

Chapter 2

Nonequilibrium Effects on the Phase Interface

Abbreviations

BC	Boundary condition
CPS	Condensed-phase surface
DF	Distribution function

2.1 Conservation Equations of Molecular Flows

2.1.1 *The Distribution Function*

The description of intense phase changes calls for the solution to the flow problem in the ambient spaces of evaporating (condensing) matter, as described by gas dynamic equations. The specific feature of an intense phase change lies in the formation near the condensed-phase surface (CPS) of the Knudsen layer of thickness of order of the mean free path of molecules. The existence of the Knudsen layer depends on the nonequilibrium character of evaporation (condensation) resulting in the anisotropy of the velocity distribution function (DF) near CPS. In this setting, the gasdynamic description becomes unjustified—the phenomenological gas parameters (temperature, pressure, density, velocity), as defined according to the conventional rules of statistical averaging, lose their macroscopic sense. Such a situation can be described at a simplified level with the help of an “imaginary experiment”. Assume that the Knudsen layer has hypothetical micrometers of pressure and temperature. Then their readings will not agree with the statistically averaged values, but will rather depend on the structure of a micrometer. Such anomalies disappear beyond the Knudsen layer, in the outer region, where the Navier-Stokes equations hold. The outer region is also called the “Navier–Stokes region”.

Under a rigorous approach one needs to specify the boundary condition (BC) for the equations of gas dynamics in the Navier–Stokes region on the outer boundary of the Knudsen layer. To this aim one needs to know the DF on this interface. This, in

turn, leads to the problem of the solution of the Boltzmann equation in the Knudsen layer. Only in this case one may evaluate the corresponding gasdynamic parameters as the corresponding moments of the DF. It should be also pointed out that the outer boundary of the Knudsen layer is defined only up to several mean free paths of molecules. So, setting of the BC for the equations of gas dynamics is a highly nontrivial macroscopic problem. Its relation with the problem of microscopic parameters for the Boltzmann equation in the Knudsen layer governs the specifics and difficulty of the kinetic analysis of the intense phase changes [1].

The spectrum of molecules in the Knudsen layer is formed by the two oppositely directed molecular flows the one emitted by the CPS and the one incident on it from the Navier–Stokes region. In a somewhat simplified form the physical scheme of emission of molecules can be described as follows. Some part of liquid molecules, which are near the CPS and are in the state of chaotic thermal motion, temporarily acquire the kinetic energy, which exceeds the bond energy of molecules. As a consequence, “fast molecules” escape from the surface into the gaseous domain. This suggests that the intensity of the surface emission of molecules are uniquely determined by the temperature T_w of the CPS. This leads to the physically plausible conjecture: the spectrum of the emitted molecules are described by the equilibrium Maxwell distribution [2, 3]

$$f_w^+ = \frac{n_w}{\pi^{3/2} v_w^3} \exp\left(-\left(\frac{\mathbf{c}}{v_w}\right)^2\right) \quad (2.1)$$

Here $n_w = p_w/k_B T_w$ is the molecular gas density, $\mathbf{c}$, $\mathbf{u}_\infty$ are, respectively, the vectors of molecular and hydrodynamic velocity, c_z is the normal component of molecular velocity, $v_\infty = \sqrt{2R_g T_\infty}$, $v_w = \sqrt{2R_g T_w}$ is the thermal velocity of molecules, the index “w” denotes conditions on the CPS, the index “ ∞ ” denotes the conditions at infinity, $R_g = k_B/m$ is the individual gas constant, is the Boltzmann constant, m is the mass of molecule.

Maxwell considered gas as an ensemble of perfectly elastic balls moving chaotically in a closed volume and colliding with each other. Ball molecules can be subdivided into three groups in terms of their velocities, in a stationary state the number of molecules in each group being constant, even though they may change their velocities after collisions. This setting suggests that in equilibrium particles have different velocities, their velocities distributed according to the Gauss curve (the Maxwell distribution). Using the so-obtained DF, Maxwell calculated a number of quantities of great value in transport phenomena: the number of particles in a definite rage of velocities, the average velocity and the average squared velocity. The complete DF was calculated as the product of DF for each of the coordinates.¹

¹This implied their independence, which at this time was unclear to many researchers and required justification (which was done later).

Flow of molecules flying towards CPS is formed as a result of their collisions away from the CPS over the entire Knudsen layer. Hence, its DF should reflect certain averaged state of vapor in the surface region. As a result, the total DF on the CPS can be conventionally split into two parts, which “genetically” differ from each other

$$\begin{aligned} 0 \leq c_z < \infty : f_w &= f_w^+ \\ -\infty < c_z \leq 0 : f_w &= f_w^- \end{aligned} \quad (2.2)$$

Thus, the distribution of molecules in terms of velocities on the CPS (Fig. 2.1) should be discontinuous. Away from the phase interface the discontinuity in the DF is smoothed due to intermolecular collisions, the principal reconstruction occurring within the Knudsen layer.

2.1.2 Molecular Flows

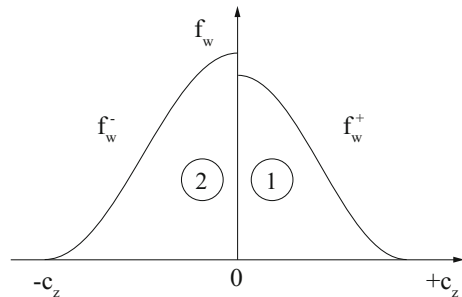
Let us consider the one-dimensional problem of evaporation/condensation in the half space for a vapor (of monatomic perfect gas) at rest. In this case, the vector of hydrodynamic velocity $\mathbf{u}_\infty$ is degenerated into the scalar velocity u_∞ in the direction of the evaporation flow. It is assumed that on the phase interface the constant temperature T_w is maintained by virtue of an external heat surface. On the phase interface there are coexisting molecular flows: the emitting ones J_i^+ and the incident ones J_i^- . In the equilibrium case we have: $J_i^+ = J_i^-$. For $J_i^+ \neq J_i^-$ in the Navier–Stokes region there are flows ($j_i \neq 0$), respectively, of mass ($i = 1$), momentum ($i = 2$) and energy ($i = 3$)

$$J_1^+ - J_1^- = j_1 \quad (2.3)$$

$$J_2^+ - J_2^- = j_2 \quad (2.4)$$

$$J_3^+ - J_3^- = j_3 \quad (2.5)$$

Fig. 2.1 Distribution function of molecules on the condensed-phase surface



So, the flows of evaporation/condensation in the Navier–Stokes region appear as the difference between the one-way gas flows for CPS. These net transfers are written in terms of the macroscopic parameters in the Navier–Stokes region

$$j_1 = \rho_\infty u_\infty \quad (2.3a)$$

$$j_2 = \rho_\infty u_\infty^2 + p_\infty \quad (2.4a)$$

$$j_3 = \frac{\rho_\infty u_\infty^3}{2} + \frac{5}{2} \rho_\infty u_\infty \quad (2.5a)$$

Here ρ_∞ is the density, p is the pressure, u_∞ is the hydrodynamic velocity, $J_i^+ > J_i^-$, $j_i > 0$ during evaporation, $J_i^+ < J_i^-$, $j_i < 0$ during condensation. Equations (2.3)–(2.5) can be looked upon as conservation equations of mass, momentum and energy for the Knudsen layer.² According to the theory [1], the flows of quantities are calculated by integrating the DF with the corresponding over the three-dimensional field of molecular velocities c_x , c_y , c_z . Accordingly, equations for the flows are as follows: for the emitting ones J_i^+ we have

$$\left. \begin{aligned} J_1^+ &= m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z f_w^+) \\ J_2^+ &= m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z^2 f_w^+) \\ J_3^+ &= \frac{1}{2} m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z^2 f_w^+) \end{aligned} \right\} \quad (2.6)$$

and for the incident ones J_i^-

$$\left. \begin{aligned} J_1^- &= m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_{-\infty}^0 dc_z (c_z f_w^-) \\ J_2^- &= m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_{-\infty}^0 dc_z (c_z^2 f_w^-) \\ J_3^- &= \frac{1}{2} m \int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_{-\infty}^0 dc_z (c_z^2 f_w^-) \end{aligned} \right\} \quad (2.7)$$

²Here it is assumed that the mass, momentum and energy flows in stationary state are equal through any plane parallel to the CPS.

Substituting the positive part f_w^+ of the DF from (2.1) into Eqs. (2.6) and integrating, we arrive at the following expressions for the emitting flows

$$J_1^+ = \frac{1}{2\sqrt{\pi}} \rho_w v_w \quad (2.8)$$

$$J_2^+ = \frac{1}{4} \rho_w v_w^2 \quad (2.9)$$

$$J_3^+ = \frac{1}{2\sqrt{\pi}} \rho_w v_w^3 \quad (2.10)$$

The quantity J_1^+ is also known as the “one-way Maxwell flow”. In order to evaluate the incident flows from integrals (2.7), one needs to specify the negative part f_w^- of the DF, which is unknown a priori. Theoretically it can be found from the solution of the Boltzmann equation in the Knudsen layer. It should be pointed out that on the hypothetical precise solution to the Boltzmann equation the system of conservation equations becomes the system of identities by definition. However, at present strong solutions of this highly involved integro-differential equation are available only in some special cases.

If f_w^- is given from some or other model view, then the system of Eqs. (2.3)–(2.5) is superdefinite. Hence, to close the problem this system must be augmented with a free parameter, which give the semi-empirical character to the solution. It is worth noting that departures from the local thermodynamic equilibrium are manifested exclusively in the gas phase. In most cases, the nonequilibrium effects in the condensed phase can be neglected: if they nevertheless occur, this happens only with anom intensities of transport processes.

2.2 Evaporation into Vacuum

The kinetic molecular theory was founded by Maxwell [2, 3], who in 1860 obtained his famous formula (2.1) for velocity distribution function (DF) for gas molecules in thermal equilibrium. In 1872, Boltzmann put forward an equation describing the statistical distribution of gas molecules (the Boltzmann equation) [4]. Function (2.1) is a particular solution to the Boltzmann equation for the case of statistical equilibrium in the absence of external forces. Being highly involved, for a long time the Boltzmann equation was considered as a mathematical abstraction. It seems that only in 1960s it was understood that problems related with low gas density, high velocities of its motions and with noticeable departures from the thermodynamic equilibrium can be investigated solely on the basis of the Boltzmann equation.

Historically, the first applied kinetic molecular problem was the problem of “evaporation into vacuum”. In 1882, Hertz published his classical paper [5] on evaporation of mercury at low pressure. Analyzing the results of his experiments,

Hertz arrived at the following fundamental conclusion: for any substance there exists the maximal evaporation flux, which depends only on the temperature of the surface and the specific properties of a given substance. The maximal evaporation flux cannot be higher than the number of molecules of vapor that hit in unit time the surface of condensate in the state of equilibrium. Hence, the upper limit during the evaporation is the achievement of the one-way Maxwell mass flow, as defined by relation (2.8). In 1913, Langmuir [6] employed formula (2.8) to evaluate the vapor pressure of tungsten during its evaporation in a vacuum tube.

2.2.1 The Hertz–Knudsen Equation

In 1915, Knudsen [7] performed new experiments on mercury evaporation. He found that the maximal velocity of evaporation is in line with relation (2.8). However, this pertained only to highly purified mercury: velocity of evaporation of impure mercury was found to be lower by almost three orders. To interpret these experimental data, Knudsen introduced into formula (2.8) the “evaporation coefficient” β as a cofactor.

$$j_1 \equiv J_1^+ = \frac{\beta}{2\sqrt{\pi}} \rho_w v_w \quad (2.11)$$

The evaporation coefficient shows that among all vapor molecules that hit the CPS only the part β is absorbed by it, the remained part $1 - \beta$ of molecules is reflected from the interface and goes off into the vapor. Knudsen [7] also introduced the “condensation coefficient”. In the majority of cases one adopts the assumption that the coefficients of evaporation and condensation are equal. In the present chapter, we shall adopt this hypothesis and use the “evaporation-condensation coefficient”.

Taking into account the ideal gas law

$$p = \rho R_g T = \frac{1}{2} \rho v^2 \quad (2.12)$$

relation (2.11) can be rewritten as

$$j_1 = \beta \frac{p_w}{\sqrt{2\pi R_g T_w}} \quad (2.13)$$

It is very interesting that both Langmuir and Knudsen came to use formulas of (2.13) from very different positions. Langmuir was led to inquire about the evaporation flux by examining the reactions of tungsten with oxygen. Knudsen’s interest in the problem of evaporation appeared in connection with the study of the dynamics of rarefied gases and in connections with the development of the effusion method for

finding the vapor pressure. In the papers by Hertz, Langmuir and Knudsen, relations (2.11) and (2.13) were interpreted as the maximal intensity of evaporation into vacuum (see the survey [8]). It was clear for the classics of the kinetic molecular theory that in the framework of the one-dimensional problem the stationary process of evaporation into vacuum is in reality impossible, and hence, the mass flux, as defined by formulas (2.11) and (2.13), cannot be achieved. In the actual fact, the presence of a “cloud of molecules” in the CPS (a typical expression from the early period of investigations) with density ρ_∞ and pressure p_∞ will result in a decrease of the velocity of evaporation. This decelerating effect can be taken into account by introducing into relation (2.13) the corresponding difference of pressures

$$j_1 = \beta \frac{p_w - p_\infty}{\sqrt{2\pi R_g T_w}} \quad (2.14)$$

Relation (2.14), which is known in the literature as the Hertz–Knudsen equation, is widely useful in calculations of processes of evaporation/condensation (in particular, for experimental evaluation of β), to the present day. Relation (2.14) says that the net transfer is proportional to the difference of two one-way Maxwell flows. This introduces the following two assumptions: near a macroscopic surface the vapor is at rest; the vapor state can be described by the local equilibrium of the Maxwell distribution.

2.2.2 Modifications of the Hertz–Knudsen Equation

In 1933, Risch [9] proposed a modification of the Hertz–Knudsen equation, by assuming that the flow incident to the CPS has an equilibrium Maxwell spectrum with density ρ_∞ and pressure p_∞

$$j_1 = \beta \left(\frac{p_w}{\sqrt{2\pi R_g T_w}} - \frac{p_\infty}{\sqrt{2\pi R_g T_\infty}} \right) \quad (2.15)$$

The Hertz–Knudsen Eq. (2.14) is a consequence of (2.15) with $T_w \approx T_\infty$. In 1956, Schrage [10] modified the empirical set-up of [9] by taking into account the effect of the flow of evaporation/condensation on the molecular flow incident to the CPS

$$J_1^- = \frac{p_\infty}{\sqrt{2\pi R_g T_\infty}} \Gamma(s) \quad (2.16)$$

Here $\Gamma(s) = \exp(-s^2) - \sqrt{\pi} s \operatorname{erfc}(s)$, $s = u_\infty/v_\infty$ is the velocity factor, u_∞ is the hydrodynamic velocity, $v_\infty = \sqrt{2R_g T_\infty}$ is the thermal velocity (all the quantities are taken on the infinity).

The Hertz–Knudsen equation modified in this way reads as

$$j_1 = \beta \left(\frac{p_w}{\sqrt{2\pi R_g T_w}} - \Gamma(s) \frac{p_\infty}{\sqrt{2\pi R_g T_\infty}} \right) \quad (2.17)$$

For $u_\infty = 0$ ($\Gamma = 1$) the relations (2.15) and (2.16) are identical. The backflow will become slower during evaporation by the motion of vapor: $u_\infty > 0 \Rightarrow \Gamma < 1$. On the other hand, during condensation the hydrodynamic velocity will be summed with the velocity of the backflow, thereby accelerating it: $u_\infty < 0 \Rightarrow \Gamma > 1$. A detailed survey of the early period of the kinetic molecular analysis may be found in the old survey [8], which is still relevant.

Here it is worth mentioning that the aforementioned attempts to modify the Hertz–Knudsen equation on the same basis had led to unsatisfactory results. The thing is that the momentum conservation Eq. (2.4) and the energy conservation Eq. (2.5) must be satisfied in addition to the mass conservation Eq. (2.3) for a correct description of a phase change. An attempt to satisfy all three conservation equations within the same rigid scheme results in the superdefiniteness of mathematical description and physical absurdity. The above incorrectness of Eqs. (2.14) and (2.15), (2.17) results, in particular, in the uncertainty of the temperature T_∞ . These difficulties demonstrate the necessity of a stringent kinetic molecular formulation of the problem of phase change, which would reside in the actual picture of nonequilibrium gas state near the CPS.

An important step in the kinetic molecular study of evaporation was made in 1960 by Kucherov and Rikenglaz [11]. As distinct from the empirical approach of Schrage, Kucherov and Rikenglaz correctly took into account the actual motion of vapor in the normal direction to the surface with the velocity u_∞ and wrote the DF of the molecular backflow in the form of the displaced Maxwell distribution

$$f_w^- = \frac{n_w}{\pi^{3/2} v_w^3} \exp \left(- \left(\frac{\mathbf{c} - \mathbf{u}_\infty}{v_w} \right)^2 \right) \quad (2.18)$$

The function f_w^- is also called the “volume DF”. This function and various modifications thereof were successfully used in the majority of theoretical studies on the processes of evaporation and condensation from the positions of the kinetic molecular theory.

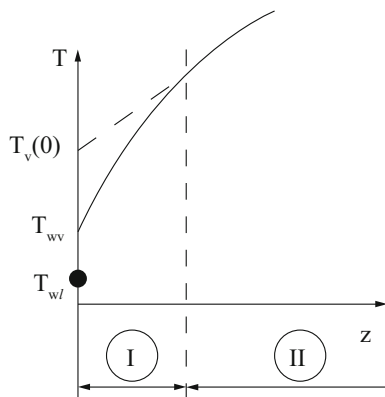
Parameters of strong evaporation were numerically calculated in [12–14]. In [12] the method of molecular dynamic was employed to demonstrate the legitimacy of using the equilibrium Maxwell spectrum for the emitted flow [relation (2.1)]. In [13, 14] the Lennard-Jones potential of intermolecular interaction was used to show that the molecular flow of mass exceeds by 3.6 times the quantity calculated from the Hertz–Knudsen equation. The conclusion [12] on the equilibrium Maxwell spectrume of the emitted flow was also justified. In a number of papers, the inadequacy to real physical process of collisions was numerically demonstrated, which occurs due to the fact that the frequency of collisions does not depend on the velocities of collided particles.

2.3 Extrapolated Boundary Conditions

The degree of rarefaction of gas near the CPS is characterized by the Knudsen number $Kn = l_{mol} / l_0$ [1]. Here, l_0 is the linear scale of the region in which transport processes in the gas phase occur (the thickness of the Prandtl boundary layer, the transverse section of the channel), l_{mol} is the mean free path of molecules. In the limit case $Kn \gg 1$ (actually, already for $Kn \geq 1$) the gas flow can be calculated without consideration of collisions of molecules between each other, taking into account only impacts of molecules on the CPS. Such a flow regime, which is also called the free molecule regime, is manifested in practice already when $Kn \sim 1$. In the limit case, $Kn \ll 1$ (actually, already for $Kn \leq 0.1$) the phenomenological prescriptions of continuum mechanics hold in the gas region. In such a continuum regime the thickness of the Knudsen layer is immaterial in comparison with the macroscopic geometrical scales: $l_{mol} \ll l_0$. Here, the flow can be calculated on the basis of the Navier–Stokes equations. However, the BC for them are obtained by gluing together the Knudsen layer with the Navier–Stokes region. The continual method is approximately valid and is used in practice already for $Kn \leq 10^{-3}$. In the range $10^{-3} \leq Kn < 1$, various flow regimes of rarefied gas, which lie between the free molecule regime and the continuum regime, are realized.

Outside the Knudsen layer, the phenomenological laws of heat transfer (Fourier’s law) and momentum transfer (Newton’s friction law) now apply. The scheme of the region near the CPS (see Fig. 2.2) consists of the Knudsen layer I with the adjacent Navier–Stokes region II. In comparison with the outer linear scale $l_{mol} \ll l_0$, the Knudsen layer in the majority of cases has vanishingly small thickness. Hence, the detailed description of the fields of quantities (velocities, temperatures, pressures, densities) in region I is purely theoretical. If these parameters are imagined to be extrapolated from the transverse coordinate up to the CPS, ignoring the Knudsen layer, we obtain some conditional values of the quantities. The difference between these extrapolated values from the true parameters results in the appearance of “kinetic jumps” on the CPS (which, of course,

Fig. 2.2 Temperature distribution in the region near the condensed-phase surface



have only conditional character). It is worth remarking that the ultimate purpose of the applied kinetic molecular analysis is the evaluation of the extrapolated BC.

As an example, we shall consider the heat transfer through an impermeable surface. Figure 2.2 schematically shows the actual distribution of the gas temperature near the CPS, including the Knudsen layer. The extrapolation of the temperature profile from the Navier-Stokes region is shown by dotted lines. As a result, on the CPS we have two temperature jumps: the actual $\Delta T_w = T_{wl} - T_{wv}$ and the extrapolated $\Delta T = T_{wl} - T_v(0)$ ones. Here, T_{wv}, T_{wl} is the actual gas temperature on the surface, respectively, from the gas and liquid side, $T_v(0)$ is the extrapolated value of the gas temperature on the surface (the conditional quantity). Thus, we have two alternative settings of the problem:

- The minimum program. To set the BC on the CPS for the equations of gas dynamics in the Navier-Stokes region it suffices to specify the extrapolated temperature jump. Hence, giving the available conditional gas temperature, one may construct the distribution of temperatures over the entire volume of gas (except the Knudsen layer), which is important in practice.
- The maximum program. To find the distribution of temperatures within the Knudsen layer one needs to solve the Boltzmann equation for the DF. Next, using it in the corresponding integral as weight function, one may in theory obtain the precise profile of temperatures in the entire gas space. Since the Boltzmann equation is highly involved, on a certain value of the transverse coordinate one has to stop the process of solution (which can be only numerical) and “sew” the Knudsen layer with the Navier–Stokes region.

It is worth pointing out that it frequently happens that in the literature on applied problems no mention on the true parameters (or on actual jumps) is given. In the present chapter, we shall be concerned only with analytical solutions, as a part of the minimum program. This means that the purpose of the solution is to find conditional temperature jumps, whereas by parameters of the gas on the CPS we shall mean the corresponding extrapolated quantities.

2.4 Accommodation Coefficients

The concept of the accommodation coefficient was first introduced by Maxwell [2, 3], who considered two limit variants: all the molecules incident on the CPS are completely absorbed by it; all the molecules incident on the CPS are completely reflected by it.

In accordance with the conservation equations of mass, momentum and energy, one may define three corresponding accommodation coefficients. Knudsen [7] gave a concrete physical form to Maxwell’s perceptions. In particular, he wrote DB in the following form

$$f^+ = f_e + (1 - \beta)f_r \quad (2.19)$$

From relation (2.19) it follows that in the general case, among all molecules incident on the CPS, only their part defined by the quantity β is absorbed by the surface, while the other part $(1 - \beta)$ of the molecules is reflected from it. Hence, the function f^+ of the molecules flying out from the CPS can be represented in two parts. The first part (f_e) describes the evaporated molecules, while the second part (f_r) describes the molecules reflected from the interface. Knudsen calls β the coefficient of evaporation (as the vapor moves away from the CPS) or the coefficient of condensation (as the vapor moves away towards the CPS). Note that the quantity β in formula (2.19) is the accommodation coefficient of mass. In a similar way, below we shall use the concepts of the momentum coefficients and the thermal accommodation coefficient. Knudsen [7] introduced the following definitions: the condensation coefficient is ratio of the number of molecules absorbed by the surface to the total number of the molecules incident on it; the evaporation coefficient is the ratio of the flow molecules emitted by the interface to the number of flow molecules generated by the CPS in the reference case: the equilibrium Maxwell distribution, the vapor density corresponds to the CPS temperature on the saturation line.

Knudsen's scheme of evaporation is known as the "diffusion scheme". At present, there are very different approaches to the theoretical definition of the coefficients of evaporation and condensation. For a survey of theoretical and experimental studies of the coefficients of evaporation/condensation of water, we refer the reader to the paper [15].

In [16], the quantity β was defined on the basis of the transition state theory, which in turn resides on the barrier of potential energy between vapor and liquid molecules. Nagayama and Tsuruta [16] combined the potential energy of molecules and the activation energy barrier. In order to transfer a molecule from one phase into a different one, it has to gain (for evaporation) or loose (for condensation) the activation energy. In a number of papers [10, 16–19], the condensation coefficient was modeled by molecular dynamics method. Schrage [10] points out the simplified character of calculation of β from the quantity of vapor molecules reflected from the CPS. Instead, they calculated this quantity by analyzing the energy exchange between the gas and liquid molecules. Tsuruta et al. [17] used the energy criterion as a condition for the surface to capture an incident molecule: the kinetic energy of a gas molecule must decrease discontinuously to the energy of heat motion of liquid molecules. In [13], the method of molecular dynamics was employed to model various variants of processes of evaporation/condensation: a pure liquid in equilibrium and nonequilibrium conditions, liquid mixture. Four main types of behavior of gas molecule near the CPS were considered: (a) evaporation (b) reflection, (c) condensation, (d) molecular exchange. The quantity β was shown by calculations to markedly depart from the temperature. Matsumoto [19] expressed scepticism about the standard definition of the coefficients of evaporation/condensation for the case of intense phase change.

In 1916 Langmuir [20] was first to perform a theoretical analysis of condensation with due account of the energy exchange of gas and liquid molecules. He assumed that the time of energy exchange on the CPS is equal in order to the period of oscillations of liquid molecules near the equilibrium. Since this period is extremely small, the energy exchange takes place practically instantaneously, which implies that $\beta \approx 1$. It is worth noting that a similar result was obtained by modern modeling of the process of condensation by the molecular dynamics method [21].

A considerable number of papers were concerned with the experimental evaluation of the coefficients of evaporation and condensation. The experimental results from the survey [15] give the range $\beta \approx 6 \times 10^{-3} - 1.0$ for the condensation coefficient. A slightly more narrow range of experimental data is given in [21]: $\beta \approx 10^{-2} - 1.0$. It may be assumed that such a wide scatter in the experimental results is indicative of the dependence of the result on the method of measurement. The generally accepted method of experimental evaluation of the condensation coefficient is based on the kinetic molecular model. Besides, this method postulates that there exists a clear geometric boundary between gas and liquid. In reality, instead of modeling an “infinitely thin” CPS, there exists a thin (of the scale comparable to the thickness of the Knudsen layer) transient layer in which the medium density changes monotonically from the liquid state to the gas state. According to [18] the quantity of “blurriness” of the phase interface amounts to several distances between molecules in liquid.

At first sight it seems attractive to analyze the characteristics of the phase interface in the framework of the continuum mechanics. In this case, it is absolutely correct to consider the CPS as a geometrical line that has no thickness. Indeed, here the scales of blurriness of the vapor–liquid boundary are always negligible in comparison with the characteristic linear scale in the Navier-Stokes equations. However, in this case we come to a different contradiction: the standard definition of β becomes meaningless. Indeed, the molecules incident on CPS may be decelerated by numerous interactions with the “vapor cloud” long before they reach the CPS. In this case, the CPS cannot be considered as the only source of reflected molecules. Besides, in a certain limit situation a molecular flow flying away from the CPS due to evaporation completely reflects the molecular flow flying towards the interface. In this hypothetical variant none of the gas molecules will reach the CPS, hence, the experiment should yield: $\beta \rightarrow 0$. Conversely, if all the molecules flying towards CPS “adhere” to it during the time of kinetic relaxation, then the opposite limit variant should be implemented: $\beta \rightarrow 1$.

In the survey [22] on evaporation into vacuum it is noted that the Hertz–Knudsen equation is frequently used up until now to evaluate the coefficients of evaporation/condensation. Under this approach, the departure between the calculated values may be as high as three orders. Julin et al. [22] analyzed the possible causes for such a wide scatter. The analysis of a great number of theoretical and experimental papers and studies by the molecular dynamics method has shown that the Hertz–Knudsen equation is unreliable. Indeed, this equation reflects only one of the three conservation equations—the conservation law of mass flux and it does not take into account the conservation laws of the momentum and energy. Julin et al. [22]

also put forward a modified Hertz–Knudsen equation, the results of 127 experiments on the evaporation of water and ethanol being used to justify this equation. A survey of various methods for measuring the coefficients of evaporation/condensation may be found in [23].

2.5 Linear Kinetic Theory

2.5.1 Low Intensity Processes

The quantitative measure of the intensity of a phase change is the velocity factor S , which is the ratio of the absolute value of the velocity of vapor motion u and the most probable thermal velocity of molecules $\sqrt{2R_gT}$

$$s = \frac{u_\infty}{\sqrt{2R_gT}} \quad (2.20)$$

This quantity is close to the Mach number $M_\infty = u_\infty / \sqrt{(c_p/c_v)R_gT_\infty}$ and is related with it as follows

$$s = \sqrt{\frac{c_p}{2c_v}} M_\infty \quad (2.21)$$

Here, c_p, c_v are respectively, the isochoric and isobaric specific heat capacities of gas. For a number of applications, the intensity of transfer processes is quite small in comparison with that of the molecular mixing. Hence, for the kinetic molecular analysis it is admissible to use only the first powers of the departure of parameters from equilibrium and drop higher powers. Such a method is known as linearization, the linear kinetic theory is the nonequilibrium theory based on this method.

The linear kinetic theory of evaporation/condensation was first developed by Labuntsov [24] and Labuntsov and Muratova [25]. The authors [25] were concerned with the solution of the Boltzmann equation (by the method of moments) and of the Krook model relaxation equation. The main results of [25], as obtained in several variants by numerical solution of equations, determine the fields of actual and extrapolated parameters in the Knudsen layer. Moreover, the difference between the solutions on the basis of the Boltzmann and Krook equations was found to be immaterial. The linear kinetic theory was developed later, in particular, in the papers [26–29]. Below we shall consider some results obtained in the pioneering paper [25].

2.5.2 Impermeable Interface (Heat Transport)

In the absence of phase change we have an impermeable phase interface. This can be either liquid or a hard surface. Here there is no mass transport, while the heat is transported through the interface according to the mechanism of heat conductivity. In this case, the linear kinetic theory gives the conclusion that the gas temperature on the surface $T_v(0)$ does not agree with that of the condensed phase on the boundary: $T_{wl} \neq T_l(0)$ (Fig. 2.2). The temperature jump $T_l(0) - T_v(0)$ is found to be proportional to the near-surface heat flow of the gas phase: $q = -\lambda(\partial T/\partial x)_{x=0}$. The quantity $T_l(0) - T_v(0)$ also depends on the thermal accommodation coefficient α , which reflects the efficiency of the energy exchange when gas molecules interact with CPS. The concluding relation of linear kinetic theory reads as

$$\theta(0) = \sqrt{\pi} \frac{1 - 0.41\alpha}{\alpha} \tilde{q} \quad (2.22)$$

Here $\theta(0) = \frac{T_l(0) - T_v(0)}{T}$ is the dimensionless temperature jump on the surface, $\tilde{q} = \frac{q}{q_*} = \frac{q}{p_v v}$ is the dimensionless heat flow on the surface.

In the frameworks of linear analysis, as a characteristic temperature T involved in the dimensionless parameters one may take any of the temperatures phases, that is, $T \approx T_l(0) \approx T_v(0)$. The heat flow $\tilde{q}$ in relation (2.22) is considered positive if the heat is transferred from the interface towards the gas. With $\alpha = 1$ relation (2.22) implies that

$$\theta(0) = 1.05\tilde{q} \quad (2.23)$$

The scaled quantity for the heat flow q_* is proportional to the one-way flow of energy transported through the unit reference surface due to the heat motion of gas molecules: $q_* = p_v v = R_g \rho_v v T$. Hence, the relation $\tilde{q} = q/q_*$ can be looked upon as the nonequilibrium parameter in the process of heat transport in gas. Relation (2.23) is the consistency condition on the CPS, which refines the approximate equilibrium relation: $\theta(0) = 0$. It is quite natural that the equilibrium approximation is more justified the less is the value of the nonequilibrium parameter $\tilde{q}$. The decrease of the gas pressure with $q = \text{const}$ will result in an increase in the temperature jump $T_l(0) - T_v(0)$ thanks to a decrease in q_* .

Let us now consider an external flow of a surface by a high-velocity gas flow. Note that the relation for the heat flow can be expressed in terms of the Stanton number St

$$q = St \rho_v u_{v\infty} (H_{vw} - H_{v\infty}) \quad (2.24)$$

where $H_{vw} - H_{v\infty}$ is the difference of the total gas enthalpies. We have the following estimate relations

$$\frac{u_{v\infty}}{v_\infty} \equiv s \approx M, R_g \approx c_{pv} \quad (2.25)$$

Using Eq. (2.25), this gives

$$\frac{c_{pv}(T_l(0) - T_v(0))}{H_{vw} - H_{v\infty}} \approx St \cdot M \quad (2.26)$$

Thus, an increase in the Mach number leads to an increase in the temperature jump.

2.5.3 Impermeable Interface (Momentum Transport)

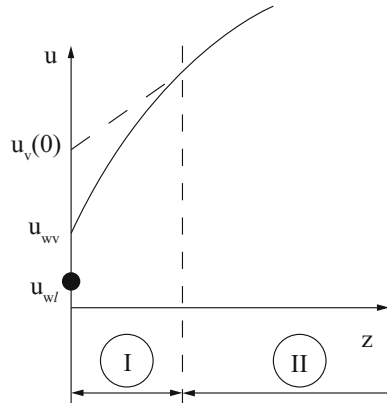
The flow of viscous gas along an impenetrable interface results in the transport through it of the tangential component of the momentum, which is responsible for the appearance of the friction stress. According to the kinetic molecular description, in the actual fact the gas velocity on the interface (in the frame where it is fixed) is not zero, as is adopted in the equilibrium scheme (Fig. 2.3).

The linear theory shows that the gas velocity on the interface $u_v(0)$ (which is called the “slip velocity”) is proportional to the tangential stress on the surface τ . Collision and reflection of molecules with the interface results in a loss of the longitudinal component of the momentum. In this case, we have

$$\tilde{u}_v(0) = \tilde{\tau} \quad (2.27)$$

where $\tilde{u}_v(0) = u_v(0)/v$ is the dimensionless slip velocity, $\tilde{\tau} = \tau/p_v = 2\tau/p_v v^2$ is the dimensionless tangential pressure. Formula (2.27) shows that for small values of the nonequilibrium parameter ($\tilde{\tau} \equiv \tau/p_v < 1$) the state will be close to

Fig. 2.3 Velocity distribution in the region near the condensed-phase surface



equilibrium ($u_v(0) = 0$). A decrease in the pressure in the system with $\tilde{\tau} = \text{const}$ increases the slip velocity. Let us now express the tangential pressure in terms of the friction coefficient c_f

$$\tau = \frac{c_f}{2} \rho_v u_{v\infty}^2 \quad (2.28)$$

Using relation (2.28) in formula (2.27) and taking into account the approximate estimate $u_{v\infty}/v \approx M$, we have

$$\frac{u_v(0)}{u_{v\infty}} \approx c_f M \quad (2.29)$$

So, $u_v(0)/u_{v\infty}$ increases with the Mach number. It immediately follows that the slip phenomena are considerable during flights of high-speed planes and space vehicles. In this case, due to high rarity of the atmosphere, the kinematical viscosity $\nu_v = \mu_v/\rho_v$ will be anomalously high. Hence, the flow pattern of an aircraft surface may prove to be laminar even for very high motion speeds. Since for a laminar flow we have $c_f \sim 1/\sqrt{\rho_v}$, the friction coefficient will increase as the gas density decreases.

2.5.4 Phase Change

The BC during evaporation and condensation on a phase interface are found to be much more involved than those assumed in the equilibrium approximation. In order to consider the results of kinetic molecular description, it is appropriate to introduce the following quantities:

- $T_l(0)$ is the surface temperature of a condensed phase.
- $p_{vw}(0)$ is the saturated pressure corresponding to the surface temperature, that is, $p_{vw} = p_{vw}(T_l(0))$
- $p_{v\infty}$ is the actual vapor pressure near the surface (beyond the Knudsen layer).
- $T_v(0)$ is the vapor temperature on the CPS (the extrapolated value).
- j is the flow of substance crossing a unit area on the CPS.
- q is the heat flow crossing a unit area on the CPS (positive values of j and q correspond to flows delivered in the vapor phase).
- β is the evaporation-condensation coefficient.

It is worth pointing out that p_{vw} is a purely theoretical value, which may be different from the actual pressure in the system. The results of the linear theory [25] may be briefly summarized as follows:

- The pressure within the Knudsen layer is constant and equal to $p_{v\infty}$, so that the condensed phase is under the same pressure as the vapor (without consideration of the surface tension on the curved boundary).

- Let T_s be the theoretical saturation temperature with the actual pressure in the vapor phase $p_{v\infty}$. Then both $T_l(0)$ and T are different from T_s .
- On the interface surface there is a temperature jump, which is proportional to the flows of mass j and heat q .
- The process is characterized by the difference $p_{vw} - p_{v\infty}$, which is the difference between the actual pressure $p_{v\infty}$ in the system and the calculated saturation pressure p_{vw} , as defined from the temperature $T_l(0)$ of the CPS.
Quantitative relations of the linear theory can be conveniently written down using the following dimensionless quantities:

- The heat flow $\tilde{q} = \frac{q}{q_s} = \frac{q}{p_{v\infty} V}$.
- The mass flow $\tilde{j} = \frac{j}{p_v V} = \frac{u_v}{V}$.
- The temperature $\theta(0) = \frac{T_l(0) - T_v(0)}{T}$.
- The pressure difference $\Delta\tilde{p} = \frac{p_{vw} - p_{v\infty}}{p}$.

2.5.5 Special Boundary Conditions

Using the above notation we may write down the special boundary conditions, which take into account the nonequilibrium effects on the CPS

$$\theta(0) = 0.45\tilde{j} + 1.05\tilde{q} \quad (2.30)$$

$$\Delta\tilde{p} = 2\sqrt{\pi} \frac{1 - 0.4\beta}{\beta} \tilde{j} + 0.44\tilde{q} \quad (2.31)$$

Relations (2.30) and (2.31) are necessary refinements of the equilibrium consistency condition. They contain very interesting information about the specifics of nonequilibrium phenomena during phase transitions. Assume that there is no mass flux through the CPS: $\tilde{j} = 0$. Then relations (2.30) and (2.31) describe the temperature and pressure jumps on an impenetrable CPS

$$\theta(0) = 1.05\tilde{q} \quad (2.32)$$

$$\Delta\tilde{p} = 0.44\tilde{q} \quad (2.33)$$

Under standard conditions of a phase transition of finite intensity, when there are no considerable overheats of vapor away from the CPS, we have the condition: $\tilde{q} \ll \tilde{j}$. Besides, relations (2.30) and (2.31) assume the form

$$\theta(0) = 0.45\tilde{j} \quad (2.34)$$

$$\Delta\tilde{p} = 2\sqrt{\pi}\frac{1 - 0.399\beta\tilde{j}}{\beta} \quad (2.35)$$

Using the Clausius–Clapeyron relation, we express the quantity $p_{ws} - p_{v\infty}$ in terms of the corresponding difference of temperatures $T_l(0) - T$

$$\left(\frac{dp}{dT}\right)_s = \frac{L\rho_v\rho_l}{(\rho_l - \rho_v)T} \approx \frac{L\rho_v}{T} = \frac{Lp_v}{R_g T^2} \quad (2.36)$$

$$p_{vw} - p_{v\infty} = \left(\frac{dp}{dT}\right)_s (T_l(0) - T_s) = \frac{L}{R_g T} \frac{T_l(0) - T_s}{T} p_v \quad (2.37)$$

Here L is the heat of phase transition. Hence, relation (2.35) assumes the form

$$\frac{T_l(0) - T_s}{T} = 2\sqrt{\pi}\frac{1 - 0.4\beta R_g T}{\beta} \frac{\tilde{j}}{L} \quad (2.38)$$

Using relations (2.32) and (2.38), we have

$$\frac{T_s - T_v(0)}{T} = \left(0.45 - 2\sqrt{\pi}\frac{1 - 0.4\beta R_g T}{\beta} \frac{\tilde{j}}{L}\right) \tilde{j} \quad (2.39)$$

From formula (2.38) it is seen that for evaporation ($\tilde{j} > 0$) we have $T_l(0) > T_s$, while for condensation ($\tilde{j} < 0$) we have $T_l(0) < T_s$. So, we have proved that the temperature on the CPS with evaporation is larger (for condensation, is lower) than the saturation temperature with the actual pressure in the system. This is a physically natural conclusion. From (2.39) it is seen that, in the same processes, the sign of the difference $T_s - T_v(0)$, and hence, of the vapor temperature $T_v(0)$ on the CPS, depends on the sign of the bracketed expression on the right of (2.39). This quantity can be estimated using the well-known Trouton's rule: $L / R_g T \approx 10$ (under the normal conditions). It turns out that the resulting signs might be different depending on the value of the evaporation-condensation coefficient. For $\beta = 1$ we have

$$0.45 - 2\sqrt{\pi}\frac{1 - 0.4\beta R_g T}{\beta} \frac{\tilde{j}}{L} \approx 0.237 > 0 \quad (2.40)$$

Hence, for $\beta = 1$, evaporation ($\tilde{j} > 0$) results in a subcooled vapor: $T_v(0) < T_s$. During a condensation the vapor on the CPS is superheated: $T_v(0) > T_s$. The difference in the temperatures decreases with β , it is zero for $\beta \approx 0.6$ and then changes the sign. So, with $\beta \approx 0.3$ in the case of evaporation we have $T_v(0) > T_s$, for condensation, $T_v(0) < T_s$. Figure 2.4 shows the relative position of the temperatures $T_l(0)$, $T_v(0)$ and T_s during evaporation and condensation with various values of β , by the results of the above analysis. Relations (2.37) and (2.38) show that the quantity.

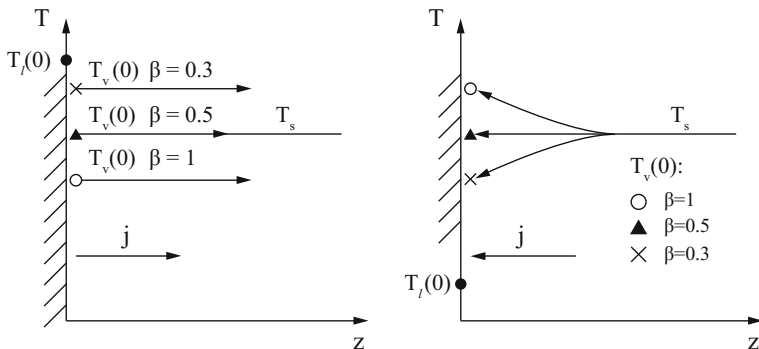


Fig. 2.4 Relative position of the temperatures $T_l(0)$, $T_v(0)$ and T_s during evaporation and condensation with various values of β

$$\tilde{j} = \frac{j}{\rho_v v} \quad (2.41)$$

is the nonequilibrium parameter during phase transitions. The smallness of this parameter ($\tilde{j} \rightarrow 0$) justifies the approximation of the local thermodynamic equilibrium. So, the relations (2.38) and (2.39) from the pioneering paper [25] contain very interesting subtle information about the actual parameters of vapor on the CPS during evaporation/condensation.

2.6 Introduction into the Problem of Strong Evaporation

2.6.1 Conservation Equations

Of special importance in the analysis of the strong evaporation is establishing its limit possible intensity. Landau and Lifshitz [30] gave a detailed analysis of the development of small disturbance of phase interface. In the general case it splits into two acoustic waves (propagating upstream and downstream the gas flow), the perturbation of entropy (upstream and downstream the gas flow) and the propagation of entropy (propagating together with the gas flow).

If the velocity of evaporation reaches the sound velocity, then the acoustic wave propagating upstream the gas flow “stands” on the interface. It is a common belief nowadays that supersonic evaporation is impossible. Indeed, assume that the gas flow in the outside region is described by the equations for a perfect gas. Then the analysis of the characteristic properties of the system of Euler equations shows that in the supersonic flow any perturbation is moved away from the interface. Thus, even if the domain of supersonic flow would exist ab initio, it must eventually separate from the interface. It immediately implies the physical impossibility of

supersonic evaporation for which no perturbation propagates from the gas domain towards the interface. Hence, the attainment of the sonic evaporation state should be looked upon as the limit possible case.

Let us estimate the nonlinear effects for the evaporation problem. Assume that the spectrum of incident molecules is described by the volume DF (2.18), which takes into account the effect of evaporation flow with velocity u_∞ . Substituting f_w^- into the integrals (2.7) and transforming, we obtain a system of equations consisting of the mass, momentum, and energy conservation laws

$$\frac{\sqrt{\tilde{T}_\infty}}{\sqrt{\pi\tilde{p}_\infty}} + s \operatorname{erfc}(s) - \frac{\exp(-s^2)}{\sqrt{\pi}} = 2s \quad (2.42)$$

$$\frac{1}{2\tilde{p}_\infty} + \left(\frac{1}{2} + s^2\right) \operatorname{erfc}(s) - \frac{s \exp(-s^2)}{\sqrt{\pi}} = 1 + 2s^2 \quad (2.43)$$

$$\frac{1}{\sqrt{\pi\tilde{p}_\infty}\sqrt{\tilde{T}_\infty}} + s\left(\frac{5}{4} + \frac{s^2}{2}\right) \operatorname{erfc}(s) - \left(1 + \frac{s^2}{2}\right) \frac{\exp(-s^2)}{\sqrt{\pi}} = \frac{5s}{2} + s^3 \quad (2.44)$$

Here $\tilde{p}_\infty = p_\infty/p_w$, $\tilde{T}_\infty = T_\infty/T_w$ are the dimensionless values, respectively, of pressure, temperature, s is the velocity factor given by formula (2.20). It should be noted that this system of equations was obtained for the limit case of complete absorption of molecules incident on the CPS: $\beta = 1$.

The evaporation problem can be stated as follows in the form natural for applications. Assume that we know the temperature T_w of the CPS, and hence, the density of saturated vapor with this temperature: $\rho_w = \rho_s(T_w)$. Assume further that we are given some parameter of vapor in the Navier–Stokes region (for example, the pressure p_∞). It is required to find two unknowns: the temperature T_∞ and the mass flux $j_1 = \rho_\infty u_\infty$. The form of system of Eqs. (2.42)–(2.44) suggest the following more formal statement of the same problem: find the dependences $\tilde{T}_\infty(M_\infty)$, $\tilde{p}_\infty(M_\infty)$. Here M_∞ is the Mach number related with the velocity factor by formula (2.21).

This system of three equation is superdefinite. This is a direct corollary to the stringent setting of the negative part of the DF as relation (2.18). With this point of view we consider the above early analytical solutions to the problem of evaporation into vacuum:

- The solution (2.13) by Langmuir and Knudsen was obtained from the mass conservation law (2.42) using the DF (2.18) with $u_\infty = 0$.
- The Hertz–Knudsen Eq. (2.14) was obtained by heuristic introduction of the difference of pressures into relation (2.13), which takes into account the presence of the “cloud of molecules” for the CPS.
- The “improved” relations (2.15) and (2.17) were obtained by semi-empirical modifications of the Hertz–Knudsen equation.

- The authors of [11], [29] used, in the linear approximation, the mass and energy conservation laws (respectively, (2.42) and (2.44)) and ignored the momentum conservation law (2.43).

Let us now consider the results of solutions [11], [29] in the linear approximation

$$\theta(0) = 0.443s \quad (2.45)$$

$$\Delta\tilde{p} = 1.995s \quad (2.46)$$

We write the relations of the linear theory (2.34) and (2.35) with $\beta = 1$

$$\theta(0) = 0.45s \quad (2.47)$$

$$\Delta\tilde{p} = 2.13s \quad (2.48)$$

So, strange as it seems, in the linear approximation the results of [11], [29] differ from the precise ones by 2.5% (the temperature jump) and 6.5% (the pressure jump).

The solution to the system of Eqs. (2.42) and (2.44) is written as very cumbersome analytical relations. The dimensionless mass flux

$$\tilde{J} = 2\sqrt{\pi} \frac{\rho_{\infty} u_{\infty}}{\rho_w v_w} \quad (2.49)$$

is the additional parameter of the solution. The quantity $\tilde{J}$ is the ratio of the mass flux and the one-way Maxwell flow of molecules emitted by the CPS and defined by relation (2.8). It can be evaluated using the relation following from the Clausius-Clapeyron equation, as written for the CPS conditions and the Navier-Stokes region

$$\tilde{p}_{\infty} = \tilde{p}_{\infty} \tilde{T}_{\infty} \quad (2.50)$$

Here $\tilde{p}_{\infty} = p_{\infty}/p_w$ is the dimensionless value density.

The numerical results of [31, 32] were used as reference results for verification of the solution obtained from Eqs. (2.42) and (2.44). In these papers, the processes in vapor were described by the spatially one-dimensional Boltzmann equation with the Bhatnagar–Gross–Krook collision term [1]. From Figs. 2.5, 2.6, 2.7 it is seen that in the nonlinear approximation, the solutions of [11, 29] agree with the numerical solutions of [31, 32] with marked error, which attains its maximum value with sonic evaporation ($M_{\infty} = 1$): $\approx 10\%$ for $\tilde{T}_{\infty}$, $\approx 20\%$ for $\tilde{p}_{\infty}$, $\approx 30\%$ for $\tilde{J}$.

The method of papers [11, 29] based on ignoring one of the three conservation equations does not provide any proof, and in addition, has quantitative errors. With this proviso, the two remaining combinations of the conservation equations have

Fig. 2.5 Dependence of the dimensionless mass flux in the Navier–Stokes region on the Mach number. 1 numerical solutions of [32]; 2 solutions of [11]

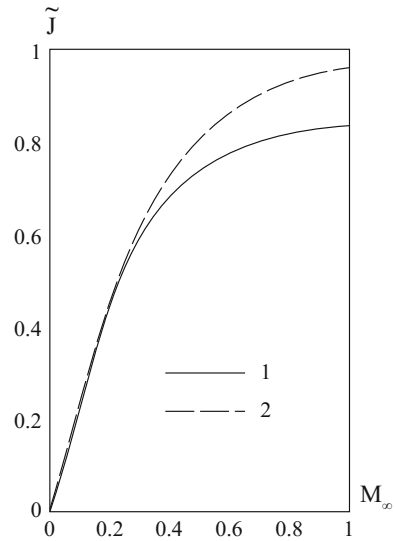


Fig. 2.6 Dependence of the dimensionless temperature in the Navier–Stokes region on the Mach number. 1 numerical solutions of [32]; 2 solutions of [11]

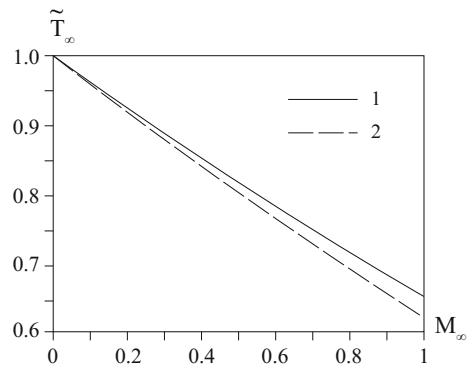
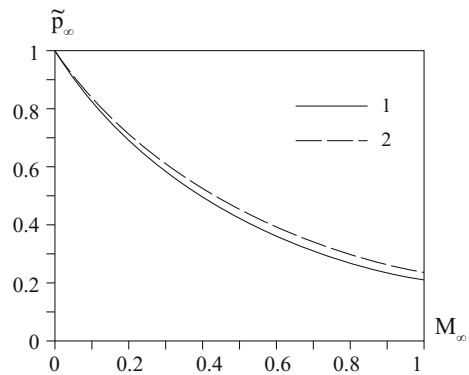


Fig. 2.7 Dependence of the dimensionless pressure in the Navier–Stokes region on the Mach number. 1 numerical solutions of [32]; 2 solutions of [11]



the same “right to life”: the “mass+momentum” and the “momentum+energy” equations. However, calculations with these pairs of equations lead to anomalous results. Thus, the above example clearly suggests the necessity of having a correct analytical solution of the problem of evaporation.

2.6.2 The Model of Crout

In 1936, Crout [33] proposed the first correct model of strong evaporation. In this pioneering paper, the description of the process was built on the physical analysis of the evolution of the DF of emitted molecules between CPS (the section “w”) and the conditional section “e” inside the Knudsen layer. Crout [33] used the following two main assumptions:

- Initially, the equilibrium spectrum (2.1) of the emitted molecular flow under the effect of intermolecular collisions in the Knudsen layer is “blurred” and in the section “e” acquires the “ellipsoidal character”

$$f_e^+ = \frac{n_e}{\pi^{3/2} v_r^2 v_z} \exp \left(- \left(\frac{c_x^2 + c_y^2}{v_r^2} \right) - \left(\frac{(c_z - u_z)^2}{v_z^2} \right) \right) \quad (2.51)$$

Here $v_r = \sqrt{2R_g T_r}$; $v_z = \sqrt{2R_g T_z}$; T_r , T_z are, respectively, the longitudinal and transverse temperatures, c_z is the normal component of the molecular velocity, c_x, c_y are the molecular velocities parallel to the CPS, $v_\infty = \sqrt{2R_g T_\infty}$, $v_w = \sqrt{2R_g T_w}$ is the thermal velocity of molecules, the index “w” denotes the conditions on the CPS, the index “ ∞ ” denotes the conditions at infinity. Since the flow is one-dimensional, we have $c_x = c_y = c_r$, where c_r is the transverse molecular velocity. The ellipsoidal distribution function f_e^+ differs from the Maxwell distribution function f_w^+ by the presence of different measures of the mean velocity of motion of molecules in the longitudinal and transverse directions (the longitudinal and transverse temperatures). Besides, relation (2.51) takes into account the shift of u_z over the axis of longitudinal velocities c_z .

- Between the sections “w” and “e”, the molecular flows of mass

$$\int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z (f_e^+ - f_w^+)) = 0 \quad (2.52)$$

is conserved, as well as the molecular flows of the momentum

$$\int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z^2 (f_e^+ - f_w^+)) = 0 \quad (2.53)$$

and the energy

$$\int_{-\infty}^{\infty} dc_x \int_{-\infty}^{\infty} dc_y \int_0^{\infty} dc_z (c_z^3 (f_e^+ - f_w^+)) = 0 \quad (2.54)$$

The function f_e^+ involves four unknowns: the hydrodynamic velocity u_z , the density n_e and two thermal velocity: the longitudinal v_z and the transverse v_r ones. The same unknowns come over to Eqs. (2.52)–(2.54). In turn, Eqs. (2.42)–(2.44) involve two unknowns: the temperature T_∞ and the pressure p_∞ . Thus, the system of Eqs. (2.42)–(2.44), (2.52)–(2.54) involves four unknowns and is closed. As a result, Crout obtained a complete and qualitatively correct solution of the evaporation problem of arbitrary intensity. A flaw of [33] is that the adopted approximation of the distribution function on the surface is adapted to the boundary conditions on the surface evaporation only in the mean (in the terminology of the book [1]). Besides, in the domain of small intensity of the process, this solution is inaccurate, it quantitatively poorly agrees with relations (2.34) and (2.35) of the linear theory.

2.6.3 The Model of Anisimov

In 1968, Anisimov [34] proposed an original idea of the closure of the system of Eqs. (2.42)–(2.44). He assumed that the DF of the molecules incident on the CPS is proportional to the volume DF

$$f_w^- = A f_{w0}^- \quad (2.55)$$

Here,

$$f_{w0}^- = \frac{n_w}{\pi^{3/2} v_w^3} \exp \left(-\frac{2c_r^2}{v_r^2} - \left(\frac{c_z - u_\infty}{v_w} \right)^2 \right) \quad (2.56)$$

A is the free parameter. Substituting f_w^- from Eqs. (2.55) and (2.56) into integrals (2.7), we obtain the following system of equations

$$\frac{\sqrt{\tilde{T}_\infty}}{\sqrt{\pi\tilde{p}_\infty}} + A \left(s \operatorname{erfc}(s) - \frac{\exp(-s^2)}{\sqrt{\pi}} \right) = 2s \quad (2.57)$$

$$\frac{1}{2\tilde{p}_\infty} + A \left(\left(\frac{1}{2} + s^2 \right) \operatorname{erfc}(s) - \frac{s \exp(-s^2)}{\sqrt{\pi}} \right) = 1 + 2s^2 \quad (2.58)$$

$$\frac{1}{\sqrt{\pi\tilde{p}_\infty}\sqrt{\tilde{T}_\infty}} + A \left(s \left(\frac{5}{4} + \frac{s^2}{2} \right) \operatorname{erfc}(s) - \left(1 + \frac{s^2}{2} \right) \frac{\exp(-s^2)}{\sqrt{\pi}} \right) = \frac{5s}{2} + s^3 \quad (2.59)$$

With a given velocity, the factor s of the system of Eqs. (2.57)–(2.59) involves three unknowns: $\tilde{p}_\infty$, $\tilde{T}_\infty$, A . For the case of monatomic gas we have: $M_\infty = u_\infty / \sqrt{5/3 RT_\infty}$, $s = \sqrt{5/6} M_\infty$. In [34], the limit case of sonic evaporation ($M_\infty = 1$; $s = \sqrt{5/6}$) was considered and the following limit parameters were calculated

$$M_\infty = 1 : \tilde{T}_\infty = 0.6691, \tilde{p}_\infty = 0.2062, \tilde{J}_\infty = 0.8157 \quad (2.60)$$

Relations (2.60) show that acoustic evaporation generates vapor with the parameters: $T_\infty \approx 2/3 T_w$, $p_\infty \approx 1/5 p_w$, $J_\infty \approx 4/5 J_1^+$. Here, J_1^+ is the one-way Maxwell flow emitted by the CPS' it can be found by formula (2.8). Physically this means that, with the maximal velocity of evaporation, approximately 1/5 of the emitted molecules are decelerated by the incident flow. Accordingly, they come back to the interface and are condensed on it. As many pioneers, Anisimov wrote a small very informal note [34] (only three pages!). However, the brilliant idea of [34] opened a line of research on the strong evaporation on the basis of mass, momentum, and energy conservation laws. In this connection, it suffices to mention the papers [35–43].

In 1977, Labuntsov and Kryukov [35] and independently Ytrehus [36] applied the method of [34] to the entire region of variation of the Mach number: $0 \leq M_\infty \leq 1$. The resulting analytical solution [35, 36] reads as

$$\sqrt{\tilde{T}_\infty} = \sqrt{1 + B^2} - B \quad (2.61)$$

$$\tilde{p}_\infty = \frac{1}{2} \exp(s^2) \left(C + D \sqrt{\tilde{T}_\infty} \right) \quad (2.62)$$

$$\tilde{J}_\infty = 2\sqrt{\pi} \frac{s\tilde{p}_\infty}{\sqrt{\tilde{T}_\infty}} \quad (2.63)$$

Here we used the following notation: $B = \sqrt{\pi}/8 s$, $C = \exp(-s^2) - \sqrt{\pi}s \operatorname{erfc}(s)$, $D = (1 + 2s^2)s \operatorname{erfc}(s) - 2/\sqrt{\pi}s \exp(-s^2)$. In 1979, Labuntsov and

Kryukov [37] in more detail their method of [35]. The results of [37] accord well with the numerical results of [31, 32], the departure of the dependence $\tilde{T}_\infty(M_\infty)$ being the greatest ($\approx 5\%$).

Later, Knight [38, 39] used the system of Eqs. (2.61)–(2.63) to construct the thermal model of laser ablation in outer atmosphere. This model relates the gas parameters with the intensity of evaporation. The author of [38, 39] deal with the dual problem, which involves the system of equations of gas dynamics and heat-transfer equation in a radiated target.

2.6.4 The Model of Rose

In 2000, Rose [40] proposed a model of strong evaporation, which is a modification of Schrage's old model [10]. Schrage [10] defined the negative part of DF as follows

$$f_w^- = (1 + Ac_z)f_{w0}^+, \quad c_z < 0 \quad (2.64)$$

here f_{w0}^+ is the equilibrium Maxwell distribution, as defined by formula (2.1), A is the free parameter. The form of Eq. (2.64) was based on the work on diffusion in binary systems by the author of [44]. Rose [40] replaced in formula (2.64) f_{w0}^+ by the function f_{w0}^- , as given by relation (2.56). The results of [40] in the form of the dependences $\tilde{p}_\infty$, $\tilde{T}_\infty$, $\tilde{J}_\infty$ on the Mach number agree quite well with the numerical results [31, 32], the dependence $\tilde{T}_\infty(M_\infty)$ being even better than that of Ytrehus [36] and Labuntsov and Kryukov [37].

2.6.5 The Mixing Model

Inside the Knudsen layer we introduce the conditional mixing surface “m” and write for it the mass, momentum, and energy conservation laws (2.3)–(2.5)

$$\rho_w v_w - \rho_m v_m I_1 = 2\sqrt{\pi}\rho_\infty u_\infty \quad (2.65)$$

$$\rho_w v_w^2 - \rho_m v_m^2 I_2 = 4\rho_\infty u_\infty^2 + 2\rho_\infty v_\infty^2 \quad (2.66)$$

$$\rho_w v_w^3 - \rho_m v_m^3 I_3 = \sqrt{\pi}\rho_\infty u_\infty^3 + \frac{5}{2}\sqrt{\pi}\rho_\infty v_\infty^2 u_\infty \quad (2.67)$$

Equations (2.65)–(2.67) take into account the state equation for a perfect gas $p = \rho v^2/2$, the following notations were used

$$I_1 = \exp(-s_m^2) - \sqrt{\pi} s_m \operatorname{erfc}(s_m) \quad (2.68)$$

$$I_2 = \frac{2}{\sqrt{\pi}} s_m \exp(-s_m^2) - (1 + 2s_m^2) \operatorname{erfc}(s_m) \quad (2.69)$$

$$I_3 = \left(1 + \frac{s_m^2}{2}\right) \exp(-s_m^2) - \left(\frac{5\sqrt{\pi}}{4} s_m + \frac{\sqrt{\pi}}{2} s_m^3\right) \operatorname{erfc}(s_m) \quad (2.70)$$

Here $s_m = u_m/v_m$ is the velocity factor, u_m is the hydrodynamic velocity, $v_m = \sqrt{2R_g T_m}$ is the thermal velocity (all the quantities are taken on the mixing surface).

It is assumed that due to the molecular flow the mixing parameters in the section will differ from those in the Navier–Stokes region. We shall assume that between the sections “ ∞ ” and “ m ” the molecular mass flows are conserved (the condition mixing)

$$\rho_\infty u_\infty = \rho_m u_m \quad (2.71)$$

Let us consider the solution of system of Eqs. (2.68)–(2.71). Assume that we are given the following quantities: the density ρ_w and the thermal velocity v_w on the CPS and the hydrodynamic velocity u_∞ in the Navier–Stokes region. Then the system of Eqs. (2.68)–(2.71) contains 5 unknowns: the density ρ_m , the thermal velocity v_m and the hydrodynamic velocity u_m on the mixing surface, as well as the density ρ_∞ and the thermal velocity v_∞ in the Navier–Stokes region. For the closure of the system of equations we adopt the following assumption $v_m = v_\infty$, which physically means the equality of temperatures: $T_m = T_\infty$.

The mixing model was developed in the papers of the author of the present book [42–43]. If we assume that $u_m = u_\infty$ and exclude the mixing condition (2.71), we arrive at Anisimov’s model. Thus, the mixing model is a further development of the last one. We note that the introduction inside the Knudsen layer of some conditional surface correlates in a certain sense with Crout’s model, even though there are principal differences here: in Crout’s model one modifies the positive part of the DF, whereas in the mixing model, the negative part.

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