Effect of Condensation Heat on the Condensation Coefficient

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To account for the effect of condensation heat on the condensation coefficient (α), a semiempirical model is proposed. The model contains two free parameters: a characteristic size of the "hot spot" where the heat release occurs and its lifetime. At reasonable values of the parameters, the model agrees well with experimental and computer-simulated data for both simple and associating liquids. For nonequilibrium conditions, the model leads to the Hertz–Knudsen equation with α dependent not only on characteristics of the liquid but also on those of ambient vapor. This offers an explanation for the existing scattering of experimental data in α. Among other things, the expression for α obtained shows that for the net evaporation process α is always higher than that for the net condensation, and moreover, $\alpha = 1$ for all liquids if evaporation occurs in vacuum. The model also indicates that for complex associating liquids like glycerol α may be quite sensitive to peculiarities of the liquid state under consideration.

Introduction

A correct evaluation of the molecular exchange rate between a liquid surface and ambient vapor is of importance in many fields of chemical engineering. A key characteristic of the process is the condensation coefficient, α, which is usually defined as the flux ratio of condensed molecules to incident vapor ones (i.e., as a probability for an incident molecule to augment the liquid phase). The condensation coefficient was introduced at the beginning of this century (Knudsen, 1915) but still remains a matter of discussion for both its nature and value (see, e.g., a comprehensive review by Cammenga, 1980; as well as recent papers by Fujikawa and Maerefat, 1990; and Matsumoto et al., 1995).

Two problems manifest themselves as the most challenging. The first one is a characteristic difference in the condensation coefficient between simple and polar, particularly associating liquids. It is generally recognized that for the former α is close to unity, while for the latter, most authors agree that α is significantly less than unity. The second problem is a large scattering in experimental data for α. A characteristic example is glycerol: within a close temperature range, Wyllie (1949), Heideger and Boudart (1962), and Baranova et al. (1966) found $\alpha \approx 0.05$, whereas Trevoy (1953), Lednovich and Fenn (1977), and Cammenga et al. (1977) obtained $\alpha \approx 1$.

A theoretical consideration has been given mainly to the first problem. It was Wyllie (1949) who pointed out that for polar liquids the condensation coefficient is remarkably close to the free-angle ratio $\delta = q_l^r/q_v^r$ (q_l^r and q_v^r are the molecular rotational partition functions in the liquid and vapor, respectively), which was introduced by Kincaid and Eyring (1938) in their kinetic theory of liquids. Following this notion, Penner (1952), Mortinsen and Eyring (1960), and Fujikawa and Maerefat (1990) applied the transition state theory to calculate the condensation coefficient: they equated α with δ calculating q_l^r and q_v^r, respectively, at the transition state, being associated with the liquid surface, and in the ambient vapor. Since molecular rotations are hindered in the surface, for polar liquids $q_l^r < q_v^r$, and α is thus always less than unity for them. This approach enables a reasonable explanation of experimental data for polar liquids (Penner, 1952; Mortinsen and Eyring, 1960; Fujikawa and Maerefat, 1990), but it cannot explain why α may differ noticeably from unity for simple ones (as it was recently found for Ar, $\alpha = 0.7–0.8$, Matsumoto et al., 1994a,b).

As for the other problem—the scattering of experimental data—its probable solution was related with either refining experimental methods or giving due consideration to secondary effects such as the rate control by heat flux, or both (Cammenga, 1980). At the same time, no one seriously doubted that α is a physical characteristic for a given liquid, being only temperature dependent for pure liquids. Otherwise, it might be expected that α is dependent on the specific, nonequilibrium conditions in which it is measured, and therefore the scattering of experimental data in α is just a reflection of these conditions.

In this respect, recent results of molecular dynamics simulations of the condensation-evaporation process by Matsumoto et al. (1994a) are very remarkable. Contrary to popular belief, the authors found that there existed a correlation between the fluxes of molecules striking the liquid surface and leaving it. This correlation manifested itself either in the rebound of incident molecules (the reevaporation phenomenon), or in that the incident molecules caused evaporation of other molecules (the exchange process). This may suggest that in nonequilibrium conditions the condensation coefficient should be dependent on these conditions, in particular, on ambient vapor pressure. The publication of this article was followed by a detailed study of the condensation–evaporation process (Matsumoto et al., 1994b, 1995; Yasuoka et al., 1994, 1995), including its energetics (Matsumoto et al., 1995).

This article presents a semiempirical model that considers condensation heat release to be responsible for the correlation between the fluxes of molecules striking and leaving the surface: when a vapor molecule sticks to the liquid surface, local overheating of the surface (in the form of "hot spot") occurs due to the condensation heat release. As a result, molecules evaporate from the hot spot with a higher probability than from an undisturbed surface. This mechanism of evaporation is supported by the latest results of molecular dynamics study by Matsumoto et al. (1995). The model contains two free parameters: a characteristic size of the hot spot and its lifetime. At reasonable values of these parameters, it is in good agreement with experimental and computer-simulation data for both simple and associating liquids. The model shows that the characteristic difference in α for simple and associating liquids is due to their difference in the entropy of vaporization and the free-angle ratio. For nonequilibrium conditions, the model leads to the Hertz–Knudsen equation with the condensation coefficient α dependent not only on the characteristics of the liquid but also on those of the ambient vapor. This offers an explanation for the scattering of experimental data in α. Among other things, the expression for α obtained shows that for the net evaporation process α is always higher than that for the net condensation. Moreover, for all liquids, α is equal to unity when evaporation takes place in a vacuum. These conclusions, together with the previously mentioned difference in α for simple and associating liquids, correspond to the most general trends in experimental data (Cammenga, 1980).

Model

Let us consider a vapor being in equilibrium with its liquid at temperature T_∞ (see Figure 1). Assume the vapor to be an ideal gas. Then, the number of molecules incident upon a unit area of the liquid surface in unit time is given by the well-known relation from the kinetic theory of gases:

$$j_{\text{inc}} = \frac{1}{4} n_{vs} \bar{c}, \tag{1}$$

where $n_{vs} = p_{vs}/k_B T_\infty$ is the saturated vapor number density, and $\bar{c} = \sqrt{8 k_B T_\infty / \pi m}$ is the average velocity of molecules (k_B is the Boltzmann constant, m is the molecular mass, and p_{vs} is the saturation vapor pressure at temperature T_∞). Equation 1 allows an interpretation that is more convenient for future consideration: with an average distance between vapor molecules introduced as:

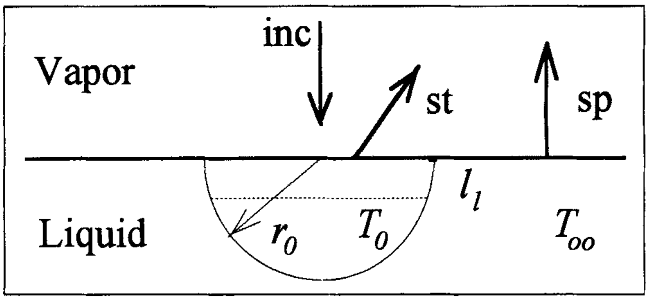

Figure 1. Condensation–evaporation process.

$$l_v = n_{vs}^{-1/3},$$

one may think, in accordance with Eq. 1, that the area of the liquid surface,

$$S_m = l_v^2 = n_{vs}^{-2/3} \tag{2}$$

experiences, on average, an impact of one vapor molecule during the time interval:

$$t_m = 4\frac{l_v}{\bar{c}} = \frac{4}{n_{vs}^{1/3}\bar{c}}. \tag{3}$$

When a vapor molecule approaches the liquid surface, the energy of cohesion between the vapor and surface molecules converts into kinetic energy. In thermodynamic terms, this phenomenon may be described as release of the heat $\epsilon = \Delta E/N_A$, where $\Delta E = \Delta H - RT_\infty$ is the condensation heat per mole (N_A is the Avogadro number, ΔH is the molar heat of vaporization, and R is the gas constant). The heat release leads to local overheating of the liquid at the point where the incident molecule collides with the surface. The excess heat acquired by the molecules involved in the energy-conversion process stimulates the molecules to evaporate from the surface, and if the act of evaporation does not happen in a short time, it rapidly dissipates into the liquid by heat conductivity.

A rigorous analytical description of this process is rather problematic, in particular because the process takes place in the interphase region, which is rather complex for analytical description itself. Some severe simplifying assumptions should be made.

Specifically, in this article it is assumed that at the moment when an incident molecule sticks to the liquid surface, a "hot spot" is instantaneously created (see Figure 1). The hot spot consists of N_0 molecules in the liquid, at and near the surface, and the molecule that stuck to the surface, with the condensation heat ϵ homogeneously distributed among all of these molecules. For a time interval t_0, the hot spot retains its state, and then it instantaneously decays (disappears). (A finite rate of the hot-spot decay due to heat conductivity is considered in the Appendix.)

Let the hot spot be as a half-sphere with radius r_0. Then, the total number of molecules in it, $N_{0t} = N_0 + 1$, is related to the radius as

$$N_{0t} = \frac{2}{3}\pi r_0^3 n_l,$$

where n_l is the number density of the liquid. Among these N_{0t} molecules, part of them, N_{0s}, constitutes a surface layer that comes in contact with the vapor by the area:

$$S_0 = \pi r_0^2.$$

Assuming the width of the layer to be equal to

$$l_l = n_l^{-1/3},$$

the following is obtained:

$$N_{0s} = \pi\left(r_0^2 n_l^{2/3} - \frac{1}{3}\right).$$

The temperature in the hot spot is

$$T_0 = T_\infty + \frac{\Delta E}{C_l N_{0t}}, \tag{4}$$

where C_l is the heat capacity of the liquid per mole.

In equilibrium, the flux of the molecules incident upon the liquid surface is equal to that of the molecules leaving it. Specifically, according to the preceding interpretation of Eq. 1, the surface area S_m in time t_m should lose, on average, one molecule. Let the rate of evaporation from surface unit area be written as $A\exp(-\Delta E/RT) = A\exp(1 - \Delta S/R)$, where $\Delta S = \Delta H/T$ is the entropy of vaporization. For solids, A is the product of the characteristic frequency of molecular vibrations in the surface by the surface number density (see, e.g., Frenkel, 1955). For liquids, A is, in general, of a more complex nature. For our present purposes, however, A does not need to be specified in detail since it drops out of the final relations. The balance equation is written as

$$1 = Ae^{-\Delta E/RT_0}S_0 t_0 + Ae^{-\Delta E/RT_\infty}(S_m - S_0)t_0 + Ae^{-\Delta E/RT_\infty}S_m(t_m - t_0).$$

The first and second terms in the righthand side of this equation represent the probabilities for a molecule to evaporate from the surface, respectively, from the hot spot and the remaining area of S_m, while the hot spot exists. The last term is the probability of evaporation from the whole area S_m during the remainder of t_m, when the hot spot has disappeared.

The preceding equation can be written as

$$1 = Ae^{-\Delta E/RT_\infty}S_m t_m + A(e^{-\Delta E/RT_0} - e^{-\Delta E/RT_\infty})S_0 t_0. \tag{5}$$

The quantity $A\exp(-\Delta E/RT_\infty)S_m t_m$ represents the probability of spontaneous evaporation, that is, the evaporation that would occur if the liquid surface were undisturbed by collisions of vapor molecules. Then, the second term in the righthand side of Eq. 5 should be considered as the probability of stimulated evaporation, as a result of the condensation heat release. Since stimulated evaporation implies either the reevaporation or exchange process, it is natural to equate the condensation coefficient α with the probability of spontaneous evaporation (Matsumoto et al., 1994a), that is, $\alpha = A\exp(-\Delta E/RT_\infty)S_m t_m$. Eliminating A with the help of Eq. 5 yields:

$$\alpha = \left\{1 + \frac{S_0 t_0}{S_m t_m}\left[\exp\left(-\frac{\Delta E}{RT_\infty}\left(\frac{T_\infty}{T_0} - 1\right)\right) - 1\right]\right\}^{-1}. \tag{6}$$

The model also allows one to estimate the probability of condensation of an incident molecule itself, α_{self}. According to the previous discussions, the probability of stimulated evaporation is equal to $1 - \alpha$. Then, assuming that the incident molecule contributes to this quantity simply as one molecule from the total number of molecules in the hot-spot surface layer, one obtains for α_{self}:

$$1 - \alpha_{\text{self}} = \frac{1-\alpha}{N_{0s}} = \alpha\frac{S_0 t_0}{S_m t_m}\left[\exp\left(-\frac{\Delta E}{RT_\infty}\left(\frac{T_\infty}{T_0} - 1\right)\right) - 1\right]\frac{1}{N_{0s}}. \tag{7}$$

It seems reasonable to introduce a dimensionless parameter instead of t_0. For this purpose, t_0 may be measured in the time units characteristic to the liquid:

$$\tau_0 = t_0\frac{\bar{c}}{l_l} = t_0\bar{c}n_l^{1/3} \tag{8}$$

Then in Eqs. 6 and 7:

$$\frac{S_0 t_0}{S_m t_m} = \left(\frac{9\pi}{256}\right)^{1/3}\frac{n_{vs}}{n_l}\tau_0 N_{0t}^{2/3}, \tag{9}$$

where $N_{0t} = N_0 + 1$.

The free parameters N_0 and τ_0 are supposed to be identical for all liquids. One may argue that a better choice for N_0 would probably be its proportionality to the mean number of the nearest-neighbor molecules in the liquid of interest. This suggestion will also be discussed below.

Comparison with Experimental Data. Fitting N_0 and t_0

Although rough estimates of N_0 and τ_0 might be made by physical reasoning (N_0 is likely close to the number of the nearest neighbors for a surface molecule, and τ_0 is of the order of 1), for closer specification, it is necessary to invoke experimental data (in this chapter, "experimental data" refers to both laboratory experiments and computer simulations). For this purpose, the method of least squares can be used.

Table 1. Predicted Values of Condensation Coefficient vs. Experimental and Computer Simulation Data

Liquid	T_∞ K	Exp.		Eqs. 6 and 7 $N_0 = 2.75$ and $\tau_0 = 4.0$		Eqs. 6 and 7 $N_0/N_c = 0.08$, $\tau_0 = 0.25$	
		α	α_{self}	α	α_{self}	α	α_{self}
Argon	80	0.75*	0.94*	0.64	0.90	0.88	0.93
Carbon tetrachloride	297	0.64†	—	0.55	0.88	0.79	0.87
Water	293	0.35†	—	0.30	0.81	0.29	0.46
Methanol	288	0.16‡	—	0.19	0.77	0.18	0.23
Methanol	300	0.25*	0.89*	0.24	0.79	0.26	0.31
Glycerol	342	0.05§	—	0.05	0.73	0.01	0.08

*Computer simulation data by Matsumoto et al. (1994) ($\alpha = 0.7$–0.8 for argon, and $\alpha = 0.2$–0.3 for methanol).
†Experimental data by Fujikawa and Maerefat (1990) (for water $\alpha = 0.27$–0.43).
‡Experimental data by Maerefat et al. (1989) ($\alpha = 0.13$–0.17).
§Experimental data by Baranova et al. (1966).

Specifically, assuming the relative standard deviation to be the same in all measurements, consider the functional:

$$\Phi = \sum_i \left(\frac{\alpha_i}{\alpha_i^{\exp}} - 1 \right)^2, \qquad (10)$$

where i labels the experimental points concerned, $\alpha_i^{\exp}$ and α_i are the experimental and predicted values of the condensation coefficient, respectively. The quantity $\sqrt{\Phi}$ characterizes the relative root-mean-square deviation of the theoretical predictions from the experimental data.

In Table 1, experimental data employed for fitting N_0 and τ_0 are given, and also some results of calculations. The choice of the data is a compromise between our intention to consider different types of liquids and the availability of reliable experimental data for quasi-equilibrium conditions.

Table 2 contains the thermodynamic data used for the calculations. A part of them (generally, the saturated vapor pressure and heat of vaporization, with the latter being either given or extracted from the pressure data) were taken from corresponding references, superscripted by *, †, ‡, and § in Table 1. The other necessary data were borrowed from sources of thermodynamic data (Kaye and Laby, 1959; Reid et al., 1977; Weast, 1972).

Figure 2a shows the surface $\Phi = \Phi(N_0, \tau_0)$ (Eq. 10), with α_i calculated on the assumption that $C_l = C_{pl}$. It may be seen that within a range of reasonable values of N_0 and τ_0, the surface does not show any evidence of a minimum.

That this attempt has failed should probably be attributed to the inappropriate specification of C_l. First, in line with the known results of Kincaid and Eyring (1938), who found that a satisfactory agreement of theoretical heat conductivity with the experimental data in liquids is achieved at $C_{vl} = 3R$, it seems reasonable to assume that in the hot spot both molecular rotations and vibrations are frozen rather than active. Next, the effect of a liquid's expansion in the hot spot on the hot-spot energy is likely to be small; therefore, the heat capacity at constant volume is applicable rather than that at constant pressure. This leads to assigning $C_l = 3R$ for all liquids (for argon this value is close to the measured one, $C_{vl} \approx 24$ J/mol·K, see, e.g., Kaye and Laby, 1959). The result is shown in Figure 2b. As is seen, a pronounced minimum at $N_0 \approx 2.75$ and $\tau_0 \approx 4.0$ now appears (at the minimum $\sqrt{\Phi} \approx 0.14$). Corresponding values of α and α_{self} are given in Table 1. It is important to note that a satisfactory correlation with the experimental data exists not only for α but also for α_{self}, which were not involved in the fitting procedure.

Ignoring either of these assumptions, that is, that both rotations and vibrations are frozen or C_l is specified as the heat capacity at constant volume, led to an inappropriate surface pattern: in the first case, the surface was similar to that in Figure 2a, and in the second, a valley appeared in the surface although it did not exhibit a minimum.

To find out how the choice of experimental data for α may affect the results, the surfaces (Eq. 10) were calculated for all possible combinations of the points given in Table 1, with one or two of these six points being omitted (this resulted in 6 and 15 combinations of the points, respectively). Each of the surfaces was of the same pattern as in Figure 2b. The minima of the surfaces are mapped in Figure 3 together with the minimum and two contour lines from Figure 2b. This figure shows how successfully the model would predict α for the whole set of experimental data if N_0 and τ_0 were determined on the base of truncated sets of the data. Several conclusions can be drawn from the figure. First, essentially all

Table 2. Thermodynamic Data Used for Calculations

Liquid	m a.m.u.	T_∞ K	ΔH kJ/mol	p_{vs} kPa	ρ_l 10^3 kg/m^3	C_{pl} J/mol·K	N_c
Argon	40	80	6.8	43.5	1.37	44.0	8.5*
Carbon tetrachloride	154	297	31.0	12.7	1.58	135.0	8.5
Water	18	293	44.0	2.3	1.00	75.6	4.4**
Methanol	32	288	38.8	8.9	0.79	79.0	2.0†
Methanol	32	300	37.6	16.8	0.79	81.3	2.0†
Glycerol	92	342	78.0	$1.5 \cdot 10^{-3}$	1.26	250.0	2.0

*Experimental data by Harris and Clayton (1967).
**Experimental data by Morgan and Warren (1938).
†Computer simulation data by Matsumoto and Gubbins (1990).

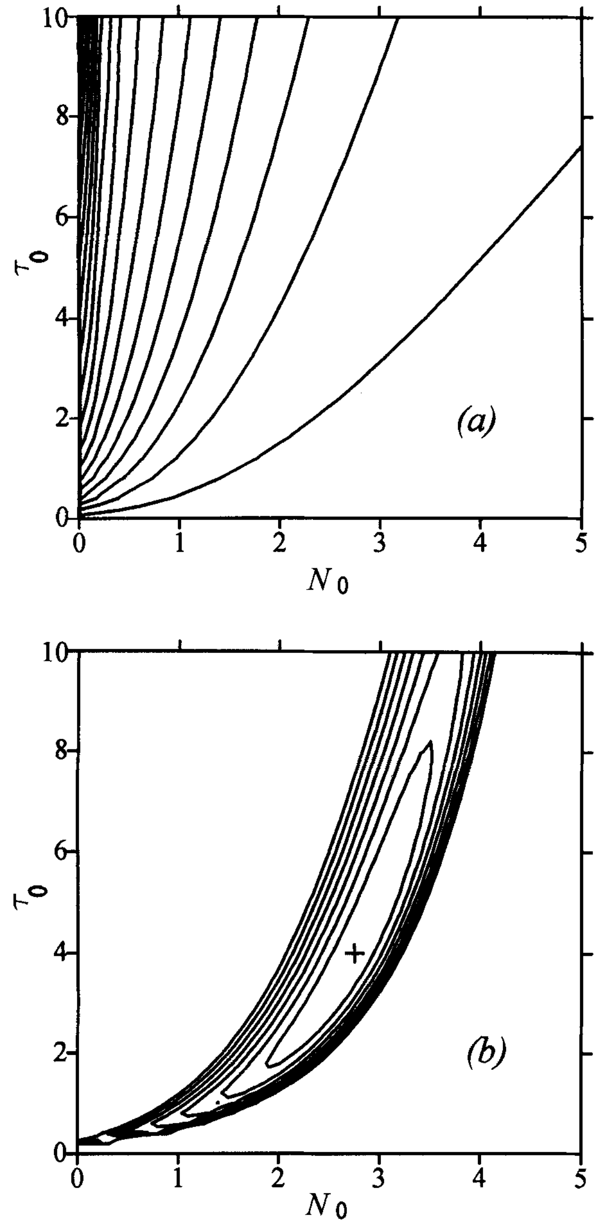

Figure 2. Contour map of the surfaces for the least-square functional $\Phi(N_0, \tau_0)$.

(a) $C_l = C_{pl}$ for all liquids: the interval between contour lines $\Delta\Phi = 0.5$; (b) $C_l = C_{vl}$, with molecular rotations and vibrations in all liquids being frozen ($C_l = 3R$): $\Delta\Phi = 0.02$, + indicates a minimum at $N_0 = 2.75$ and $\tau_0 = 4.0$ ($\Phi = 0.02$).

the minima are within the range of $\sqrt{\Phi} \approx 0.2$ (with only one exception at $N_0 \approx 1.1$ and $\tau_0 \approx 0.8$, which corresponds to the disregarded points 3 and 6). Second, the greater number of experimental points taken into account to specify N_0 and τ_0 results in less scattering of the minima. Finally, as our examination of the results shows, the minima tend to shift up or down depending upon which points are disregarded: up if points 1 and 2, and down if the others. This latter observation hints that N_0 and τ_0 may be different for different types of liquids, in particular, for simple and associating ones. Unfortunately, the variety of experimental data is not sufficient to come to an ultimate conclusion.

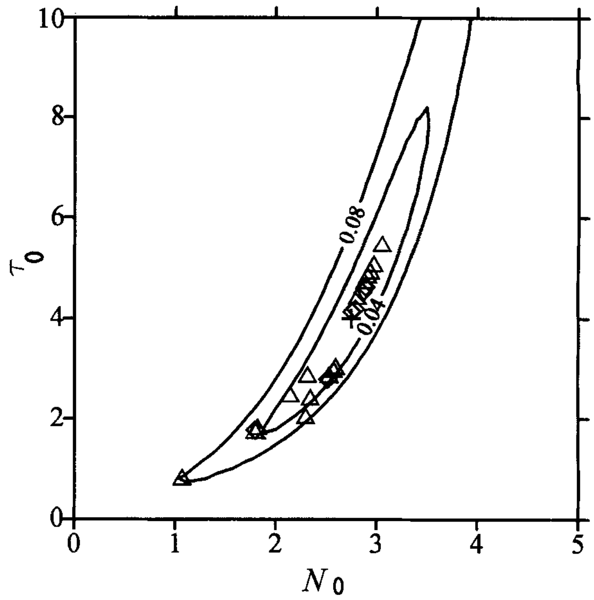

Figure 3. Contour lines and minima of the surfaces for the least-square functional $\Phi(N_0, \tau_0)$; $C_l = C_{vl}$, with molecular rotations and vibrations in all liquids being frozen ($C_l = 3R$).

Contour lines (——) and the minimum (+) of the surface based on the whole set of experimental points (as in Figure 2b); ◇ and △ are the minima of the surfaces based on the truncated sets of the points containing 5 and 4 points, respectively.

Figure 4 shows the surface defined by Eq. 10 under the assumption that N_0 is proportional to the mean number of the nearest-neighbor molecules in the liquid, N_c (and at $C_l = 3R$). The values of N_c used for the calculations are given in Table 2. N_c for carbon tetrachloride was taken as for argon, and N_c for glycerol was set equal to that for methanol. The surface also exhibits a minimum similar to that in Figure 2b, in this case at $N_0/N_c \approx 0.08$ and $\tau_0 \approx 0.25$. However, the values of N_0 seem to be unreasonably low, and besides, the accuracy of the correlation with the experimental data is lower, $\sqrt{\Phi} \approx 0.33$. The corresponding values of α and α_{self} are given in Table 1. It may be noticed that the predicted value of α_{self} for methanol is also much worse than before, which is due to the unreasonably small value of N_0 (≈ 0.16). Similar results, including such low values of N_0 ($N_0/N_c \approx 0.18$), were obtained when carbon tetrachloride and glycerol were not taken into consideration to determine the free parameters.

Thus, the former approach (N_0 is identical for all liquids) proves to be more successful than the latter (N_0 is proportional to N_c). This finding may be attributed to the nonequilibrium character of the process of evaporation, as well as to the fact that the process takes place in interphase region: it looks reasonable that under these conditions, the molecules do not manifest their coordination peculiarities in such a pronounced manner as they do in the equilibrium bulk liquid.

As mentioned in the Introduction, Matsumoto et al. (1995) also investigated energetics of the process via molecular dynamics simulation. Specifically, they found that the fluctuations of temperature exhibited a maximum at the surface (that was related to condensation heat release), and estimated the value of these fluctuations and their relaxation time. This of-

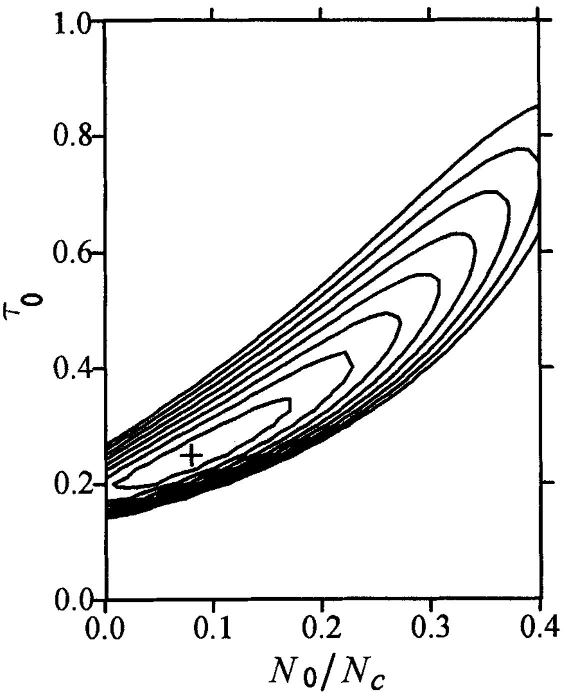

Figure 4. Contour map of the surface for the least-square functional $\Phi(N_0/N_c, \tau_0)$; $C_l = C_{vl}$, with molecular rotations and vibrations in all liquids being frozen ($C_l = 3R$).

The interval between contour lines $\Delta\Phi = 0.005$; + indicates a minimum at $N_0/N_c = 0.08$ and $\tau_0 = 0.25$ ($\Phi = 0.11$).

fers an opportunity for a direct verification of the physical mechanism underlying the model.

Let us estimate the previously cited quantities following the model.

Because of the relation between A and α, $\alpha = A\exp(-\Delta E/RT_\infty)S_m t_m$, the second term in the righthand side of Eq. 5 is proportional to α. This implies that the temperature fluctuations responsible for stimulated evaporation in general correlate with those responsible for spontaneous evaporation. To estimate the maximum value of temperature fluctuations, let the correlation coefficient be equal to unity. Then we can write (Feller, 1970):

$$\langle(\Delta T)^2\rangle = \left[\langle(\Delta T)^2\rangle_{sp}^{1/2} + \langle(\Delta T)^2\rangle_{st}^{1/2}\right]^2$$

where $\langle(\Delta T)^2\rangle_{sp}^{1/2}$ and $\langle(\Delta T)^2\rangle_{st}^{1/2}$ are the root-mean-square deviations of temperature due to spontaneous and stimulated fluctuations, respectively. For methanol at $T_\infty = 300$ K Matsumoto et al. (1995) found $\langle(\Delta T)^2\rangle_{sp}^{1/2} \approx 100$ K and $\langle(\Delta T)^2\rangle^{1/2} \approx 120$ K (the latter indicates the maximum value of the fluctuations in the interphase region). According to the model, $\langle(\Delta T)^2\rangle_{st}^{1/2}$ can be evaluated as

$$\langle(\Delta T)^2\rangle_{st} = (T_0 - T_\infty)^2 \frac{V_0 t_0}{S_m t_m r_0},$$

where $V_0 = (2\pi/3)r_0^3$ is the hot spot's volume. Since $V_0 = 2S_0 r_0/3$, this equation can be rewritten as

$$\langle(\Delta T)^2\rangle_{st} = \frac{2}{3}(T_0 - T_\infty)^2 \frac{S_0 t_0}{S_m t_m},$$

where $S_0 t_0/S_m t_m$ is given by Eq. 9. At $N_0 = 2.75$ and $t_0 = 4.0$ [the first value, in particular, gives $T_0/T_\infty = 2.25$ (Eq. 4)], and using the preceding value of $\langle(\Delta T)^2\rangle_{sp}^{1/2}$ from direct simulations, we find $\langle(\Delta T)^2\rangle^{1/2} \approx 111$ K in comparison with 120 K in the paper of Matsumoto et al. (1995). In fact, the obtained value of $\langle(\Delta T)^2\rangle^{1/2}$ should be compared with the value averaged over the layer by width r_0 ($\approx 5\times10^{-10}$ m) rather than with the actual maximum value (120 K); this averaged value is equal to approximately 115 K.

The relaxation time of the fluctuations (exponential decay time) was estimated by Matsumoto et al. (1995) for argon at 80 K as 2.1 ps to 22 ps (in the bulk liquid and at its surface, respectively), and as 2.6 ps to 11 ps for methanol at 300 K. This time may be compared with the hot spot lifetime $t_0 = \tau_0/\bar{c}n_l^{1/3}$, which is obtained to be equal to 7.1 ps in the case of argon and 4.3 ps for methanol.

We can thus infer that the proposed mechanism of the condensation–evaporation process is well supported by direct molecular dynamics simulations.

To conclude this section, note that the condensation coefficient at a given temperature, Eqs. 6, 8, and 9, is essentially dependent on two thermodynamical characteristics that vary significantly in passing from simple to associating liquids: the condensation heat ΔE (or the heat of vaporization $\Delta H = \Delta E + RT_\infty$), and saturated vapor number density n_{vs} (or the saturated vapor pressure $p_{vs} = n_{vs}k_B T_\infty$). According to the free-volume (lattice) theory of liquids (see, e.g., Hirschfelder et al., 1954), the latter can be evaluated as $n_{vs} \approx n_l(\Delta E/2RT_\infty)^3\exp(-\Delta H/RT_\infty)/\delta$, where δ is the free-angle ratio. Then, taking the expression for T_0 (Eq. 4) into account, α (Eq. 6) may be written in the form of:

$$\alpha = \left\{1 + \frac{1}{8\delta}\left(\frac{9\pi}{256}\right)^{1/3} \tau_0 N_{0t}^{2/3}\left(\frac{\Delta S}{R} - 1\right)^3 \exp(-\Delta S/R) \times \left[\exp\left(\frac{(\Delta S/R - 1)^2}{\Delta S/R - 1 + N_{0t}C_l/R}\right) - 1\right]\right\}^{-1}.$$

It follows that the condensation coefficient is completely determined by the entropy of vaporization $\Delta S = \Delta H/T_\infty$ and free-angle ratio δ. The latter, in turn, can be roughly evaluated as $\exp(-\Delta S_{p,s})$, where $\Delta S_{p,s}$ is the difference between the vaporization entropy for polar liquid and its usual mean value for simple liquids (Cammenga, 1980).

Nonequilibrium Conditions

At equilibrium:

$$j_{\mathrm{inc}} = j_{ev}^{sp} + j_{ev}^{st} = \alpha j_{\mathrm{inc}} + (1 - \alpha) j_{\mathrm{inc}},$$

where j_{ev}^{sp} and j_{ev}^{st} are the molecular fluxes corresponding to the spontaneous and stimulated evaporation, respectively.

Now consider nonequilibrium conditions, assuming for simplicity that each of the subsystems, vapor and liquid, is in equilibrium itself (and can thus be described in thermodynamic terms). For this purpose, let us shift the values of vapor temperature and density from their equilibrium values $T_v = T_\infty$ and $n_v = n_{vs}$. Using the prime to mark these modified conditions, we find that the net (condensation) flux is

$$\Delta j_{(c)} = j'_{\text{inc}} - (j'^{sp}_{ev} + j'^{st}_{ev})$$
$$= j'_{\text{inc}} - [\alpha' j_{\text{inc}} + (1-\alpha') j'_{\text{inc}}] = \alpha'(j'_{\text{inc}} - j_{\text{inc}}),$$

where α' is given by Eq. 6 as before, except that the expression for $S_0 t_0 / S_m t_m$ (Eq. 9), in accordance with Eqs. 2, 3, and 8, includes additional factors n_v/n_{vs} and T_v/T_l, which are responsible for the nonequilibrium conditions:

$$\frac{S_0 t_0}{S_m t_m} = \left(\frac{9\pi}{256}\right)^{1/3} \frac{n_{vs}}{n_l} \tau_0 N_{0t}^{2/3} \frac{n_v}{n_{vs}} \left(\frac{T_v}{T_l}\right)^{1/2}, \tag{9a}$$

here $T_l = T_\infty$.

We thus arrive at the Hertz–Knudsen equation with the condensation coefficient dependent upon the characteristics of the nonequilibrium state under consideration. As a result, when using the Hertz–Knudsen equation to calculate α from experimental data (by relating the measured value of Δj to $j'_{\text{inc}} - j_{\text{inc}}$), different values of a at the same surface conditions may be found, depending upon vapor pressure and temperature. Therefore, the scattering in experimental data for the condensation coefficient is not necessarily due to the limitations of the experimental methods but may just display the conditions under which the measurements were conducted. In particular, as is seen from Eqs. 6 and 9a, for net evaporation ($n_{vs} > n_v$, $\Delta j_{(c)} < 0$), α is always higher than that for net condensation ($n_{vs} < n_v$, $\Delta j_{(c)} > 0$). Moreover, for the evaporation in a vacuum ($n_v \to 0$), α is equal to unity for all liquids. These conclusions are the two most general ones that have been drawn from the analysis of experimental data on α (Cammenga, 1980).

For more details, consider the case of glycerol. As mentioned earlier, within a close temperature range Wyllie (1949), Heideger and Boudart (1962), and Baranova et al. (1966) found $\alpha \approx 0.05$, whereas Trevoy (1953), Lednovich and Fenn (1977), and Cammenga et al. (1977) obtained $\alpha \approx 1$. In the papers of Heideger and Boudart (1962) and Baranova et al. (1966), the experiments were conducted under conditions not far from equilibrium, and, as a result, the value of α obtained is in good correlation with the values of α for other liquids (Table 1). In the papers of Trevoy (1953), Lednovich and Fenn (1977), and Cammenga et al. (1977), the evaporation in a vacuum was investigated to obtain α, and that $\alpha \approx 1$ was found is also explained by the model, as indicated earlier. However, Wyllie (1949) found $\alpha \approx 0.05$ under the evaporation in a vacuum, and Cammenga et al. (1977) obtained $\alpha \approx 1$ not only for the evaporation in a vacuum but also at quasi-equilibrium conditions. While the results of an early study by Wyllie (1949) might be attributed to the presence of a trace of water, as was supposed by Cammenga (1980), every precaution was taken by Cammenga et al. (1977) in their experiments. Thus, the value $\alpha \approx 1$ obtained under quasi-equilibrium conditions needs an explanation. For this purpose, α was calculated for the conditions of the paper by Cammenga et al. (1977) ($T_\infty = 313.4$, $\Delta H = 86.8$ kJ/mol, and $p_{vs} = 1.4 \times 10^{-4}$ kPa; the other properties were as in Table 2) at different values of C_l (Table 3). It can be seen that the increase of C_l from $3.0R$ to $4.5R$ is sufficient to give a value for α close to that in Table 1. A further rise in C_l up to $10.5R$ leads to the value of α found by Cammenga et al. (1977). For glycerol $C_{pl} \approx 28R$ (≈ 230 J/mol·K; see e.g., Pryde, 1966); therefore, such variations in C_l do not seem to be incredible, particularly if one takes into account that glycerol may happen to be in a glassy state (Pryde, 1966; Cammenga et al., 1977). According to the model, a similar strong effect on the condensation coefficient is also possible due to relatively small variations in ΔH and p_{vs}, for example, being a result of thermal decomposition of glycerol during distillation at high temperatures (Heideger and Boudart, 1962). This suggests that the condensation coefficient, primarily in complex liquids like glycerol, may be extremely dependent upon the peculiarities of the liquid state under consideration.

Table 3. Condensation Coefficient for Glycerol in Relation to the Heat Capacity, $T_\infty = 313.4$

C_l/R	3.0	4.5	7.5	10.5
α	0.002	0.034	0.643	0.964

Conclusion

This article proposed a semiempirical model to account for the effect of condensation heat release on the condensation coefficient α. The key idea is that a local overheating of the surface (in the form of a "hot-spot") occurs because of the condensation heat release when a vapor molecule sticks to the liquid surface. As a result, molecules more readily evaporate from the hot spot than from an undisturbed surface. The model contains two free parameters, the characteristic size of the hot spot plus its lifetime. Two cases have been considered: (1) both of the parameters are identical for all liquids; and (2) the characteristic size of the hot spot is proportional to the mean number of the nearest-neighbor molecules in the liquid of interest. Testing these suggestions by the experimental and computer-simulation data for a characteristic set of liquids (argon, carbon tetrachloride, water, methanol, and glycerol), it is found that in the first case the data correlate with each other considerably better and the values of the free parameters just given look more reasonable than in the second case. It was also found that the heat capacity of the liquid in the hot spot must be specified as that at a constant volume, with molecular rotations and vibrations being frozen. With the free parameters fitted, the theoretical predictions are in good agreement with experimental and computer-simulation data for both simple and associating liquids. The model suggests that the characteristic difference in α for simple and associating liquids is primarily due to their difference in the condensation heat ΔE and saturated vapor pressure p_{vs}. Invoking the free-volume (lattice) theory of liquids to define p_{vs} shows that this dependence may be expressed in terms of the entropy of vaporization and free-angle ratio. The proposed mechanism of the condensation-evaporation process agrees well with the results of the molecular dynamics study of its energetics by Matsumoto et al. (1995).

For nonequilibrium conditions, the model leads to the Hertz–Knudsen equation with α dependent not only on the characteristics of liquid but also on those of ambient vapor. This offers an explanation for the scattering of experimental data in α. Among other things, the expression for α obtained shows that for the net evaporation process α is always higher than that for the net condensation. Moreover, for all liquids, α is equal to unity when evaporation takes place in a vacuum. These conclusions, together with the just mentioned difference in α for simple and associating liquids, correspond to the most general trends in experimental data (Commenga, 1980). The model also shows that for complex associating liquids like glycerol, α may be quite sensitive to peculiarities of the liquid state under consideration.

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Notation

A = constant specific to the liquid
C_v = molar heat capacity at constant volume
C_p = molar heat capacity at constant pressure
Δj = net flux
v_f = free volume
τ = reduced time

Subscripts

c = condensation
exch = exchange

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Appendix: Account for a Finite Rate of the Hot-Spot Decay

Due to heat conductivity, the hot spot expands in size and cools down. To evaluate how the hot spot's characteristics vary with time, it is assumed that (1) the hot spot holds its half-spherical form, (2) all thermodynamic parameters of the liquid in the hot spot are uniformly distributed and temperature independent, and (3) the front of heat conductivity is a discontinuity that travels according to the Einstein equation $dr_b^2 = 6a_l dt$ (here, r_b is the current radius of the hot spot, and $a_l = k_l / c_l n_l$ is the thermal diffusivity in the liquid, where k_l is the heat conductivity, and $c_l = C_l / N_A$ is the heat capacity per molecule). Integrating the equation for r_b, one obtains:

$$r_b^2 = r_0^2 + 6a_l(t - t_0). \tag{A1}$$

The relations for other current characteristics of the hot spot, namely, for its temperature T, the area of the surface layer, S, and the numbers of the molecules in the volume, N_t, and on the surface, N_s, are the same as for the initial hot spot's characteristics, except that r_b appears instead of r_0.

A finite rate of the hot-spot decay results in an additional evaporation from the expanding hot spot. Then, Eq. 5 is rewritten as

$$1 = Ae^{-\Delta E/RT_\infty} S_m t_m + A(e^{-\Delta E/RT_0} - e^{-\Delta E/RT_\infty}) S_0 t_0 + A\int_{t_0}^{t_m} (e^{-\Delta E/RT} - e^{-\Delta E/RT_\infty}) S\, dt,$$

where the last term in the righthand side represents this additional evaporation. Correspondingly, Eq. 6 takes the form of:

$$\alpha = \left\{ 1 + \frac{S_0 t_0}{S_m t_m} \left[\exp\left(-\frac{\Delta E}{RT_\infty} \left(\frac{T_\infty}{T_0} - 1 \right) \right) - 1 \right] + \frac{1}{S_m t_m} \int_{t_0}^{t_m} \left[\exp\left(-\frac{\Delta E}{RT_\infty} \left(\frac{T_\infty}{T} - 1 \right) \right) - 1 \right] S\,dt \right\}^{-1}. \quad \text{(A2)}$$

In dimensionless variables this latter equation can be written as

$$\alpha = \left\{ 1 + \frac{S_0 t_0}{S_m t_m} \left[\exp\left(-\frac{\Delta E}{RT_\infty} \left(\frac{T_\infty}{T_0} - 1 \right) \right) - 1 \right] + \frac{S_0 t_0}{S_m t_m} \int_{1}^{t_m/t_0} \left[\exp\left(-\frac{\Delta E}{RT_\infty} \left(\frac{T_\infty}{T} - 1 \right) \right) - 1 \right] \frac{S}{S_0} dt' \right\}^{-1},$$

where $S_0 t_0 / S_m t_m$ is given by Eq. 9 as before and

$$\frac{t_m}{t_0} = 4 \left(\frac{n_l}{n_{vs}} \right)^{1/3} \frac{1}{\tau_0}$$

$$\frac{S}{S_0} = \left(\frac{r_b}{r_0} \right)^2$$

$$\frac{T}{T_\infty} = 1 + \frac{\Delta E}{RT_\infty} \frac{R}{C_l} \frac{1}{N_{0l}} \left(\frac{r_0}{r_b} \right)^3,$$

where according to Eq. A1,

$$\frac{r_b}{r_0} = \left[1 + \left(\frac{256\pi^2}{9} \right)^{1/3} \frac{n_l^{1/3} a_l}{\bar{c}} \frac{\tau_0}{N_{0l}^{2/3}} (t' - 1) \right]^{1/2}.$$

Under the conditions of Table 1, the relative value of the last term in the curly brackets in Eq. A2 was about 0.15 for glycerol and did not exceed 0.015 for the other liquids.

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