The dynamics of the expansion of a vapor when evaporated into a vacuum

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(Submitted October 3, 1972)
Zh. Eksp. Teor. Fiz. **64**, 869-876 (March 1973)

The gas-kinetic problem of the motion of the vapor of a condensed body during the nonstationary vaporization of the body into a vacuum is solved. The transition from the free-molecule vapor expansion regime, which obtains at the initial stage of the evaporation, to the regime in which the vapor moves like a continuous medium is studied. The time of transition to the limiting flow regime in which the motion of the bulk of the vapor is described by the equations of gas dynamics is determined. Boundary conditions on the surface from which the evaporation takes place are determined for the gas-dynamics equations. The reflux of atoms to the surface of the condensed body due to collisions in the gaseous phase is computed.

INTRODUCTION

The rate of evaporation into a vacuum of a condensed body of temperature much less than the binding energy of the atoms is determined by two processes: the departure of atoms from the surface owing to the thermal motion and their return to the surface owing to collisions in the gaseous phase. For a sufficiently slow evaporation into the vacuum, the vapor density near the surface is small and the second process can be neglected. In fact, in papers devoted to the kinetics of the evaporation of solids and liquids only this simplest case is considered[1-3]. An effective method for computing the probability of escape of an atom from the surface turned out in this case to be a method based on the theory of absolute reaction rates[3].

For an intense (as well as prolonged) evaporation, the neglect of the reflux of atoms becomes incorrect. Such a case is realized, for example, during the action of a high-power laser or electron beam on the surface of a solid[4]. Under conditions typical of such experiments, the motion of the bulk of the vapor can be described by the equations of hydrodynamics. Two questions then arise as to: 1) what the "pure" evaporation rate is and 2) what boundary conditions the solutions of the gas-dynamics equations should satisfy at the vaporizing surface. The second question is connected with the fact that the hydrodynamic approximation is clearly inapplicable in a thin (a few atomic mean free paths thick) Knudsen layer at the surface of the solid, where the distribution function strongly differs from the locally stable distribution function. From the hydrodynamic point of view the Knudsen layer is a discontinuity surface. In order to obtain the effective boundary conditions at such a discontinuity, we must find the velocity distribution function for the atoms inside the Knudsen layer. The solution to this problem was given in[5] and was subsequently confirmed by a more circumstantial computation carried out in[6] (see also chapter IV of the book[4]). It was established that the vapor temperature at the outer boundary of the Knudsen layer is roughly equal to $0.67T_0$ (where T_0 is the temperature of the condensed phase), while the vapor density is close to $0.31n_0$ (n_0 is the equilibrium vapor density at the temperature T_0). From this it is easy to obtain the magnitude of the reflux during evaporation into a vacuum. It is approximately equal to $j_- = 0.2j_+$, where j_+ is the flux in the absence of collisions. Thus, the relative jumps in the variables in the Knudsen layer during evaporation into a vacuum turn out to be of the order of unity. Such a result seems reasonable, since the problem does not contain any small parameters.

It should be noted that allowance for the boundary conditions given above is extremely important in the study of the evaporation of solids under the action of light. In this case there arises the question of light absorption in the vapor stream and of screening at the vaporizing surface[4]. Since under conditions of weak screening the absorption coefficient very strongly depends on the vapor density and temperature, even a slight error in the boundary conditions will entail a considerable error in the determination of the optical thickness of the vapor layer[1)].

The description of the flow by the equations of gas dynamics with effective boundary conditions is possible in the case when the mass of the evaporated matter is sufficiently large and a hydrodynamic motion of the bulk of the vapor has been formed. This phase is preceded by a transition process the analysis of which requires the solution of the kinetic problem of vapor motion not only for the Knudsen surface layer, but for the entire flow. A hydrodynamic expansion regime will be established in a region where the density is fairly large. However, in an expansion into a vacuum the rarefaction wave always has a "tail" in which the flow remains a free-molecule flow. Therefore, the hydrodynamic description of the expansion of a gas into a vacuum always contains an inaccuracy connected with the fact that the vanishing of the density and pressure at finite (for finite t) distances that follows from the hydrodynamic solution is, strictly speaking, incorrect (for a discussion on the correctness of the hydrodynamic formulation of the problem of gas expansion into a vacuum, see[8]).

Thus, the correct approach to the problem of evaporation into a vacuum presupposes the solution of the kinetic equation for the expanding vapor over a sufficiently large time interval. Such a solution allows us to follow the transition from the free-molecule dispersion of the vapor to the hydrodynamic dispersion, to determine the nature of the flow in the low-density region, where the equations of hydrodynamics are inapplicable, and to find the effective boundary conditions on the vaporizing surface. Such a solution is obtained in the present paper by a numerical method. Since the numerical solution of the kinetic equation with the Boltzmann collision term requires an extraordinarily large expenditure of machine time, we thought it advisable to carry out the basic computations for the so-called BGK model of the collision integral[9]. The considerable number of kinetic problems solved with such a model allows us to conclude that the model is highly accurate in a wide range of Knudsen numbers (see[10])$^{2)}$.

We restricted ourselves to the solution of the one-dimensional non-stationary problem and assumed the surface temperature and the distribution function of the particles emitted from the surface to be time independent. The simultaneous solution of the heat equation for the solid phase and the kinetic equation for the vapor would have corresponded more closely to the experimental conditions. Such calculations do not require a fundamental complication of the formulation adopted in this paper for the problem and they are carried out at present.

1. FORMULATION OF THE PROBLEM

We shall consider the evaporation into an initially vacuous half-space of a semi-infinite solid of temperature T_0. Let us choose a system of coordinates in which the phase interface is at rest. The solid phase occupies the half-space $x < 0$ and the gas, the half-space $x > 0$. The motion of the gas is described by the Boltzmann equation

$$\frac{\partial f}{\partial t}+(\mathbf{v}, \nabla) f=I(f). \tag{1}$$

We assume for the collision integral the model expression[9]

$$I(f)=\nu(f_0-f), \tag{2}$$

where

$$f_0(x, t, \mathbf{v})=n(x, t)[\alpha(x, t)/\pi]^{3/2}\exp\{-\alpha(x, t)[\mathbf{v}-\mathbf{u}(x, t)]^2\},$$
$$\alpha(x, t)=M/2kT(x, t).$$

The functions $n(x, t)$, $\mathbf{u}(x, t)$, and $T(x, t)$ entering into (2) are not known in advance and are determined in terms of the function $f(x, t, \mathbf{v})$ by the integral relations

$$n=\int f\,d^3v, \qquad n\mathbf{u}=\int \mathbf{v} f\,d^3v, \tag{3}$$
$$3nkT+Mnu^2=m\int v^2 f\,d^3v.$$

The collision rate $\nu = A(T)n$ entering into (2) depends on the law of interaction between the atoms. We shall henceforth consider the rigid-sphere model, for which $A \sim \sqrt{T}$. As the boundary condition for (1)—(2), we must specify the distribution function of the atoms entering into the half-space $x > 0$. In accordance with[2], we shall assume it to be Maxwellian for the particles with $v_x > 0$:

$$f_+(\mathbf{v})=n_0(\alpha_0/\pi)^{3/2}\exp(-\alpha_0 v^2), \tag{4}$$

where $\alpha_0 = M/2kT_0$, M is the atomic mass, T_0 is the surface temperature, and n_0 is the equilibrium vapor density corresponding to this temperature. Since the evaporation of a metal is of the greatest practical interest, we assume the probability of sticking of the particles to the surface to be equal to unity. Besides (4), there are the obvious conditions which can be imposed on the function $f(x, t, \mathbf{v})$:

$$\lim_{x\to\infty} f(x, t, \mathbf{v})=0, \qquad \lim_{|\mathbf{v}|\to\infty} f(x, t, \mathbf{v})=0, \qquad f(x, 0, \mathbf{v})=0.$$

It is convenient for what follows to go over to dimensionless variables. Let us introduce them in the following fashion. As the unit of length, let us choose the atomic mean free path at the density n_0; as the unit of velocity, the quantity $(2\alpha_0)^{-1/2}$; we shall measure temperature and density in units of T_0 and n_0 respectively. Since we shall henceforth use only dimensionless quantities, we preserve for them the same symbols as for the dimensional quantities. The problem can then be formulated as follows:

$$\frac{\partial f}{\partial t}+v_x\frac{\partial f}{\partial x}=\nu(f_0-f),$$
$$f_0=n(2\pi T)^{-3/2}\exp[-(\mathbf{v}-\mathbf{u})^2/2T],$$
$$f_+=(2\pi)^{-3/2}\exp(-v^2/2), \quad \nu=n\sqrt{T}.$$

The dimensionless expressions for n and **u** coincide with (3); the relation determining T will be written out below (see (6)).

The integration in the formulas (3) is over the entire velocity space, i.e., the integrals in (3) are, with allowance for the symmetry of the problem, double integrals. It is convenient, bearing in mind the numerical solution of the problem, to go over from $f(x, t, \mathbf{v})$ to new unknown functions which depend only on one component v_x of the velocity. We can formulate a closed system of equations in terms of these equations and compute all the hydrodynamic variables that characterize the vapor stream. Let us introduce the new functions $\varphi(x, t, v_x)$ and $\psi(x, t, v_x)$ according to the relations

$$\psi(x, t, v_x)=\int f(x, t, \mathbf{v})\,d^2v_\perp,$$

$$\varphi(x, t, v_x)=\int f(x, t, \mathbf{v})\,v_\perp^2 d^2v_\perp,$$

where the vector $\mathbf{v}_\perp$ has the components (v_y, v_z). The equations for φ and ψ have the form

$$\frac{\partial\psi}{\partial t}+v_x\frac{\partial\psi}{\partial x}=n\sqrt{T}(\psi_0-\psi),$$
$$\frac{\partial\varphi}{\partial t}+v_x\frac{\partial\varphi}{\partial x}=n\sqrt{T}(\varphi_0-\varphi). \tag{5}$$

Here

$$\psi_0=n(2\pi T)^{-1/2}\exp[-(v_x-u)^2/2T], \quad \varphi_0=2T\psi_0,$$

while the function $T(x, t)$ is defined by the relation

$$T(x, t)=(3n)^{-1}\Big\{\int_{-\infty}^{\infty} v^2\psi(x, t, v)\,dv$$
$$+\int_{-\infty}^{\infty}\varphi(x, t, v)\,dv-n^{-1}\Big[\int_{-\infty}^{\infty} v\psi(x, t, v)\,dv\Big]^2\Big\}. \tag{6}$$

For $n(x, t)$ and $u(x, t)$ the relations (3) remain valid, except that f is replaced by ψ and the integration is a single integration over v_x.

2. METHOD OF SOLUTION

To solve the system of equations (5) numerically, we use an iterative method for the collisions. As the initial approximation in each time spacing, we shall use the distribution functions computed for the previous spacing.

For small times the dispersion of the vapor takes place without collisions, and therefore the values of the distribution functions along the characteristic curves $dx/dt = v_x$ are conserved. In the presence of collisions, the variation of the functions φ and ψ along the characteristic curves is determined by the collision term. Before expounding the procedure for integrating Eqs. (5), let us write out the solution for the collisionless case, since this solution will be needed below. Taking the conservation of φ and ψ along the characteristic curves into account, and using the boundary conditions at $x = 0$ and $t = 0$, we easily derive the following formulas for the hydrodynamic averages:

$$n(x,t)=\tfrac{1}{2}\operatorname{erfc}\mu,\quad u(x,t)=(2/\pi)^{1/2}(e^{\mu^2}\operatorname{erfc}\mu)^{-1},$$
$$T(x,t)=1+\frac{2}{3\sqrt{\pi}}(e^{\mu^2}\operatorname{erfc}\mu)^{-1}[\mu-(\sqrt{\pi}\,e^{\mu^2}\operatorname{erfc}\mu)^{-1}],\tag{7}$$
$$\mu=\frac{x}{t\sqrt{2}},\qquad \operatorname{erfc}\mu=\frac{2}{\sqrt{\pi}}\int_{\mu}^{\infty}e^{-z^2}dz.$$

For $x \gg t\sqrt{2}$ we obtain the following asymptotic distributions for the variables:

$$n(x,t)\sim\frac{t}{x\sqrt{2\pi}}\exp\left(-\frac{x^2}{2t^2}\right)$$
$$u(x,t)\sim x/t,\quad T(x,t)\sim {}^2/_3.$$

Notice that the mean energy density T(x, t) of the thermal motion in the free-molecule dispersion tends at large distances from the surface not to zero (as would have been in the hydrodynamic solution), but to $\frac{2}{3}$. The reason is that in the absence of collisions, only the longitudinal component of the velocity of the thermal motion contributes to the kinetic energy of the ordered motion of the vapor. The "transverse" temperature remains "frozen."

The free-molecule motion is evidently self-similar and depends on the variable x/t. The hydrodynamic motion, which subsequently develops, is a centered rarefaction wave. It is also self-similar and depends on the same variable. However, the profiles of the functions computed on the basis of both approximations substantially differ from each other.

To solve the system (5), we iterate with respect to the collisions. After integrating (5) along the characteristic curves, we can easily derive the formulas: for $x > v_x t$

$$\psi(x,t,v_x)=\psi(x-v_x t,0,v_x)\exp\left[-\int_0^t\nu(\xi_1,t_1)dt_1\right]$$
$$+\int_0^t\psi_0(\xi_1,t,v_x)\nu(\xi_1,t_1)\exp\left[-\int_{t_1}^t\nu(\xi_2,t_2)dt_2\right]dt_1,\tag{8}$$

and for $x < v_x t$

$$\psi(x,t,v_x)=\psi\left(0,t-\frac{x}{v_x},v_x\right)\exp\left[-\int_0^x\nu(x_1,\eta_1)\frac{dx_1}{v_x}\right]$$
$$+\int_0^x\psi_0(x_1,\eta_1,v_x)\nu(x_1,\eta_1)\exp\left[-\int_{x_1}^x\nu(x_2,\eta_2)\frac{dx_2}{v_x}\right]\frac{dx_1}{v_x},$$

where $\xi_h = x - v_x(t - t_h)$; $\eta_k = t - v_x^{-1}(x - x_k)$ and the quantities n, u, and T are given by the relations (3) and (6).

Similar expressions can be written down for the function φ. Given the values of the functions $\psi(x, t_{l+1}, v_x)$ and $\varphi(x, t_{l+1}, v_x)$ at $t = t_l$ as the zeroth approximation to them, we can solve the system (5) by iterating with respect to the collisions. These iterations, however, converge relatively slowly, and, to hasten the convergence, we use a quasi-diffusion type of procedure[11]. As an intermediate step in the iterations, we solve the "quasi-gas-dynamic" system

$$\frac{\partial n}{\partial t}+\frac{\partial j}{\partial x}=0,\qquad\frac{\partial j}{\partial t}+\frac{\partial W}{\partial x}=0,\tag{9}$$

where j = nu is the particle flux density and

$$W=\int_{-\infty}^{\infty}v_x^2\psi\,dv_x.$$

The use of (9) enables us to substantially shorten the computation time and to obtain a solution to the kinetic equation over a long interval of time. A detailed exposition of the mathematical method will be given in a separate article.

3. DISCUSSION OF THE RESULTS

The qualitative picture of the solution is as follows. At the beginning of the process, when t < 1, the motion of the vapor is collisionless, and the profiles of the variables are given by the formulas (7). Then the collisionless profiles begin to get distorted, owing to the collisions, and a hydrodynamic flow begins to form at distances from the surface of the order of unity. The hydrodynamic flow gradually encompasses a larger and larger spatial region and assumes more and more the structure of a centered rarefaction wave. It is interesting to follow how the energy-density profile for the thermal motion of the atoms varies (in the equilibrium state this quantity is called the temperature, and we shall, for brevity, call it thus in the nonequilibrium case being studied here). Figure 1 shows the temperature profiles at different moments of time (the time is indicated by the numbers on the corresponding curves). It can be seen that at t = 0.5, the temperature profile corresponds to a free-molecule dispersion: the temperature varies monotonically from the value 0.78 at x = 0 to 0.67 when x → ∞. For t > 1 the curve T(x, t) has a minimum. The minimum evidently arises because a portion of the "transverse" energy of the thermal motion is converted as a result of collisions into kinetic energy for the ordered dispersion, so that the vapor temperature turns out to be less than the temperature in the collisionless motion. As time goes on, the minimum of the temperature profile becomes deeper. The temperature profile approaches the Riemann solution for a rarefaction wave. At the same time the flow in the region of large x remains, as before, a free-molecule flow. In particular, the asymptotic value of the temperature for x → ∞ is equal to $\frac{2}{3}$ for all moments of time.

The dashed curve in Fig. 1 shows how the temperature in the centered rarefaction wave varies. Comparison of the hydrodynamic solution with the true kinetic solution shows that the former is valid in about half of the region between the surface of the solid phase and the "front," where, according to hydrodynamics, the temperature should vanish. If we extrapolate the hydrodynamic solution to the surface x = 0 (where the solution is, in fact, incorrect), then the limiting value of the temperature turns out to be equal to 0.69, which is in good agreement with the asymptotic solution obtained in[5,6] for the Knudsen layer.

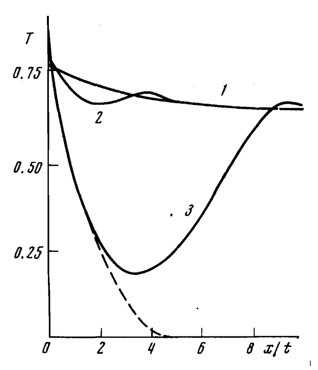

FIG. 1

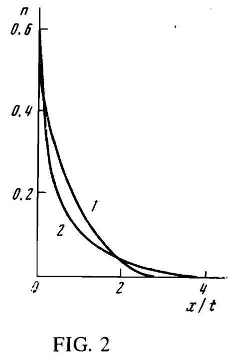

FIG. 2

FIG. 1. "Temperature" distribution at different moments of time. 1–t = 0.5; 2–t = 3.0; 3–t = 15.0.

FIG. 2. Vapor density distribution: 1–t = 0.5; 2–t = 15.0

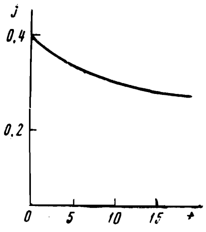

FIG. 3

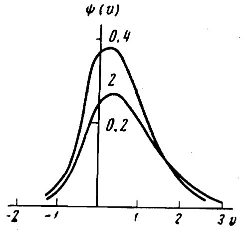

FIG. 4

FIG. 3. Flux density of the vaporized atoms at the surface.

FIG. 4. The distribution function ψ (v) at t = 5.0 for 1–x = 0 and 2–x = 5.0.

Figure 2 shows the density profiles corresponding to different moments of time. It can be seen that the density profile as a function of the self-similar variable x/t does not change very drastically on going over from the free-molecule dispersion to the centered rarefaction wave. The change amounts first and foremost to a reconstruction of the surface Knudsen layer and to the formation at large x of a low-density "tail."

Atomic collisions in the vapor lead to the appearance of a reflux and a decrease in the "pure" evaporation rate. Figure 3 shows how the flux density of the vaporized atoms varies in time. The highest flux density that corresponds to a collisionless flow (equal in our units to 0.398) decreases by roughly 20% during the transition process. This is also in good agreement with the results of[4-6]. The time during which stabilization of the reflux occurs is about 20 times the mean free time. This time may be conventionally regarded as the establishment time for the hydrodynamic regime of the motion of the vapor. In fact, the hydrodynamic regime is attained not inside the Knudsen layer, but in the "tail" of the rarefaction wave. However, since an exponentially small portion of the vaporized matter moves in the "tail," and the energy contained in this region is small, the asymptotic motion can be described with sufficient accuracy by the equations of gas dynamics with the boundary conditions obtained in[5,6]. Thus, the flow structure proposed in[5] is, in fact, attained after a fairly prolonged evaporation. The establishment time for such a flow is much longer than the mean free time of the atoms near the surface of the condensed phase; therefore, in an impulsive heating, conditions can be realized when the hydrodynamic evaporation regime does not set in at all. The last remark pertains, for example, to the evaporation of absorber bodies under the action of laser pulses obtained in a Q-modulated regime.

The variation of the distribution function $\psi(x, t, v)$ of the atoms in the course of the dispersion is shown in Fig. 4. At large distances the reconstruction of the distribution function is connected only with the kinematic transformation of the flow. At small distances the primary changes are due to collisions.

In conclusion, we express our sincere thanks to Yu. I. Lysikov, who performed a great deal of the work at the initial stage of the present investigation.

[1)] Touching upon the screening problem, we must note that, in general, its correct solution falls outside the framework of the simple one-dimensional gas-dynamical problem. For example, in the initiation of a luminous breakdown of the vapor, an important role may be played by liquid drops, which are, according to [7], often observable in the stream even at the initial stage of the evaporation.

[2)] An additional justification for using the model follows from the good agreement of the results of [5] and [6].

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Translated by A. K. Agyei
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