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# Non-Equilibrium Phenomena near Vapor-Liquid Interfaces

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# Chapter 2
# Background for Pure (One Component) Substance

One way to develop accurate boundary conditions is the application of molecular-kinetic theory to creation of these conditions. From point of this theory view intensity of evaporation and condensation processes (mass flux density *j*) can be defined. Brief history of study development about mass flux density *j* determination at evaporation and condensation of pure vapor is following.

First correlation, which should be mentioned, is famous Herts-Knudsen (HK) formula attributed to Herts [1] and Knudsen [2]. Possible version of this formula at $\beta_E = \beta_C = \beta$, where $\beta_E$ is the evaporation coefficient, $\beta_C$ is the condensation coefficient:

$$j = \beta\left[\rho_S\sqrt{RT_S/2\pi} - \rho_\infty\sqrt{RT_\infty/2\pi}\right] \tag{2.1}$$

Evaporation coefficient is defined as ratio of vapor mass flux density in evaporation process near the liquid (solid)—vapor interface $j_E$ to mass flux density calculated in accordance with positive half of Maxwell distribution function with temperature of interface $T_S$ and equilibrium (saturated vapor) density $\rho_S$ corresponding to this temperature $\rho_S\sqrt{RT_s/2\pi}$. Thus $\beta_E = j_E/\rho_S\sqrt{RT_s/2\pi}$. Condensation coefficient $\beta_C$ is defined as ratio of mass flux density of condensing on the interface molecules $j_C$ to mass flux density of whole flux of molecules striking with interface $j_-$: $\beta_C = j_C/j_-$.

HK formula is based on the assumption that as emitted (evaporated) from interface molecules and as molecules moving to this surface are described by half Maxwellian velocity distributions with constant in any point of space occupied by vapor $\rho_s$, $T_s$, $\rho_\infty$, $T_\infty$. Schematically this distribution function is illustrated by Fig. 2.1.

Hence relationship (2.1) is valid only for free-molecular flow that is at Kn → ∞ where Kn is Knudsen number—ratio of mean free path of vapor molecules *l* to typical system size *L*. Thus Herts-Knudsen formula cannot be used for determination of mass flux density at Kn → 0.

In continuum limit at Kn → 0 velocity distribution function for vapor far (in the scale of mean free path) from interface cannot be presented by two-side

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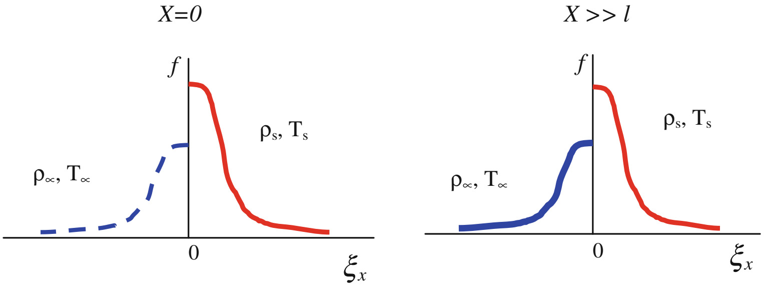

**Fig. 2.1** Half-Maxwellians

Maxwellian like in HK formula because there is the motion of bulk vapor and corresponding distribution function looks like in Fig. 2.2.

First attempts to take into account velocity of bulk vapor, directed away from interface, were made in papers [3–5]. Crout was first who used a distribution function for the vapor remote from the interface which would give the bulk vapor velocity $u_\infty$. However, Schrage in [5] has criticized such application of ellipsoidal Crout's distribution because this function is incompatible with distribution of molecules evaporated from the interface. R. W. Schrage has proposed two types of distribution function for molecules moving to the interface near it. In the first of them this distribution function is just part of distribution far from interface with same bulk velocity, temperature and density for molecules moving to the interface $u_\infty, \rho_\infty, T_\infty$.

Kucherov and Rikenglaz [6] have applied thirteen-moment distribution for study of weak evaporation and condensation at which vapor bulk velocity is much smaller the vapor sonic velocity. Due to this strong inequality the description has been simplified considerably, became linear and distribution function has been transformed in shifted Maxwellian distribution like in Schrage's approach. As a result the authors have deduced evident formula for determination of mass flux density in this process at $\beta_E = \beta_C = \beta = 1$ in continuum limit. Calculation in accordance with this formula was in two times more value obtained from Herts-Knudsen correlation

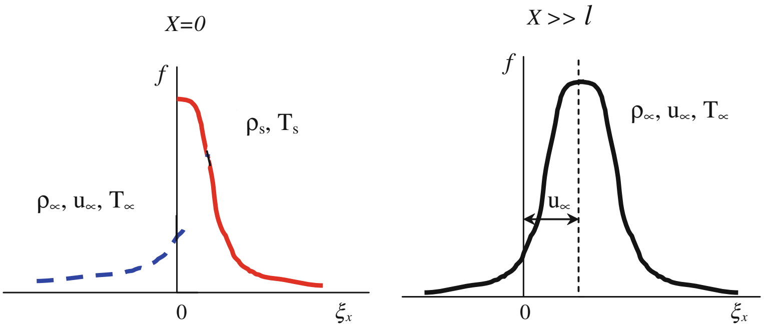

**Fig. 2.2** Distribution functions

(2.1). Same result can be derived from [5] where relationship $j$, $\rho_s$, $T_s$, $\rho_\infty$, $T_\infty$ is presented but in implicit form concerning $j$. A little later in paper [7] Kucherov and Rikenglaz have made generalization for arbitrary evaporation–condensation coefficient at the assumption $\beta_E = \beta_C = \beta$ and have presented the following formula:

$$j = \frac{\beta}{1 - 0.5\beta}\left[\rho_S\sqrt{RT_S/2\pi} - \rho_\infty\sqrt{RT_\infty/2\pi}\right] \tag{2.2}$$

For further analysis we need the generalization (2.2) for the case $\beta_E \neq \beta_C$. In order to derive this correlation let us to repeat deduction in Kucherov's and Rikenglaz's manner but taking into account that $\beta_E \neq \beta_C$. This procedure can be done for linearized statement (weak evaporation) that is at $V_\infty/\sqrt{2RT_\infty} << 1$, $\rho_s \approx \rho_\infty$, $T_s \approx T_\infty$. Resulting correlation is following:

$$j = \frac{1}{1 - 0.5\beta_C}\sqrt{RT/2\pi}[\beta_E\rho_S - \beta_C\rho_\infty] \tag{2.3}$$

where $T \approx T_s \approx T_\infty$. At $\beta_E = \beta_C = \beta$ formula (2.3) transforms in (2.2). For weak evaporation and condensation $P_S = \rho_s RT_S \approx \rho_s RT$ and $P_\infty = \rho_\infty RT_\infty \approx \rho_\infty RT$. Hence (2.3) can be presented as:

$$j = \frac{1}{1 - 0.5\beta_C}\frac{[\beta_E P_S - \beta_C P_\infty]}{\sqrt{2\pi RT}} \tag{2.3a}$$

Relationships (2.2) and (2.3) have been obtained on the base only conservation equations and known prescribed distribution function for molecules moving to the interface. Labuntsov [8], Muratova and Labuntsov [9] have solved the Boltzmann kinetic equation for weak evaporation and condensation and deduced from these solutions more accurate formula for $\beta_E = \beta_C = \beta$ instead (2.2):

$$j = \frac{\beta}{1 - 0.4\beta}\frac{(P_S - P_\infty)}{\sqrt{2\pi RT}} \tag{2.4}$$

Comparison (2.2) with (2.4) shows that at $\beta_E \neq \beta_C$ instead (2.3a) more accurate correlation should be used:

$$j = \frac{1}{1 - 0.4\beta_C}\frac{(\beta_E P_S - \beta_C P_\infty)}{\sqrt{2\pi RT}} \tag{2.4a}$$

Correlation (2.2) and (2.4) above are valid only for weak processes when bulk velocity of vapor flow is much smaller sound velocity. At the rising evaporation or condensation intensity non-equilibrium of vapor increases and distribution function changes more strongly. The good enough solutions of this problem on the base of the Boltzmann kinetic equation and its models for high evaporation intensity have been studied and were presented in different papers [10–19]. For calculation of mass flux density in evaporation problem in paper [15] the following formula were suggested for $\beta = 1$:

$$j = 0.6\sqrt{2RT_S}(\rho_S - \rho_\infty)\sqrt{\frac{\rho_\infty}{\rho_S}} \tag{2.5}$$

For calculation of subsonic strong condensation the correlation below were obtained on the base corresponding molecular-kinetic approaches:

$$j = 1.67\frac{P - P_S}{\sqrt{2\pi RT_\infty}} \cdot \left\{1 + 0.51 \cdot \ln\left[\frac{P\sqrt{T_\infty}}{P_S\sqrt{T_S}}\right]\right\} \tag{2.6}$$

As example the comparison of application of equilibrium and non-equilibrium boundary conditions to condensation in solid state (de-sublimation) transfer process is presented bellow.

Condensation of gas carbon dioxide ($CO_2$) on a flat surface is studied in steady statement. Temperature of this surface $T_w$ is known and constant during condensation process (see Fig. 2.3).

Gas (vapor) parameters far from the interface in comparison with of gas molecules mean free path are considered as known. It is supposed that on the plate surface layer of solid carbon dioxide exists. Thickness of this deposit $\delta$ is known and does not change during the whole process. Four unknown values are needed to determine: temperature of condensate interface—$T_s$, vapor pressure corresponding to this temperature in accordance with saturation conditions—$P_s$, mass flux density—$j$ and also heat flux density—$q$.

Thus for determination of four unknown values four equations should be used. First of them is the expression of Fourier thermal conductivity law for one-dimensional case $q = \lambda_{CO_2}\frac{(T_S - T_W)}{\delta}$, where $\lambda_{CO_2}$ is thermal conductivity of $CO_2$ deposit. It is considered that the $\lambda_{CO_2}$ value is known. Second is $q = j \cdot r$, where $r$ is the latent heat of de-sublimation per mass unit. Third is the empirical correlation between saturation pressure and corresponding temperature $P_s = T^{-\frac{1361}{T_S}+12.01}$. Traditional approach suggests in the role of the fourth equation same relationship between saturation pressure and corresponding temperature, that is temperature near the interface is determined in accordance with saturation line. The solution of these four

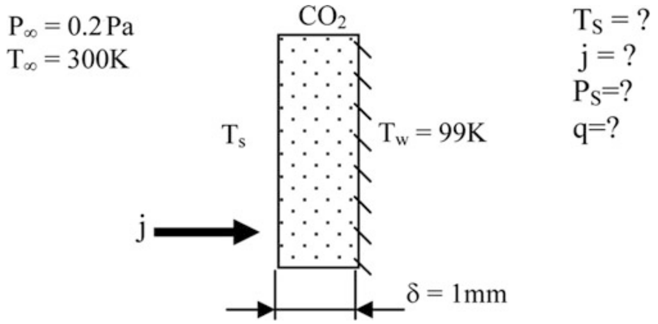

**Fig. 2.3** Condensation of gas carbon dioxide ($CO_2$)

equations gives as a result temperature difference across the deposit layer is about 8 K. But if instead of traditional approach we use the non-equilibrium correlation (2.6) then the value of this temperature difference and mass flux density *j* becomes in almost fifteen times smaller than at traditional calculations.

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