THE MOTION OF AN AEROSOL DROP IN A THERMAL DIFFUSION CHAMBER†

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A mathematical model of the motion of aerosol drops in a thermal diffusion chamber due to the action of thermodiffusiophoresis and the gravity force is proposed, taking into account phase transitions on the drop surface. The model includes the equation of motion of the drop and an equation describing the change in its radius during condensation. The dependence of the kinetic coefficients on the temperature and composition of the mixture is neglected, which imposes certain limitations on the permissible value of the temperature change in the region considered. A formula is obtained for the height of maximum ascent of the drop. The results of calculations using this formula are compared with experimental data [1] and with the results obtained using the free-molecular theory. The proposed model gives more satisfactory agreement with experimental results. © 2002 Elsevier Science Ltd. All rights reserved.

Thermal diffusion chambers in which aerosol particles are formed during homogeneous nucleation are widely used to investigate aerosol systems. The particles formed move due to the action of a temperature gradient and the non-uniformity of the composition of the gaseous mixture (thermo-diffusiophoresis) and the gravity force, thereby increasing the dimensions due to condensation of vapour on the surface of the particles. The results of experimental investigations of the behaviour of a drop of dioctylphthalate liquid, formed in a vapour–gas mixture of dioctylphthalate and an inert gas (hydrogen and/or helium) were presented in [1]. The experimental data were compared with calculations based on the free-molecular model (the "dusty-gas" model) [2], developed for a multicomponent mixture [3]. However, the drops traverse a considerable fraction of the trajectory in a continuous medium. This obviously explains the observed disagreement between the results of calculations using the model described in [3] and the measurements presented in [1].

Below, in developing the approach in [4–6] to the analysis of the thermophoresis of an aerosol when a phase transition occurs on the drop surface, we propose a mathematical model of the motion of aerosol drops in a thermal diffusion chamber in a continuous-medium approximation.

1. FORMULATION OF THE PROBLEM

The thermal diffusion chamber. Schematically, a thermal diffusion chamber is a system, bounded by two surfaces, on which a different temperature is maintained (Fig. 1). The vapour of a liquid, evaporated onto the lower heated plate (the temperature of which is T_+), is lifted upwards, diffusing through an inert gas which fills the whole space between the plates and condenses on the upper cooled plate (the temperature of which is T_-). In the steady state, the temperature T_∞ and the pressure p_∞ of the vapour increase quasi-linearly from the lower plate to the upper plate. Supersaturation (the ratio of the vapour pressure to the pressure of the saturated vapour p_∞/p_s) reaches the maximum value in the upper zone of the chamber close to the point $z = z_0$. At this point, where the rate of nucleation is a maximum, as a result of homogeneous nucleation, a drop is produced which, as a result of thermodiffusiophoresis, begins to move upwards and to grow due to condensation of the vapour on its surface. As the drop grows, the influence of the gravity force, which acts on the drop in addition to the thermophoresis forces, increases. At a certain height $z = z_{max}$ the ascent of the drop ceases, and it begins to fall. The coordinate $z = z_{max}$ was measured experimentally in [1].
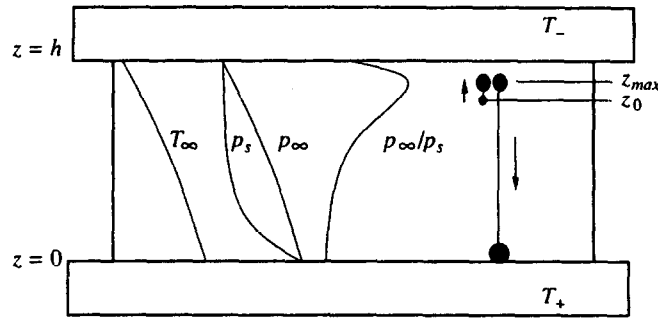
Fig. 1

The equations of motion and mass exchange of the drop. Boundary conditions. Consider the motion of a spherical drop of radius R in a thermal diffusion chamber. The velocity of relative motion of the drop and the gas, and also the characteristic times, are fairly small, so that the velocity field in the gas is described by Stokes' equation, while the temperature outside the drop is T and inside the drop is T_i, and the vapour concentration of the working substance C (the transfer coefficients are constant) obey Laplace's equation

$$\Delta T_i = 0, \quad r \leqslant R; \quad \Delta T = 0, \quad \Delta C = 0, \quad r \geqslant R \tag{1.1}$$

In the zero approximation with respect to the Knudsen number, the boundary conditions on the drop surface $(r = R)$ can be written in the form [7, 8]

$$v_{cr} - \frac{\rho_i v_{ir}}{\rho} = 0, \quad \frac{\rho_i v_{ir}}{\rho_i} = (\bar{v}_1 - \bar{v}_2)_r = -\frac{N}{\rho_1 L}\left(\frac{\partial C}{\partial r} + \frac{k_t}{T}\frac{\partial T}{\partial r}\right) \tag{1.2}$$

$$(\bar{v}_c - \bar{v}_i)_\theta = k_{ts}\frac{\mu}{\rho T}\frac{1}{R}\frac{\partial T}{\partial \theta} + Dk_{ds}\frac{1}{R}\frac{\partial C}{\partial \theta} \tag{1.3}$$

$$k\frac{\partial T}{\partial r} + N\left(\frac{\partial C}{\partial r} + \frac{k_t}{T}\frac{\partial T}{\partial r}\right) + k_p N\frac{\partial C}{\partial r} = k_i\frac{\partial T_i}{\partial r} \tag{1.4}$$

$$T = T_i, \quad C = C_S(T) \tag{1.5}$$

$$N = \frac{LD\rho_1}{C(1-C)}, \quad k_p = \frac{k_t P}{L\rho_1}$$

Here $\bar{v}$ is the velocity in a laboratory system of coordinates connected with the fixed surfaces of the thermal diffusion chamber (the bar denotes averaging over the ensemble of gas molecules), the subscripts $c, i, s, 1$ and 2 denote quantities at the centre of mass of the gas mixture, the condensed phase, the saturated vapour and the volatile component (dioctylphthalate) – subscript 1, or to the non-volatile component (the inert gas) – subscript 2; the subscripts r and θ indicate the radial and tangential components, P, ρ, k and μ are the pressure, density, thermal conductivity and dynamic viscosity of the gas, respectively, $C = n_1/n$ is the concentration of dioctylphthalate vapour (n is the number of molecules per unit volume of the gas), D is the coefficient of mutual diffusion of the components of the mixture, L is the specific heat of the phase transition, and k_t, k_{ts} and k_{ds} are the coefficients of thermal diffusion, thermal slip and diffusion slip.

Relation (1.2) describes the flow of the volatile component on the drop surface, and relation (1.3) describes the slip (thermal and diffusion) of the gas along the drop surface. The second term on the left-hand side of heat-balance equation (1.4) takes into account the flow of heat liberated (absorbed) as a result of any physical–chemical transition of the volatile component, while the third term takes into account the heat flux due to the Dufour effect.

At an infinite distance from the drop $T = T_\infty(z)$, $C = C_\infty(z)$, and at its centre $T = T_0$.

2. THE TEMPERATURE AND CONCENTRATION DISTRIBUTION IN THE REGION OF THE DROP

We will write the solutions of Eqs (1.1) in the form

$$T_i = T_0 + Ar\cos\theta, \quad r \leq R \tag{2.1}$$

$$T = T_\infty + \delta T \frac{R}{r} + \frac{dT}{dz} r\cos\theta + Br\cos\theta \frac{R^3}{r^3}, \quad r \geq R$$

$$C = C_\infty + \delta C \frac{R}{r} + \frac{dC}{dz} r\cos\theta + Gr\cos\theta \frac{R^3}{r^3}, \quad r \geq R \tag{2.2}$$

Assuming that the non-uniformity of the temperature within the drop $\delta T_i = T_i(R) - T_0$ is small, the concentration of saturated vapour in the region of the phase boundary can be expressed in the form

$$C_s(T) = C_s(T_0) + \frac{\partial C_s}{\partial T} \delta T_i \tag{2.3}$$

From boundary condition (1.4), taking relations (2.1) and (2.2) into account, we obtain

$$\delta T = T_0 - T_\infty, \quad A = \frac{dT}{dz} + B, \quad \delta T_i = T_i(R) - T_0 = AR\cos\theta$$

$$A \frac{\partial C_s}{\partial T} = G + \frac{dC}{dz}, \quad \delta C = C_s(T_0) - C_\infty \tag{2.4}$$

Substituting the values of the derivatives of T, T_i and C with respect to r when $r = R$ into condition (1.4), we obtain the following transcendental equation for determining δT

$$\delta T = -N(1 + k_p)(k + k_t N/T)^{-1}\delta C \tag{2.5}$$

and the following expression for the function A

$$A = \frac{3}{2}\left[\left(1 + k_t \frac{N}{kT}\right)\frac{dT}{dz} + \frac{N}{kT}(1 + k_p)T\frac{dC}{dz}\right]\left(1 + \frac{k_i}{2k} + \frac{N}{kT}\left(k_t + T\frac{\partial C_s}{\partial T} + T\frac{\partial C_s}{\partial T}k_p\right)\right)^{-1} \tag{2.6}$$

Relations (2.1)–(2.6) determine the temperature distribution inside and outside the drop, and also the concentration distribution of the volatile component.

The temperature distribution of the medium and the concentration distribution of the saturated vapour over the height of the chamber h, can be calculated in the linear approximation from the formulae

$$dT/dz = (T_+ - T_-)/h, \quad dC/dz = (C_s(T_+) - C_s(T_-))/h$$

The temperature dependence of the relative concentration of the saturated vapour of the working material can be represented by the formula

$$C_s(T) = p_s(T)/P$$

The following approximate relations are assumed for k_i and k_{ds} [9, 10]

$$k_t(T) = \frac{1}{2} C_s(T) \frac{M_1 - M_2}{|M_1 - M_2|}, \quad k_{ds} = -\frac{M_1}{M_2} + \left(\frac{M_1}{M_2}\right)^{\frac{1}{2}}$$

where M_1 is the molecular mass of the working material of dioctylphthalate, and M_2 is the molecular mass of the inert gas-carrier. A value of k_{ts} equal to unity is used in the calculations. The coefficient of viscosity of the gaseous mixture is found from the formula

$$\mu = \frac{(1-C)\mu_k}{1-C+C\phi_{k2}} + \frac{C\mu_2}{C+(1-C)\phi_{2k}}, \quad \phi_{k2} = \frac{[1+(\mu_k/\mu_2)^{\frac{1}{2}}(M_2/M_k)^{\frac{1}{4}}]^2}{[8(1+M_k/M_2)]^{\frac{1}{2}}}$$

The subscript k denotes that the corresponding value of the viscosity is taken for helium or hydrogen. The vapour density and the density of the gaseous mixture are calculated from the following formulae (R_g is the universal gas constant)

$$\rho_1 = \frac{p_\infty M_1}{R_g T_\infty}, \quad \rho = \rho_1\left[1 + \frac{M_1}{M_2}\left(\frac{1}{C_\infty} - 1\right)\right]$$

The functions and coefficients in the dioctylphthalate–hydrogen and dioctylphthalate–helium systems, used in the calculations, are taken from [11].

3. CALCULATION OF THE THERMODIFFUSIOPHORESIS FORCE

To calculate the force acting on the drop from the non-uniform gaseous mixture (the thermodiffusiophoresis force), we will use Stokes' solution for the gas velocity field. According to this solution, the components of the gas velocity on the drop surface can be represented in the form (v_c is the velocity of the centre of mass of the gas relative to the drop)

$$v_r = v_c \cos\theta(1 - 2a + 2b), \quad v_\theta = -v_c \sin\theta(1 - a - b) \tag{3.1}$$

On the other hand, the radial and tangential velocities on the drop surface can be expressed in terms of the diffusion velocity v_d and the slip velocity v_{sl} in the form

$$v_r = v^{(0)} + v_d \cos\theta, \quad v_\theta = v_{sl} \sin\theta \tag{3.2}$$

($v^{(0)}$ is the spherically symmetrical part of the radial velocity). Taking the second condition of (1.2) and condition (1.3) into account, we obtain when $r = R$

$$v^{(0)} = \frac{N}{\rho L}\frac{1}{R}\left(\delta C + \frac{k_t}{T}\delta T\right)$$

$$v_d = \frac{N}{\rho L}\left[2A\frac{\partial C_s}{\partial T} - 3\frac{dC}{dz} + \frac{k_t}{T}\left(2A - 3\frac{dT}{dz}\right)\right] \tag{3.3}$$

$$v_{sl} = -A\left[k_{ts}\frac{\mu}{\rho T} + Dk_{ds}\frac{\partial C_s}{\partial T}\right]$$

Taking expressions (3.1) and (3.2) into account, we can write the aerodynamic drag force, and, taking expression (2.6) into account, the heat flux per unit area of the drop surface

$$\mathbf{F} = 2\pi\mu R(3v_c + 2v_{sl} - v_d), \quad I = \frac{k\delta T}{(1+k_p)}\left(1 - \frac{k_t N k_p}{kT}\right) \tag{3.4}$$

The spherically symmetrical part of the radial velocity $v^{(0)}$ defines the change in the mass of the drop (the integral is taken over the drop surface S)

$$\frac{dm}{dt} = \iint_S \rho v_r \, dS = \frac{N}{L}\left(\delta C + \frac{k_t}{T}\delta T\right)4\pi R = 4\pi\frac{R}{L}I \tag{3.5}$$

On the other hand, the change in the mass of a spherical drop of density ρ_i can be written in the form

$$\frac{dm}{dt} = 4\pi R^2 \rho_i \frac{dR}{dt} \tag{3.6}$$

Comparing expressions (3.5) and (3.6) we obtain the following equation for the square of the radius of the drop

$$\frac{dR^2}{dt} = I_0, \quad I_0 = \frac{2I}{\rho_i L} \tag{3.7}$$

The conditions on the boundary of the working volume, describing the phase transition of one of the components of the gaseous mixture and the unpermeability of the boundary for the other component, determine the velocity of the centre of mass of the gaseous mixture (usually called the Stefan flow velocity)

$$v_{st} = -\frac{N}{\rho L}\left(\frac{dC}{dz} + \frac{k_t}{T}\frac{dT}{dz}\right) \tag{3.8}$$

4. THE HEIGHT OF ASCENT OF THE DROP

The equation of motion of the drop from the instant of nucleation, taking into account the change in its mass due to condensation, can be represented in the form

$$\frac{d(m\mathbf{v})}{dt} - \mathbf{v}_m \frac{dm}{dt} = \mathbf{F} - m\mathbf{g}, \quad v_m = v_{st}\frac{\rho}{\rho_1} \tag{4.1}$$

The velocity $\mathbf{v}$ of the drop in a system of coordinates connected with the fixed walls of the chamber, is equal to the difference $\mathbf{v} = \mathbf{v}_{st} - \mathbf{v}_c$. Then, taking the second expression of (3.4) and formula (3.6) into account, we write Eq. (4.1) in the form

$$\frac{d\mathbf{v}}{dt} = \frac{\Phi - \Psi v(t)}{R^2(t)} - \mathbf{g} \tag{4.2}$$

$$\Phi = \frac{3\mu}{\rho_i}\mathbf{f}_d, \quad \mathbf{f}_d = \left(\left(\frac{3}{2} + \frac{I}{L\mu}\frac{\rho}{\rho_1}\right)\mathbf{v}_{st} + \mathbf{v}_{sl} - \frac{1}{2}\mathbf{v}_d\right), \quad \Psi = \frac{3\mu}{\rho_i}\left(\frac{I}{L\mu} + \frac{3}{2}\right)$$

We will consider the system of two first-order ordinary differential equations (3.7) and (4.2) with the following initial conditions

$$R^2(0) = R_0^2$$

$$v(0) = v_{st} + \frac{2}{3}v_{sl} - \frac{1}{3}v_d = -\frac{2}{3}A\left[\frac{N}{\rho L}\left(\frac{\partial C_s}{\partial T} + \frac{k_t}{T}\right) + k_{ts}\frac{\mu}{\rho T} + k_{ds}D\frac{\partial C_s}{\partial T}\right] \tag{4.3}$$

To determine the heat flux I we need to obtain from transcendental equation (2.5) the temperature difference between the drop and the gas surrounding it $\delta T(z)$, and also the temperature at the centre of the drop $T_0(z)$, which is used, in turn, to calculate the temperature functions in system (3.7) and (4.2). Hence, I_0, Φ and Ψ are functions of time, since they depend on the temperature, which varies along the height of the chamber. However, in the first approximation, we will assume them to be constant quantities. (A numerical solution of the problem showed that, under the conditions considered, this assumption is completely acceptable for practical purposes). This enables us to write immediately an analytical solution of Eq. (3.7) with the first boundary condition (4.3) in the form

$$R^2 = I_0 t + R_0^2 \tag{4.4}$$

Taking expression (4.4) into account, Eq. (4.2) can be integrated in explicit form

$$v(t) = (v(0) - a_1)\left(\frac{t}{\gamma} + 1\right)^\beta + a_2 t + a_1 \tag{4.5}$$

$$a_1 = \frac{\Psi}{\Phi} - \frac{gR_0^2}{\Phi + I_0} \quad a_2 = -\frac{gI_0}{\Phi + I_0} \quad \beta = -\frac{\Phi}{I_0} \quad \gamma = \frac{R_0^2}{I_0}$$

Integrating Eq. (4.5), we obtain the following expression for the coordinate of the ascent of the drop

$$z(t) = \int_0^t v(t)dt = \frac{(v(0) - a_1)\gamma}{\beta + 1}\left[\left(\frac{t}{\gamma} + 1\right)^{\beta+1} - 1\right] + \frac{a_2}{2}t^2 + a_1 t + z_0 \tag{4.6}$$

For these systems $|\beta| \gg 1$, and hence the first term on the right-hand side of (4.5) is a rapidly decreasing function of time. Consequently, the expressions for the velocity and coordinates of the ascent can be written, with sufficient accuracy for practical purposes, in the form

$$v(t) = a_2 t + a_1, \quad z(t) = \frac{1}{2}a_2 t^2 + a_1 t + z_0$$

At the point of maximum ascent the velocity of the drop is equal to zero. Hence, we obtain the following formula for the maximum height of ascent

$$z_{max} - z_0 = \frac{1}{2g\chi}\left(1 + \frac{10}{9}\chi\right)\left[f_d\left(1 + \frac{2}{3}\chi\right)^{-1} - \frac{g\rho_i R_0^2}{3\mu}\left(1 + \frac{10}{9}\chi\right)^{-1}\right]^2, \quad \chi = \frac{l}{\mu L} \tag{4.7}$$

The results of calculations using formula (4.7) are practically identical with the solution obtained using the complete expression (4.6).

5. DISCUSSION OF THE RESULTS

Calculations of the maximum height of ascent of a drop for three values of the total pressure in the chamber (P = 4, 8, and 16 kPa) and four values of the chamber height (h = 14.55, 22.2, 29.4 and 37.4 mm) correspond to the data for which experiments have been carried out [1]. The initial value of the drop radius was taken to be R_0 = 1 μm. A comparison of the results of calculations and experimental data in a dioctylphthalate–hydrogen and a dioctylphthalate–helium system is presented in Fig. 2, where we have plotted the experimental values of the relative heights of ascent of the drop $\zeta = (z_{max} - z_0)/h$ along the abscissa axis, and the corresponding theoretical values along the ordinate axis. The dark circles correspond to calculations from formula (4.6) and the light circles represent the results obtained using the free-molecular theory [3]. The continuous and dashed lines are the corresponding linear approximations, calculated by the method of least squares.

As has already been noted [1], the free-molecular theory for large values of ζ predicts a higher maximum height of ascent of the drop compared with the observed values. The reason is obviously the fact that in this case a considerable part of the path of the drop takes place under conditions of a continuous medium. The proposed model gives qualitatively better agreement with experiment. In fact, it can be seen in Fig. 2 that the continuous line agrees much better with the dash-dot line than the dashed line (the dash-dot line corresponds to complete agreement between the theoretical and experimental
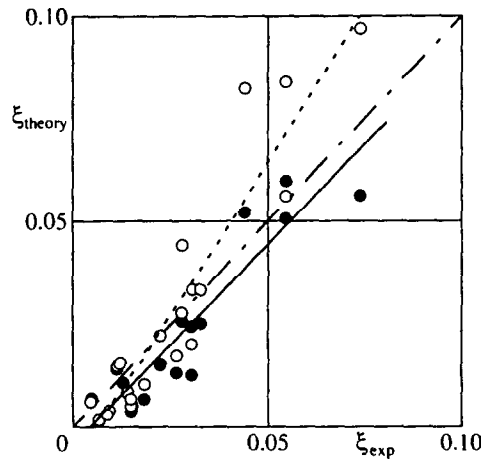

Fig. 2

results). We are inclined to think that some of the quantitative discrepancy is the result of a lack of perfection in the model and also due to the simplified assumptions which were made when carrying out the calculations.

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