Journal of Statistical Physics, Vol. 26, No. 1, 1981

The Kinetic Boundary Layer for the Fokker–Planck Equation: Selectively Absorbing Boundaries

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Received September 17, 1980

We study the joint distribution function for position and velocity of a Brownian particle near a wall. The wall absorbs all particles that hit it with sufficiently high velocity and reflects all slower ones, either specularly or diffusely. We determine in particular stationary distributions in the absence of external forces. Appreciable deviations from local equilibrium occur in a kinetic boundary layer near the wall; its details depend strongly on the way in which the slow particles are reflected. The resulting effective absorption rate is calculated and compared with the result of approximations analogous to the transition state theory of chemical reactions. The method used is a generalization of the one used in an earlier paper for the case of a completely absorbing wall; a numerical algorithm based on an expansion of the distribution function in terms of a presumably complete set of boundary layer solutions.

KEY WORDS: Fokker–Planck equation; kinetic boundary layer; diffusion-controlled reactions; transition state theory; reaction rates; half-range expansion.

1. INTRODUCTION AND SURVEY

Kinetic boundary layers[1] are regions near a wall in a fluid or, as in the case studied here, in a suspension of Brownian particles, where the assumption of approximate local equilibrium breaks down. This implies that the hydrodynamic equations (Navier–Stokes or Smoluchowski equations) cannot hold all the way to the boundary. The Chapman–Enskog solutions of the underlying kinetic equations, from which the hydrodynamic equations are derived, do not fulfill the microscopic boundary conditions; they must be supplemented by certain additional boundary layer solutions. Even so,

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0022-4715/81/0900-0059$03.00/0

one can fulfill the microscopic boundary conditions only with Chapman–Enskog solutions that obey certain additional restrictions; these can be written as boundary conditions for the hydrodynamic equations (in our case the Smoluchowski equations), when the latter are *assumed* to hold all the way to the wall. In general these macroscopic boundary conditions contain certain constants (slip or accommodation coefficients), that depend in a complicated way on the microscopic boundary conditions.

In a previous paper[2] we illustrated this state of affairs with a simple example, the Brownian motion of a particle in a half-space bounded by a completely absorbing plane wall. The dynamics of the probability distribution for velocity and position of the Brownian particle is governed by a Fokker–Planck equation of Klein–Kramers type.[3] This equation is often used to describe the flow of chemical reactants at low concentration for the case that the reacting particles are much heavier than the solvent molecules;[3] the coordinate perpendicular to the wall then corresponds to the "reaction coordinate." We further restricted ourselves to stationary solutions of this equation in the absence of external potentials. The Chapman–Enskog solutions[5] are determined completely by the probability density in position space; the latter must be of the form $n(x) = a + bx$. Solutions of the full Fokker–Planck equation that approach this density profile asymptotically and, moreover, obey the microscopic boundary condition at the wall are only possible for a particular value of $x_M = -a/b$. The so-called Milne extrapolation length x_M is the accommodation coefficient for our problem. We shall argue later that its inverse is related to an effective absorption rate at the wall. The actual value of x_M could only be determined approximately via a numerical procedure.

In the present paper we generalized these results to selectively absorbing walls. In Section 2 we adapt the formalism of Ref. 2 to treat this generalization. In Section 3 we give numerical results for a specific example, suggested by the reaction-dynamical interpretation of our model: a wall that absorbs all particles impinging on it with velocities larger than a certain threshold velocity and specularly reflects all slower particles. A pronounced feature of the solutions is an accumulation of slow particles near the wall for threshold velocities of the order of the thermal velocity or larger. Unfortunately, the convergence of our numerical procedure does not suffice to derive accurate predictions for the quantity x_M (defined in the preceding paragraph) for threshold velocities larger than the thermal velocity.

Better convergence is obtained for a modified scattering kernel for which the subthreshold particles are reemitted diffusely, i.e., with a velocity

[3] See Refs. 4 and 9. All of these contain many references to earlier work in the field.

distribution corresponding to the Maxwell distribution at the temperature of the solvent. This case is discussed in Section 4. For this case the structure of the boundary layer can be related simply to the case of a completely absorbing boundary, treated in Ref. 2. The resulting values of x_M are compared with the predictions of "transition state theory",[4] both in a naive version, and in a modified, self-consistent form. The latter yields good predictions for all but the lowest threshold velocities. For the model of Section 3 larger deviations are indicated, but convergence problems preclude definitive statements. Section 5 contains a few concluding remarks.

2. BASIC EQUATIONS AND SOLUTION PROCEDURE

In this paper we are interested in stationary solutions of the one-dimensional Fokker–Planck equation

$$\frac{\partial P(u,x,t)}{\partial t} = \left[\gamma\left(\frac{1}{m\beta}\frac{\partial^2}{\partial u^2} + \frac{\partial}{\partial u}u\right) - u\frac{\partial}{\partial x}\right]P(u,x,t) \tag{2.1}$$

where $P(u,x,t)$ is the probability distribution for the components u and x of velocity and position of the Brownian particle perpendicular to the wall, m is its mass, γ the friction coefficient, and $\beta = (k_B T)^{-1}$ with T the temperature of the solvent medium. As is shown in Section 2 of Ref. 2, this equation has the stationary solutions of Chapman–Enskog type

$$\psi_0(u,x) = (m\beta)^{1/2}\exp(-\tfrac{1}{2}m\beta u^2) \tag{2.2a}$$

and

$$\psi_0'(u,x) = m\beta\gamma(2\pi)^{-1/2}(x - \gamma^{-1}u)\exp(-\tfrac{1}{2}m\beta u^2) \tag{2.2b}$$

with corresponding position space densities $n_0(x) = (2\pi)^{1/2}$ and $n_0'(x) = x/l$ with $l = (m\beta\gamma^2)^{-1/2}$ the velocity persistence length,[2,5] the analog for our problem of the mean free path in kinetic theory. In addition we have the boundary layer solutions[2,6]

$$\psi_{\pm n}(u,x) = c_n H_n\left\{(\tfrac{1}{2}m\beta)^{1/2}\left[u \mp 2(n/m\beta)^{1/2}\right]\right\} \times \exp\left[-\tfrac{1}{2}m\beta\left\{u \mp (n/m\beta)^{1/2}\right\}^2 \mp \gamma x(nm\beta)^{1/2}\right] \quad (n = 1,2,\ldots) \tag{2.3}$$

with c_n a normalization constant.

[4] Strictly speaking, transition state theory is formulated for a particle in a bistable potential; it relates the reaction rate to the one-way flow at the top of the barrier for the equilibrium solution. We shall loosely apply the term to a similar approximation to be described more precisely in Section 4.

Our goal is to construct a solution of (2.1) for $x > 0$ that approaches the Chapman–Enskog solution $\psi_0'(u,x) + d_0\psi_0(u,x)$ for $x \to \infty$ and obeys certain boundary conditions at $x = 0$. The solution sought must have the form

$$P(u,x) = \psi_0'(u,x) + \sum_{n=0}^{+\infty} d_n \psi_{+n}(u,x) \tag{2.4}$$

since the ψ_{-n} diverge for large x.

The boundary condition at $x = 0$ will be formulated in terms of a wall scattering kernel $\sigma(u \mid u')$, where $\sigma(u \mid u')\,du$ is the probability that a particle impinging on the wall with velocity $u' < 0$ will leave it with a velocity between u and $u + du$, with $u > 0$. In terms of this quantity we must have

$$uP(u,0) = \int_{-\infty}^{0} |u'|\sigma(u \mid u')P(u',0)\,du' \qquad \text{for } u > 0 \tag{2.5a}$$

This condition relates the positive- and negative-velocity parts of $P(u,0)$, defined as

$$P^{\pm}(u,0) = P(u,0)\Theta(\pm u) \tag{2.6}$$

with $\Theta(u)$ the Heaviside step function; (2.5a) can be written symbolically as

$$P_+ = \mathfrak{R}P_- \tag{2.5b}$$

A solution of type (2.4), which contains a constant current flowing towards the wall, is possible only if there is at least some absorption: $\int \sigma(u \mid u')\,du < 1$ for at least some u'. The case of a totally absorbing wall, treated in Ref. 2, is obtained by putting σ, and hence $\mathfrak{R}$, equal to zero.

Rather than trying to satisfy (2.6) exactly, we shall construct approximate solutions

$$P^N(u,x) = \psi_0'(u,x) + \sum_{n=0}^{N-1} d_n^N \psi_{+n}(u,x) \tag{2.7}$$

such that the quantity

$$D_N^2 = \int_0^{\infty} \rho(u)\left[P_+^N(u,0) - (\mathfrak{R}P_-^N)(u,0)\right]^2 du \tag{2.8}$$

with $P_{\pm}^N$ defined in analogy with (2.6), is minimized. The function $\rho(u)$ is an as yet arbitrary positive weight function; we shall choose $\rho(u) = u\exp[\frac{1}{2}m\beta u^2]$, as in Ref. 2, for reasons discussed there. The condition that D_N^2 is minimal yields a set of inhomogeneous linear equations for d_n^N, that are solved numerically. For the choices of $\sigma(u \mid u')$ treated in the next two sections, the coefficients in this system of equations can be evaluated using the formulas in the Appendix of Ref. 2. If the $\psi_{+n}(u,0)$ with $n = 0, 1, 2, \ldots$ possess the half-range completeness property discussed in Ref. 2, the

d_n^N have unique limits for $N \to \infty$, that do not depend on the choice for $\rho(u)$. This property, though plausible, remains unproved.

3. SELECTIVELY ABSORBING WALL WITH SPECULAR REFLECTION

In this section we describe some results obtained with the method described in Section 2 for the wall scattering kernel

$$\sigma(u \mid u') = \delta(u + u')\Theta(u_t - |u'|) \tag{3.1}$$

i.e., particles hitting the wall with absolute velocities larger than the threshold velocity u_t are absorbed, while slower particles are reflected specularly. Calculations were carried out for the values $u_t = \frac{1}{2}, \sqrt{\frac{1}{2}}, 1, \sqrt{2}$, and 2 in units of the thermal velocity $(m\beta)^{-1/2}$. The calculations, as well as those reported in the following sections, were carried out on the CYBER 175 of the RWTH Computing Center. Details of the calculational procedure are given elsewhere.[7] The calculations turned out to be much more time-consuming than the corresponding ones for $u_t = 0$, and they were not carried beyond $N = 70$.

A three-dimensional picture of the $P^{70}(u, x)$ that minimizes D_{70}^2 [see (2.7) and (2.8)] for $u_t = \sqrt{2}\,(m\beta)^{-1/2}$ is given in Fig. 1. The kinetic boundary layer differs noticeably from that in Ref. 2 for a totally absorbing wall. In particular, the density seems to go through a minimum and then increases again towards the wall. Closer inspection of the figure shows that the effect occurs only in the low-velocity part of the distribution. The effect is readily understood. Particles too slow to be absorbed are reflected with a low velocity. They will tarry near the wall for some time and, if they have their first turning point close to the wall, their chances of amassing enough kinetic energy to be absorbed at their next encounter with the wall is again rather poor. A similar accumulation of unabsorbable particles near a wall was seen by Hess[8] in a system of anisotropic molecules near a wall that preferentially absorbs molecules with certain orientations. In Fig. 2 we show the density profiles

$$n^{70}(x) = \int P^{70}(u, x)\, du \tag{3.2}$$

relative to their asymptotes

$$n_{as}^{70}(x) = x/l + (2\pi)^{1/2} d_0^{70} \tag{3.3}$$

for the different values of u_t and, for comparison, for $u_t = 0$. A minimum in the density occurs for u_t of the order of the thermal velocity or higher. The interpretation of the density increase towards the wall as an accumulation of slow particles is confirmed by the data for the mean kinetic energy per

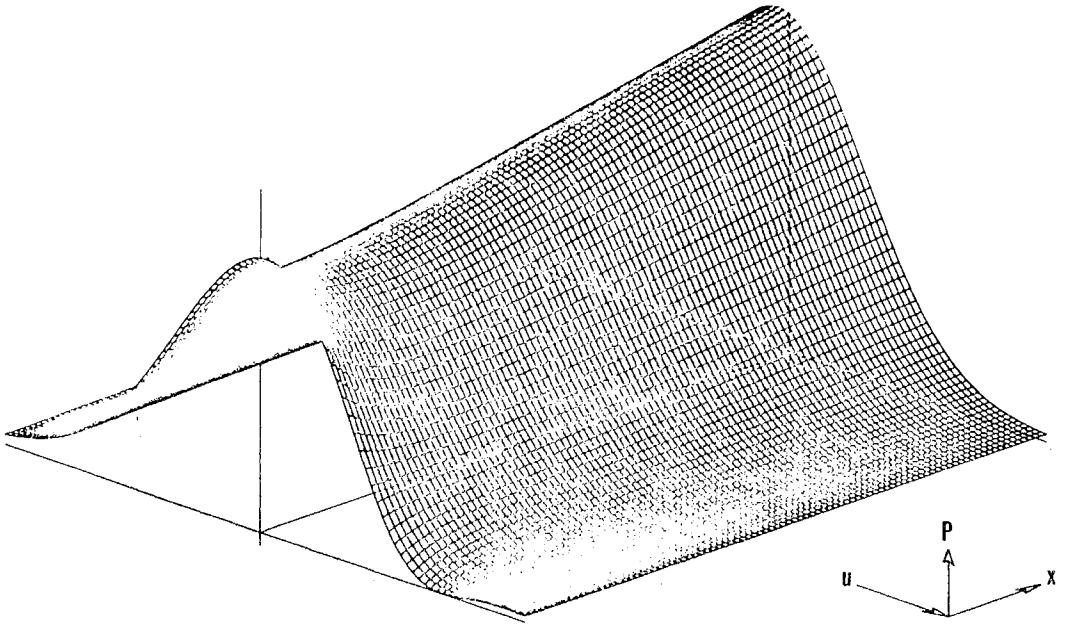

Fig. 1. The approximation $P^{70}(u, x)$ to the joint distribution of velocity u and position x of a Brownian particle near a wall (at $x = 0$) with absorption threshold $u_t = \sqrt{2}\,(m\beta)^{-1/2}$ and specular reflection of slower particles. The surface $P^{70}(u, x)$ is shown for $0 < x < 3$ in units of the velocity persistence length l and $-3 < u < 3$ in units of the thermal velocity $(m\beta)^{-1/2}$. The P axis is vertical, the x axis runs towards the rear. Note the accumulation of slow particles near the wall.

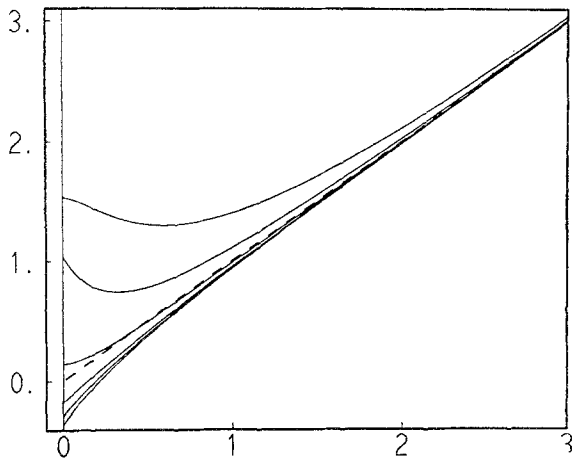

Fig. 2. The density profiles $n^{70}(x)$, cf. Eq. (3.2), for absorption thresholds 0, $\frac{1}{2}$, $\sqrt{\frac{1}{2}}$, 1, $\sqrt{2}$, and 2, in units of $(m\beta)^{-1/2}$, and specular reflection. The curves have been shifted vertically in such a way that their asymptotes $n_{\text{as}}^{70}(x)$, cf. Eq. (3.3), coincide with the dashed line in the figure. The lowest curve corresponds to $u_t = 0$, the higher ones to successively higher values of u_t. Lengths are in units of the velocity persistence length l.

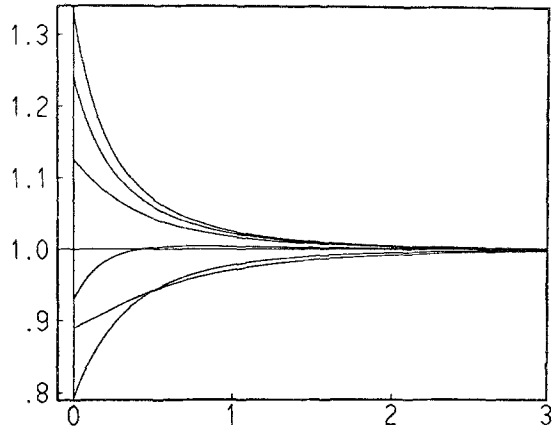

Fig. 3. The approximation obtained with 70 boundary layer solutions for the mean kinetic energy per particle, in units of $\frac{1}{2}\beta^{-1}$, as a function of x/l for specularly reflecting walls with absorption thresholds as in Fig. 2. The highest curve corresponds to $u_t = 0$; u_t increases successively as the position of the curves at the high-x side becomes lower.

particle (in units of $\frac{1}{2}\beta^{-1}$),

$$m\beta\langle u^2\rangle^{70}(x) = m\beta\int P^{70}(u,x)u^2\,du\Big[n^{70}(x)\Big]^{-1} \tag{3.4}$$

exhibited in Fig. 3. We note in passing that the occurrence of a stationary current flowing *against* a density gradient near the wall is a clear illustration of the breakdown of the hydrodynamic equation (here: the diffusion equation) inside the kinetic boundary layer.

The convergence of the results with increasing N is rather slow, but fast enough to secure the validity of the qualitative conclusions just described; a fuller discussion is given elsewhere.[7] Our values for the extrapolation length x_M for the model are given in the next section.

4. SELECTIVELY ABSORBING WALL WITH DIFFUSE REFLECTION; EFFECTIVE REACTION RATES

In this section we consider the wall scattering kernel

$$\sigma(u\,|\,u') = m\beta u\exp\left(-\tfrac{1}{2}m\beta u^2\right)\Theta(u_t - |u'|) \tag{4.1}$$

which implies that particles hitting the wall with velocities larger than u_t are absorbed, while slower particles are reemitted with a velocity distribution corresponding to a Maxwellian at the solvent temperature. The specific feature of this kernel is that the operator $\mathcal{R}$ defined by (2.5) is a multiple of the projection operator on the function $\psi_0(u,0)\Theta(u)$. This implies that the boundary condition can be fulfilled by a function $P_{[u_t]}(u,x)$ of the form

$$P_{[u_t]}(u,x) = P_{[0]}(u,x) + \Delta d_0\psi_0(u,x) \tag{4.2}$$

with $P_{[0]}(u,x)$ the solution for the case of a completely absorbing wall. Substitution in (2.5) using (4.1) shows that this fulfills the boundary condition, provided one has

$$\Delta d_0 = (m\beta)^{1/2}\int_{-\infty}^{-u_t}|u|\Big[P_{[0]}(u,0) + \Delta d_0\psi_0(u,0)\Big]\,du \tag{4.3}$$

from which Δd_0 is easily determined when $P_{[0]}(u,0)$ is known.

The form (4.2) for our solution implies that the boundary layer for the wall studied in this section is obtained from the boundary layer for a fully absorbing wall by adding a Maxwellian distribution with constant density in space. Of course this holds only for the exact solution, but we found that for the approximate solutions $P^N_{[u_t]}$ determined as described in Section 2, it remains true to at least the first six significant digits. Calculations were carried out for $(m\beta)^{1/2}u_t = \frac{1}{2}, \sqrt{\frac{1}{2}}, 1, \sqrt{2}, 2$, and 4, and for N up to 140. The interesting new information contained in our results is the value for Δd_0 or,

Table I. The Milne Extrapolation Length in Units of the Velocity Persistence Length for Various Values of the Threshold Velocity u_t[a]

u_t		$N = 35$	$N = 50$	$N = 70$	$N = 140$	Extrapolated	TST	SCTST
0		1.419	1.425	1.430	1.438	1.46	2.507	1.253
$\frac{1}{2}$	s	1.488	1.489	1.489			2.840	1.464
	d	1.606	1.610	1.613	1.618	1.63		
$\sqrt{\frac{1}{2}}$	s	1.559	1.560	1.562			3.219	1.740
	d	1.866	1.869	1.871	1.874	1.88		
1	s	1.848	1.884	1.927			4.133	2.477
	d	2.579	2.581	2.582	2.584	2.59		
$\sqrt{2}$	s	3.593	3.830	4.009			6.814	4.684
	d	4.937	4.938	4.938	4.939	4.94		
2	s	11.20	11.63	12.46			18.52	16.10
	d	16.14	16.14	16.14	16.14	16.14		
4	d	7468	7468	7468	7468	7468	7472	7468

[a] The first column gives u_t in units of the thermal velocity, both for specular (s) and for diffuse (d) reflection of subthreshold particles. Columns 2–5 give the approximate values calculated using N boundary layer solutions, column 6 the extrapolated value for $N = \infty$ (only for diffuse scattering), and columns 7 and 8 the approximations calculated from "transition state theory," both in a naive (TST) and in a self-consistent (SCTST) version. The inverse of x_M is proportional to the effective absorption rate at the wall.

equivalently, the position of the asymptote to the density profile,

$$n_{as}(x) = x/l + (2\pi)^{1/2} d_0 = (x + x_M)/l \tag{4.4}$$

where x_M is the Milne extrapolation length defined in Section 1. The approximations x_M^N to this quantity in units of the velocity persistence length $l = (\gamma^2 m\beta)^{-1/2}$ are given in Table I for various values of N and of u_t, both for the present model and that of Section 3. The length l is the distance a particle with velocity $(m\beta)^{-1/2}$ travels during the velocity equilibration time γ^{-1}. The table also contains extrapolated values for x_M found for diffusely scattering walls using the method described in Ref. 2,

Section 4. The results for different extrapolation intervals agree to the accuracy given in the table. For specularly reflecting walls reliable extrapolation was not possible.

The quantity x_M may also be related to an effective reaction rate k_{eff} defined as the ratio between the current flowing towards the wall and the density $n_{\text{as}}(0)$ obtained by extrapolating the asymptotic density towards the wall. Since in (2.4) only the term $\psi_0'(u,x)$ contributes to the current (as shown in Ref. 2), this quantity is calculated easily; using (2.2b) we obtain

$$k_{\text{eff}} = (m\beta\gamma x_M)^{-1} = (m\beta)^{-1/2} l / x_M \tag{4.5}$$

A rough approximation to k_{eff} would be obtained by replacing the velocity distribution at the wall by a Maxwellian and then determining the current carried by all particles with $u < -u_t$. This "naive transition state theory" yields

$$\begin{aligned} k_{\text{eff}} &\sim -(m\beta/2\pi)^{1/2} \int_{-\infty}^{-u_t} u \exp\left[-\tfrac{1}{2} m\beta u^2\right] du \\ &= (2\pi m\beta)^{-1/2} \exp\left[-\tfrac{1}{2} m\beta u_t^2\right] \end{aligned} \tag{4.6}$$

the approximation does not differentiate between diffuse and specular scattering. The value of x_M corresponding to (4.6) according to (4.5) is listed in Table I. Except for high u_t it gives much too low a value for k_{eff}. An obvious refinement is to approximate the velocity distribution at the wall by

$$\hat{P}(u,0) = \psi_0'(u,0) + \hat{d}_0 \psi_0(u,0) \tag{4.7a}$$

and to determine $\hat{d}_0$ by the requirement

$$\int_{-\infty}^{-u_t} u \hat{P}(u,0) = \int_{-\infty}^{+\infty} u \psi_0'(u,x)\, du = -(m\beta\gamma)^{-1} \tag{4.7b}$$

We propose to call this approximation "self-consistent transition state theory"[5]; the corresponding approximation to x_M is also shown in Table I. It yields a slight underestimate for x_M for diffusely reflecting walls, but the approximation is quite good, except for very low thresholds. Since the approximation (4.7) consists of a complete neglect of the presence of the kinetic boundary layer, we may conclude that the presence of this boundary layer has a rather small effect on the effective reaction rate for diffusely scattering walls, except at very low thresholds.

For specularly scattering walls the effect is also quite small at subthermal threshold velocities. For higher thresholds our numbers might be

[5] Note that this approximation is equal to $P^1(u,0)$ for a diffusely scattering wall, as is clear from a comparison with (4.3).

interpreted as indications of larger effects, but because of poor convergence of our results with N this evidence is not really conclusive. The only feature that seems reasonably assured is that the effective reaction rates for specular reflection are always larger than the corresponding ones for diffuse reflection. This seems reasonable; after a diffuse reflection a reflected particle obtains on the average a higher positive velocity, and hence it takes longer, on the average, to reach the wall again.

5. CONCLUDING REMARKS

The transition state theory of chemical reactions has two main defects[9]: (i) it neglects effects caused by deviations from local equilibrium; (ii) it neglects the possibility of a particle crossing the "top of the barrier," recrossing it again, and falling back without having reacted. The model treated in this paper shares the shortcoming mentioned under (ii): a particle reaching the wall with sufficient energy is always absorbed. Effects of type (i), on the other hand, are expected to be prominent. They are not even amenable to perturbative treatment; the natural expansion parameter is the ratio between the velocity persistence length (or the mean free path) and the distance over which the potential varies appreciably. The results of such a perturbative treatment can be extended to higher values of the expansion parameter by Padé-approximant techniques, as was done recently by Skinner and Wolynes.[9] In our case the variation of the potential is compressed to a single point and a nonperturbative treatment is clearly called for.

The method of expansion in boundary layer solutions, which forms the basis of our treatment, was successful in various boundary layer problems in linear transport theories.[10] These successes were obtained by sophisticated analytical methods, based on half-range completeness theorems.

Such a theorem is not available for our case, but the success of the numerical treatment gives some support to its validity there.[6] Of course, even if the set is complete, it need not be very convenient for expansion purposes. In fact it is rather awkward, as may become clear from Fig. 4, which shows $\psi_{+n}(u, 0)$ for $n = 35$, 70, and 140, and for small values of $|u|$. From the properties of the Hermite polynomials[12] it is easy to show that the first zero lies at $x_{1,n} \approx 2.338 \ldots n^{-1/6}$ and the "local wavelength" near $x = 0$ also decreases as $n^{-1/6}$. Thus it is intuitively clear, that an expansion in $\psi_n(u, 0)$ will converge much more slowly than, say, a Fourier series. This is especially true for the boundary condition of Section 3. The latter may be

[6] A similar approach was used in a recent paper by Pomraning and Larsen[11]; like ours, their numerical solution procedure was found to be highly sensitive to round-off errors.

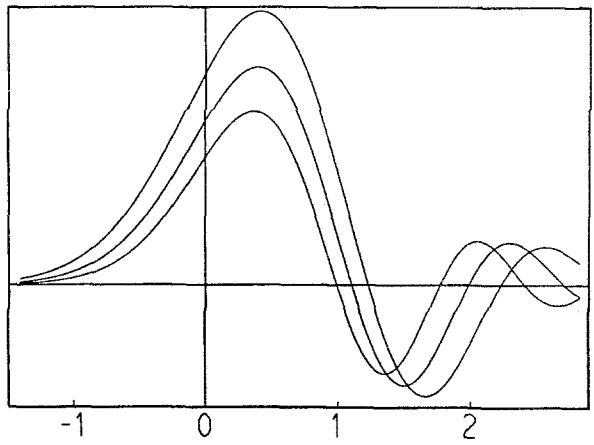

Fig. 4. The values at the wall of the boundary layer solutions $\psi_{+n}(u, x)$ for $n = 35$, 70, and 140 (n increasing as the position of the curves at low u decreases), for a range of u values, in units of $(m\beta)^{-1/2}$.

written as

$$P_+(u,0) = P_-(-u,0)\Theta(u_t - u) \tag{5.1}$$

which suggests a discontinuity at $+u_t$. On a more technical level, it is clear from Fig. 4 that in particular the integrals

$$\int_0^\infty \psi_0(u,0)\psi_{+n}(u,0)u\exp\left(\tfrac{1}{2}m\beta u^2\right)du \tag{5.2}$$

and

$$\int_0^{u_t}\psi_{+n}(-u,0)\psi_{+m}(u,0)u\exp\left(\tfrac{1}{2}m\beta u^2\right)du \tag{5.3}$$

that enter into the system of equations resulting from minimizing (2.9) with $\mathfrak{R}$ derived from (3.1), will decrease quite slowly with n, or with n and m; this leads to slow convergence of the d_n^N, and especially of the d_0^N, with increasing N.

In spite of these difficulties, we were able to obtain a good qualitative picture of the phenomena that occur in the kinetic boundary layer, even for the case of specularly reflecting walls.

ACKNOWLEDGMENTS

We thank Dr. Henk van Beijeren for several pleasant and useful discussions, Mr. N. Gwosdzyk for help and advice in obtaining the graphical computer output, and Mr. W. Juling, who provided and adapted the program used to obtain Fig. 1.

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