain

$$n_l = \frac{\pi}{4} d^2 n_v \exp\frac{V}{kT} = \frac{\pi}{4} d^2 \frac{p}{kT} \exp\frac{V}{kT}. \tag{8}$$

Expressing G in terms of gradients of $\ln p$ and $\ln T$,

$$G = G_p + \tilde{G}_T + G_{\mathrm{ph}}, \tag{9}$$

$$G_p = -\tfrac{1}{2} n_l \tau v_0^2 \nabla \ln p, \tag{10}$$

$$\tilde{G}_T = \tfrac{1}{2} n_l \tau v_0^2 (V/kT) \nabla \ln T, \tag{11}$$

with G_{ph} unchanged. Note the difference in sign and magnitude between G_T and $\tilde{G}_T$. In an experiment it will in general be $\tilde{G}_T$ that is directly observable.

From Eqs. (10) and (11) one sees that, even without the phonon flux contribution G_{ph}, appreciable differences with respect to the traditional Knudsen flow occur, where in the case of perfectly accommodating walls one has [5]

$$G_p = -\tfrac{1}{6}\sqrt{\pi} n_v v_0 d^3 \nabla p/p, \tag{12}$$

$$\tilde{G}_T = \tfrac{1}{12}\sqrt{\pi} n_v v_0 d^3 \nabla T/T. \tag{13}$$

First of all there is the effect of the potential well. It increases n_l and causes a different temperature dependence of n_l and n_v. This results in a factor V/kT in Eq. (11) for the thermally induced flux. An additional temperature dependence results from the behavior of τv_0^2. Previous investigations showed that for heavy molecules τ increases with temperature [6]. As a result of all these effects 1D molecular transport will show a temperature dependence that differs significantly from that characteristic for the normal Knudsen flow regime. The difference is less pronounced for the dependence on channel diameter. As n_l is proportional to d^2 and τ to d [7] one has a d^3 dependence also here. The situation is, however, complicated by the fact that n_l depends on V, which in turn depends on d through the amount of overlap of the contributions of the walls. When d increases the overlap decreases and so does V. All effects together will give rise to a dependence of both G_p and $\tilde{G}_T$ upon d weaker than d^3.

We will focus our attention now on the phonon-molecule drag G_{ph} [Eq. (7)]. From the point of view of nonequilibrium thermodynamics it represents a flux in one medium (the gas in the channel) as a response to a thermodynamic force applied in another medium (the solid) through an interaction at the interphase. Comparing the phonon drag (7) with the thermal creep (11) one gets

$$\left|\frac{G_{\mathrm{ph}}}{\tilde{G}_T}\right| \approx \frac{\lambda_{\mathrm{ph}}}{\tau v_0} \frac{kT}{V}. \tag{14}$$

Experimental data on gas diffusion in porous media [6] show that the relaxation length τv_0 typically varies between 0.1 and 1 nm. The characteristic value of the phonon mean free path λ_{ph} in crystals at room temperatures is about 10 nm [11]. So the phonon-molecule drag may give a contribution of the same order of magnitude as the thermal creep effect.

For an amorphous solid it is for a qualitative estimate reasonable to follow the simplified picture of a crystal with a large number of defects [11] with a mean defect concentration corresponding to the size of the characteristic short-range order region in the solid. This obviously gives $\lambda \le 1.0$ nm. Thus for an amorphous solid one expects $\lambda_{\mathrm{ph}} = \tau v_0$. According to Eq. (14), the ratio of the phonon drag flow and 1D thermal creep flow is then of the order of kT/V.

We will now consider the situation where the interaction regions of the molecules with the walls no longer overlap but where the molecules still spend most of their time in these regions and where transport through the interaction free region can be neglected; i.e., there is only two-dimensional (2D) surface flow. To describe this situation we make assumptions similar to the ones introduced earlier: The molecule-wall interaction potential is independent of the position along the channel, and the surface density of the molecules n_s is low enough to neglect molecule-molecule interaction. To obtain a relation with the gas density and pressure outside the channels we approximate the interaction by a well of constant depth V over a range L. Hence

$$n_s = n_v L \exp\frac{V}{kT} = \frac{p}{kT} L \exp\frac{V}{kT} . \qquad (15)$$

Proceeding as before we obtain G composed of three parts as in Eq. (9):

$$G_p = -\tfrac{1}{2}\pi d n_s \tau v_0^2 \nabla p/p , \qquad (16)$$

$$\tilde{G}_T = (\tfrac{1}{2}\pi d n_s \tau v_0^2 V/kT)\nabla T/T , \qquad (17)$$

$$G_{\mathrm{ph}} = -\pi d n_s v_0 C_{\mathrm{ph}} \lambda_{\mathrm{ph}} \nabla T/T . \qquad (18)$$

These results differ from those in the 1D case in one important way. As V and τ are now independent on d all three contributions have the same dependence on the diameter. Furthermore the phonon drag contribution to G becomes larger with respect to $\tilde{G}_T$ as V will be smaller than in the case of overlapping interaction regions. In comparing 2D with Knudsen flow the discussion of the temperature dependence given in the 1D case remains valid. As one expects τv_0 to be proportional to L [7] one obtains for the ratio of G_p between the two cases apart from a small numerical factor: $(L/d)^2 \exp(V/kT)$. This results in a considerable range of values for d where 2D transport is dominant. For gases like N_2 and Ar, e.g., one has $V/k \approx 1500$ K and the condition is met for $d \leq 4$ nm at $T \leq 250$ K.

The manifestations of these effects in 1D and 2D flow can experimentally most easily be assessed through the thermomolecular pressure difference (TMPD). A pressure difference, Δp, between two gas vessels with different temperatures, T and $T+\Delta T$, appears in a stationary state as a result of the balance between particle flow in the channel under the action of the given temperature gradient and the counter flow due to the resulting pressure gradient. In our case, requiring the net flux to be zero and taking into account the relations (7), (10), and (11), for 1D or (16), (17), and (18) for the 2D case one obtains in both cases:

$$\frac{\Delta p}{p} = \left[\frac{V}{kT} - 2C_{\mathrm{ph}} \frac{\lambda_{\mathrm{ph}}}{\tau v_0} \right] \frac{\Delta T}{T} . \qquad (19)$$

The result (19) is to be compared to the factor $\frac{1}{2}$ valid in a Knudsen gas [5].

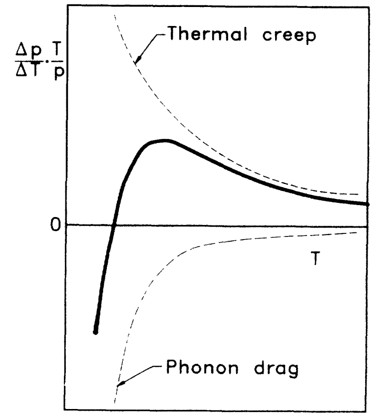

FIG. 1. Temperature dependence of TMPD in the nanometer regime (qualitative picture). The two contributions to the effect [first and second terms in Eq. (19)] are shown by dashed lines. Rough estimates for Ar, N_2, and CH_4 predict Δp changing sign at temperature around 100–140 K, while the maximum in $T\Delta p/p\Delta T$ is expected to occur at $T \sim 200$–280 K.

It is important to note from Eq. (19) that the phonon drag produces a TMPD of the opposite sign with respect to the conventional TMPD. Hence the thermomolecular pressure difference can vanish at some intermediate temperature if the quantity $C_{\mathrm{ph}}\lambda_{\mathrm{ph}}/\tau v_0$ increases faster than T^{-1} with decreasing temperature; see also Fig. 1. Since C_{ph} is assumed nearly temperature independent this is indeed what is to be expected, especially in the 2D case where V is smaller than in the 1D case. An observation of Δp changing sign would give direct evidence of the existence of the phonon-molecule drag.

Although expression (19) holds for both 1D and 2D flow there is an important difference for the behavior of the TMPD in samples with a spread in pore diameters. In the 1D case V depends on d; this results in a difference in dependence on d of G_p and $\tilde{G}_T$. The resulting TMPD depends in a complicated way on the distribution of pore size. This complication is absent for 2D flow where V

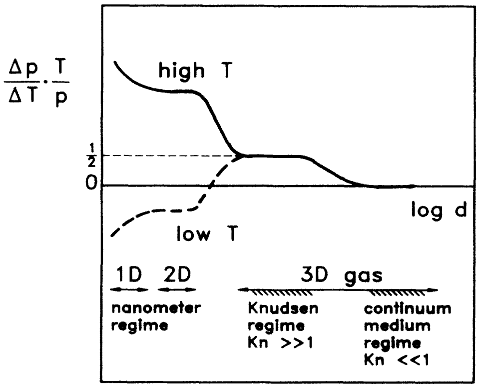

FIG. 2. The behavior of TMPD in different regimes (qualitative picture) as a function of log$d$.

does not depend on d and all contributions to the flow have the same linear dependence on d. So a spread in pore size has no effect on the value of the TMPD and a quantitative separation of the different contributions will be feasible.

To summarize our results and confront them with those valid outside the nanometer regime we plotted in Fig. 2 TMPD as a function of d. The drawn curve gives the behavior if the phonon drag can be neglected (high T). The other curve corresponds to the case that at low temperatures the phonon drag becomes the dominant contribution.

As the relative importance of surface flow and phonon drag with respect to Knudsen bulk flow behaves as d^{-2}, these contributions might still be felt for diameters in the micrometer range. They will, however, be negligible in the mm range. Hence the 10% to 15% deviations from the $T^{1/2}$ behavior observed for these diameters [12] are not covered by the theory presented here and need another explanation [13].

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