

## TEMPERATURE GRADIENT IN THE DIFFUSION REGIME OF DROPLET EVAPORATION

D.A. GAVRYUSHENKO, V.M. SYSOEV, K.V. CHEREVKO

UDC 533.15(27), 536.755  
©2007Taras Shevchenko Kyiv National University, Faculty of Physics  
(2, Academician Glushkov Ave., Kyiv 03127, Ukraine; e-mail: Kostia\_Cherevko@univ.kiev.ua)

The process of droplet evaporation has been considered on the basis of the general equations of the linear thermodynamics of nonequilibrium processes, i.e. by examining the general equation of diffusion taking into account the terms associated with gradients of the chemical potential and the temperature. An analytical expression for the temperature gradient, which arises in the diffusion regime of evaporation, has been derived. A mechanism, which explains the absence of the gas diffusion flow toward the evaporating droplet even in the case of its nonzero concentration gradient, has been proposed.

equation brings about the classical Maxwell formula for the diffusion regime of droplet evaporation

$$J = 4\pi Dr (n_0 - n_\infty), \quad (2)$$

where  $n_0 = n(r)$  is the vapor concentration in the near-surface layer and  $n_\infty$  the vapor concentration at infinity. At the same time, to describe real processes, formula (2) requires to take into account a plenty of corrections, e.g., the influence of a Stefan flow, spatial confinement, temperature decrease in the droplet during evaporation, etc. [3]. It should be noted that all corrections are made in expression (2) rather than in (1). This means that, instead of formulating the general problem, some special case is considered, and the obtained specific solution is adjusted to describe various processes by the progressive introduction of certain corrections into it.

### 1. Introduction

The process of liquid droplet evaporation in a gaseous environment plays an important role both in the nature and in human vital functions. It is crucial for such an atmospheric phenomenon as the formation and evolution of clouds, or such an ecological situations as a variation of the water evaporation rate, provided that there are certain impurities in air. The problems belonging to various other branches of science, which require the application of methods involving aerosols, can also be attributed to this scope.

In most cases, evaporation takes place in the presence of a background gas, being the environment for an evaporating droplet [1]. This process is accompanied by the diffusion of vapor molecules into the background gas. In this work, we examine just the diffusion regime of evaporation, which is established if the condition  $\frac{\lambda}{r} \ll 1$ , where  $\lambda$  is the mean free path of molecules and  $r$  is the droplet radius, holds true [1]. In the case of stationary evaporation, the diffusion flow of a droplet substance  $J$  is conventionally calculated on the basis of the Fick diffusion law which reads [1]

$$J = -4\pi\rho^2 \frac{\partial n}{\partial \rho} D \quad (1)$$

in the case of a system that was thermally stabilized initially. Here,  $\rho$  is the radial coordinate,  $D$  the vapor diffusion coefficient, and  $n$  the vapor concentration. The diffusion coefficient is considered to be constant and estimated by the methods of kinetic theory [2]. This

Therefore, a conclusion can be drawn that the construction of a thermodynamically substantiated theory for the droplet evaporation in the diffusion regime on the basis of the general equations of the linear thermodynamics of nonequilibrium processes, i.e. the general diffusion equation with regard for terms associated with the gradients of the chemical potential and the temperature, turns out an extremely challenging task.

### 2. Description of the Model

Consider the process of liquid droplet evaporation in a gaseous environment provided that the regime of diffusion evaporation is stationary. In this case, we assume that the vapor concentration near the droplet's surface is equal to the equilibrium one,  $n_0$ , i.e. the saturated vapor concentration at the droplet temperature. The background gas is considered insoluble in the droplet substance. Thus, there are no flows directed toward the droplet. The droplet shape is assumed unchangeable during the evaporation, remaining a regular sphere. The process is considered stationary and running in the absence of external fields.

During the process, the system is considered to be placed into a thermostat.

The system of equations, which describes the process indicated, is constructed on the basis of the fundamental phenomenological equation of irreversible thermodynamics [4]. This equation asserts that the flow of an evaporating substance  $\vec{J}_k$  is coupled by a linear relationship with the corresponding governing thermodynamic potential. In the case of our system, this phenomenological equation reads [4, 5]

$$\begin{aligned} \vec{J}_k &= -D_k \vec{\nabla} n_k - \sum_{i=1}^m \sum_{\substack{j=1 \\ j \neq k}}^{m-1} L_{ki} \left[ v_i \frac{\partial p}{\partial n_j} + \right. \\ &+ RT \left( \frac{\delta_{ij}}{n_i} + \frac{1}{\gamma_i} \frac{\partial \gamma_i}{\partial n_j} \right) \left. \vec{\nabla} n_j - \right. \\ &\left. - \sum_{i=1}^m L_{ki} v_i \frac{K_T}{\rho_m} \vec{\nabla} \rho_m - D_T \vec{\nabla} T, \right. \\ D_k &= \sum_{i=1}^m L_{ki} \left[ v_i \frac{\partial P}{\partial n_k} + kT \left( \frac{\delta_{ik}}{n_i} + \frac{1}{\gamma_i} \frac{\partial \gamma_i}{\partial n_k} \right) \right], \\ D_T &= \sum_{i=1}^m L_{ki} \left( P v_i \gamma_T + \frac{\partial \mu_i}{\partial T} \right) + L_{kq}, \end{aligned} \quad (3)$$

where  $m$  is the number of components in the medium,  $L_{ki}$  are the relevant phenomenological factors,  $v_i = \frac{\partial \mu_i}{\partial P}$  and  $\gamma_i$  are the partial molar volume and the activity coefficient, respectively, of the  $i$ -th component,  $R$  is the universal gas constant,  $k$  the Boltzmann constant,  $T$  the temperature,  $\delta_{ij}$  the Kronecker symbol,  $K_T = \rho_m \left( \frac{\partial P}{\partial \rho_m} \right)_T$  the isothermal compressibility modulus,  $\rho_m$  the density of the system,  $P$  the pressure, and  $\gamma_T = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V$  the thermal coefficient of pressure at a constant volume. The temperature gradient  $\vec{\nabla} T$  appears in formula (3) owing merely to the evaporation process and does not associated with the temperature gradient that is created and maintained in the system by external conditions.

In the framework of our model, we consider that the gradient of the general density in the system vanishes:  $\vec{\nabla} \rho_m = 0$ . Therefore, only those components of the flow survive, which are governed by the concentration gradient  $\vec{\nabla} n_j$  necessarily present and, as we suppose, by the temperature gradient which arises owing to such

an evaporation. In this case, the boundary conditions for the concentration look like

$$\begin{cases} n_1(r) = n_0, \\ n_1(R_\infty) = n_R, \end{cases} \quad (4)$$

where  $R_\infty$  is the boundary condition at infinity. Then, proceeding from Eq. (3), the system of differential equations to determine the flow of a diffusing substance in the stationary regime can be constructed as

$$\begin{cases} \vec{J}_1 = - \left[ L_{11} \frac{\partial \mu_1}{\partial n_1} + L_{12} \frac{\partial \mu_2}{\partial n_1} \right] \vec{\nabla} n_1 - \\ - \left[ L_{11} \frac{\partial \mu_1}{\partial n_2} + L_{12} \frac{\partial \mu_2}{\partial n_2} \right] \vec{\nabla} n_2 - \\ - \left[ L_{11} \frac{\partial \mu_1}{\partial T} + L_{12} \frac{\partial \mu_2}{\partial T} + L_{1q} \right] \vec{\nabla} T, \\ 0 = - \left[ L_{21} \frac{\partial \mu_1}{\partial n_1} + L_{22} \frac{\partial \mu_2}{\partial n_1} \right] \vec{\nabla} n_1 - \\ - \left[ L_{21} \frac{\partial \mu_1}{\partial n_2} + L_{22} \frac{\partial \mu_2}{\partial n_2} \right] \vec{\nabla} n_2 - \\ - \left[ L_{21} \frac{\partial \mu_1}{\partial T} + L_{22} \frac{\partial \mu_2}{\partial T} + L_{2q} \right] \vec{\nabla} T, \\ 0 = \vec{\nabla} n_1 + \vec{\nabla} n_2. \end{cases} \quad (5)$$

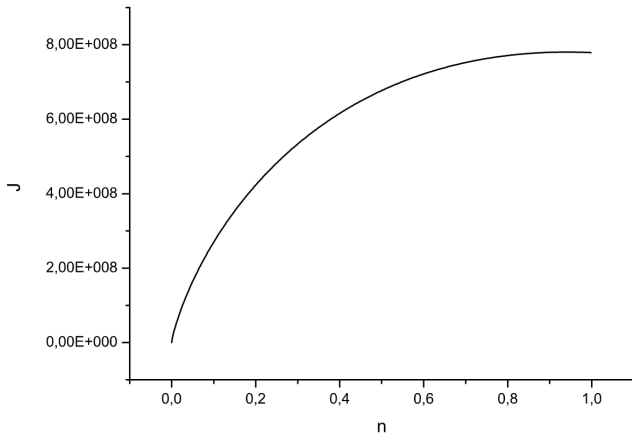
### 3. Calculation of the Temperature Gradient Occurring on the Droplet Evaporation

Proceeding from the system of differential equations (5), we obtained an expression for the temperature gradient which arises in the system owing to the evaporation. Provided the conditions for the diffusion regime that were indicated above, the following equation was obtained:

$$\vec{\nabla} T = \frac{\left[ L_{21} \left( \frac{\partial \mu_1}{\partial n_2} - \frac{\partial \mu_1}{\partial n_1} \right) + L_{22} \left( \frac{\partial \mu_2}{\partial n_2} - \frac{\partial \mu_2}{\partial n_1} \right) \right]}{L_{21} \frac{\partial \mu_1}{\partial T} + L_{22} \frac{\partial \mu_2}{\partial T} + L_{2q}} \vec{\nabla} n_1. \quad (6)$$

In our system, there is a concentration gradient of the evaporating substance. Therefore, on the basis of Eq. (5), we can draw an important conclusion that a corresponding nonzero gradient of temperature necessarily arises as well. The corresponding temperature profile can be found from expression (5):

$$\begin{aligned} \nabla &= \left[ L_{21} (s_{01} + R \ln n_1) + \right. \\ &\left. + L_{22} (s_{02} + R \ln (1 - n_1)) + L_{2q} \right]^{-2} \cdot \text{const.} \end{aligned} \quad (7)$$



The value of the constant in expression (7) can be determined using the temperature boundary conditions, namely, the given temperature at infinity,

$$T(R_\infty) = T_0$$

so that

$$\text{const} = T_0 \left[ L_{21} (s_{01} + R \ln n_1) + L_{22} (s_{02} + R \ln (1 - n_1)) + L_{2q} \right]^2.$$

The estimation of the temperature gradient that arises owing to the diffusion of the evaporating liquid into the background gas shows that the difference between the temperatures near the droplet and at infinity amounts to  $5 \div 15$  K, depending on the parameters which characterize the mixture of the background gas and the evaporating substance. This result agrees well with experimental data on the evaporation of alcohols [6].

#### 4. Calculation of the Evaporating Substance Flow

To make a comparison between the solutions of system (5) and Eq. (1), i.e. expression (2), we must specify the expression for the activity coefficient  $\gamma_i$  of the solution. Really, the expression for the diffusion flow  $\vec{J}_1$  of the evaporating substance is derived from Eq. (5) and looks like

$$\vec{J}_1 = - \left[ L_{11} \left( \frac{\partial \mu_1}{\partial n_1} - \frac{\partial \mu_1}{\partial n_2} \right) + L_{12} \left( \frac{\partial \mu_2}{\partial n_1} - \frac{\partial \mu_2}{\partial n_2} \right) - L_{21} \left( \frac{\partial \mu_1}{\partial n_2} - \frac{\partial \mu_1}{\partial n_1} \right) + \right.$$

$$\left. + L_{22} \left( \frac{\partial \mu_2}{\partial n_2} - \frac{\partial \mu_2}{\partial n_1} \right) \right] \frac{L_{11} \frac{\partial \mu_1}{\partial T} + L_{12} \frac{\partial \mu_2}{\partial T} + L_{1q}}{L_{21} \frac{\partial \mu_1}{\partial T} + L_{22} \frac{\partial \mu_2}{\partial T} + L_{2q}} \vec{\nabla} n_1. \quad (8)$$

Therefore, in order to find the dependence  $J_1(n_1)$ , one has to know the dependence  $\gamma_i(n_i)$ . The simplest case is the model of ideal solution, the activity coefficient of which  $\gamma$  equals one [7]. In this case, the final equation for the calculation of the flow  $\vec{J}_1$  reads

$$\vec{J}_1 = -2RT \left[ L_{11} \frac{1}{n_1} - L_{21} \frac{1}{1 - n_1} - \left[ L_{21} \frac{1}{n_1} - L_{22} \frac{1}{1 - n_1} \right] \times \frac{L_{11} (s_{01} + R \ln n_1) + L_{12} (s_{02} + R \ln (1 - n_1)) + L_{1q}}{L_{21} (s_{01} + R \ln n_1) + L_{22} (s_{02} + R \ln (1 - n_1)) + L_{2q}} \right] \times \vec{\nabla} n_1. \quad (9)$$

From this equation, taking the boundary conditions (4) for our process into account, it is possible to obtain the final expression for calculating the flow in the case of ideal solution. In calculations of the diffusion flow for various concentrations, we took the values of Onsager coefficients to be those characteristic of alcohols in order to make comparison with the classical theory. The dependence of the evaporating substance flow  $J$  on the substance concentration  $n$  in the near-surface layer is plotted in the figure. It is evident that, even in the case of ideal mixture, the result obtained differs substantially from expression (2) which can be derived from the classical Fick diffusion law in the framework of the approximation of a constant diffusion coefficient and the absence of a temperature gradient.

#### 5. Conclusions

In the case of the diffusion regime of the droplet evaporation, there appears a temperature gradient in the environment, caused by the evaporation. This result corresponds to the experimental data on the evaporation of alcohols [6]. The existence of the induced temperature gradient allows one to explain the absence of the background gas flow toward a droplet even if the gas concentration gradient differs from zero. This means that taking the classical Fick law with a constant diffusion coefficient into consideration is

not sufficient for examining such a process. The approach developed allows the quantitative result for the evaporating substance flow to be obtained in the general case, i.e. the expression obtained does not require to artificially introduce the further correction terms for every specific process. In addition, we derived the analytical expressions for the temperature gradient which arises during evaporation, as well as the expressions for the evaporating substance flow in the case of ideal mixture. The equations obtained allow the temperature gradient and the substance flow to be determined for other types of mixtures as well, provided that the values of the relevant activity coefficients are known.

1. N.A. Fuks, *Evaporation and Droplet Growth in Gaseous Media* (Pergamon Press, London, 1959).
2. J.O. Hirschfelder, Ch.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).
3. A.V. Kozyrev, A.G. Sitnikov, *Uspekhi Fiz. Nauk*, **171**, 765 (2001).
4. S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).

5. L.A. Bulavin, D.A. Gavryushenko, and V.M. Sysoev, *Nonequilibrium Thermodynamics. Part 1: Diffusion Equation* (Kyiv University Press, Kyiv, 2003) (in Ukrainian).
6. R.J. Hopkins and J. Reid, *J. Phys. Chem. B* **110**, 3239 (2006).
7. E.A. Moelwyn-Hughes, *Physical Chemistry* (Pergamon Press, New York, 1964).

Received 27.03.06.

Translated from Ukrainian by O.I.Voitenko

#### ВИНИКНЕННЯ ГРАДІЄНТА ТЕМПЕРАТУРИ ПРИ ДИФУЗІЙНОМУ РЕЖИМІ ВИПАРОВУВАННЯ КРАПЛІ

*Д.А. Гаврюшенко, В.М. Сисоєв, К.В. Черевко*

#### Резюме

Розглянуто процес випаровування краплі на основі загальних рівнянь лінійної термодинаміки нерівноважних процесів, тобто повного рівняння дифузії з урахуванням доданків, пов'язаних з градієнтом хімічного потенціалу та температури. Отримано аналітичний вираз для градієнта температури, що виникає при дифузійному режимі випаровування. Знайдено механізми, що пояснюють відсутність дифузії фоновому газу до краплі за наявності градієнта його концентрації.