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Abstract

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EXPERIMENTAL VERIFICATION OF THE THEORY OF THERMOPHORESIS OF LARGE AEROSOL PARTICLES

There exist two approaches to the thermophoresis of large aerosol particles: 1) one based on Maxwell' s formula (^{1}) for the velocity of thermal slip, and 2) one based on calculations showing that the true velocity of this slip is negligibly small (^{2}), but which, instead, takes into account nonequilibrium processes in the volume of an inhomogeneous gas on the basis of the Chapman–Enskog theory (^{3}). The first approach leads to Einstein' s formula (^{4}), refined by Brock (^{5}); the second, to the Derjagin–Bakanov formula (^{6}), refined by Derjagin and Yalamov (^{7}).

Brock' s formula corresponds to the thermophoretic velocity u_1:

$$u_1 = -\frac{3}{2}\frac{\eta}{\rho T}\frac{(\chi_e/\chi_i + c_t\lambda/R)\,\mathrm{grad}\,T}{(1+2c_m\lambda/R)(1+2\chi_e/\chi_i+2c_t\lambda/R)} = -k_1\frac{\eta}{\rho T}\,\mathrm{grad}\,T, \qquad (1)$$

where T is the temperature in $^\circ K$; χ_i and χ_e are the thermal conductivities of the particles and of the gas; η and ρ are the viscosity and density of the gas; c_m and c_t are constants.

The Derjagin–Yalamov formula gives, for the thermophoretic velocity,

$$u_1 = -\frac{1}{2}\frac{\eta}{\rho T}\frac{8+\chi_i/\chi_e+2c_t(\lambda/R)(\chi_i/\chi_e)}{2+\chi_i/\chi_e+2c_t(\lambda/R)(\chi_i/\chi_e)}\,\mathrm{grad}\,T = -k_2\frac{\eta}{\rho T}\,\mathrm{grad}\,T. \qquad (2)$$

In what follows, in contrast to (^{5}), we shall take $c_m = 1.09$, found theoretically in (^{8}), and for c_t, as in (^{5}), the value 2.16. For details on c_m and c_t, see (^{5,9}).

Verification of formulas (1) and (2) is made difficult by the contradictory nature of the experimental data on thermophoresis, apparently because of the impossibility of eliminating, or at least controlling, convection of the gas itself. In measurements in the Millikan condenser, thermal slip along the walls can cause convective currents independent of the action of gravity. In narrow capillaries these currents generate thermomolecular pressure (^{1,10}).

Fig. 1. Schematic of the setup

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The new method is based on observing the velocity of motion of particles in all parts of the cross section of a horizontal slit with a longitudinal temperature gradient and on eliminating the influence of convective currents by averaging the observed velocity over the cross section of the slit. The influence of particle settling is eliminated by the horizontal arrangement of the slit and additionally (in a number of experiments) by the use of a vertical electric field.

Measurement procedure. In a copper plate (Fig. 1) $30 \times 30 \times 120$ mm^3, a through slit SS, 0.98 mm high and 40 mm long, was milled. From the sides the slit was hermetically sealed with glass (2 mm thick). The ends of the slit communicated with the surrounding air through stopcocks K_1 and K_2. At the two ends of the plate, openings A and B were drilled; through them, hot and cold water was passed from two thermostats, owing to which between the ends –

a constant temperature gradient was maintained with the walls of the slit. The temperature difference was measured and controlled by a differential thermocouple t, fixed in special holes in the copper plate. With the aid of the same thermocouple it was possible to verify the strictly linear fall of temperature along the slit.

The following were studied: stearic-acid fog, vaseline (medical) oil, tobacco smoke, and MgO and NaCl smokes. An aerosol of vaseline oil was obtained by passing a stream of air through a flask with oil heated to 210—220°, entraining its vapors and passing through the capillary and tap K_1 into the slit SS, cooling on the way to its temperature. The MgO aerosol was obtained by burning magnesium wire. The NaCl aerosol was obtained by spraying a saturated NaCl solution and then passing the aerosol over the surface of concentrated sulfuric acid to absorb moisture. In all cases particles of different radii were obtained, measured by the rate of sedimentation; however, observations were made only on particles with $R = 0.3$—$0.6\,\mu$. With the aid of microscope M (eyepiece 7×, objective 10×, scale division value $105\,\mu$) with a horizontal axis directed perpendicular to the slit, the horizontal velocity of particle motion u was measured as a function of the distance z from the horizontal plane of symmetry of the slit. Illuminator O was located on the side of the slit opposite (with respect to the microscope). The illumination axis made an angle of 140° with the microscope axis. Between the illuminator and the focusing system L there was a heat-protective glass F. The entire height of the slit was in the field of view of the microscope. During the measurement the taps K_1 and K_2 were closed.

Fig. 2. $\operatorname{grad} T = 2.88$ deg/cm;
$2h = 0.5$ mm.

Table 1

Dispersing medium—air. $T = 300^{\circ}$T

Aerosol	grad T, deg/cm	u_1, μ/s	k_{exp}	Theory
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	2.48	9.3	0.72	$k_1 = 0.29$
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	2.88	11.5	0.76	$k_2 = 0.79$
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	3.85	15.3	0.76	$k_3 = 0.93$
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	4.4	16.5	0.71	$k_4 = 0.21$
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	5.06	19.6	0.74	
Oil fog ($\chi = 3.0 \cdot 10^{-1}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})			$\bar{k} = 0.74$	
NaCl aerosol ($\chi = 3.24 \cdot 10^{-2}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	3.24	9.5	0.56	$k_1 = 0.50$

Aerosol	grad T, deg/cm	u_1, μ/s	k_{exp}	Theory
NaCl aerosol ($\chi = 3.24 \cdot 10^{-2}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	3.50	9.4	0.51	$k_2 = 0.22$
NaCl aerosol ($\chi = 3.24 \cdot 10^{-2}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	4.12	13.0	0.60	$k_3 = 0.51$
NaCl aerosol ($\chi = 3.24 \cdot 10^{-2}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})	4.54	14.1	0.59	$k_4 = 0.0058$
NaCl aerosol ($\chi = 3.24 \cdot 10^{-2}$ cal $\cdot$ cm$^{-1} \cdot$ s$^{-1} \cdot$ deg^{-1})			$\bar{k} = 0.56$	
MgO smoke	2.48	8.2	0.63	
MgO smoke	3.85	12.1	0.60	
MgO smoke	4.40	14.6	0.63	
MgO smoke			$\bar{k} = 0.62$	
Tobacco smoke in a cuvette with electric field	3.0	9.4	0.60	

Aerosol	grad T, deg/cm	u_1, μ/s	k_{exp}	Theory
Tobacco smoke in a cuvette with electric field	3.3	9.5	0.55	
Tobacco smoke in a cuvette with electric field	4.0	12.4	0.59	
Tobacco smoke in a cuvette with electric field	4.6	14.0	0.58	
Tobacco smoke in a cuvette with electric field			$\bar{k} = 0.58$	

Note. The coefficients k_1, k_2, k_3, k_4 are calculated according to the formulas of Brock, Derjaguin—Yalamov, Derjaguin—Bakanov and Epstein. $\lambda/R = 0.15,\ c_m = 1.09,\ c_t = 2.16$.

In a number of experiments a cuvette was used, consisting of two copper plates insulated from one another by textolite spacers. An electric voltage was applied to the plates, compensating the weight of the charged aerosol particles, which increased the accuracy of measuring z.

The measured velocity is equal to

$$u = u_1 + u_0,$$

where u_1 is the true thermophoretic velocity (not depending on z), u_0 is the velocity of air particles, which is a function of z. From the continuity equation for steady gas flow it follows that the mean over the cross section value of $\overline{u_0(z)}$ is zero. Therefore the thermophoretic velocity can be determined by finding graphically

$$u_1 \equiv \overline{u(z)} = \frac{1}{2h} \int_{-h}^{+h} u(z)\, dz,$$

where $2h$ is the height of the slit. The measurement results are given in Table 1. For u_1 for NaCl particles we found, by measuring the time t of sedimentation of the particle from the plane of symmet-

···to the lower edge of the slit and, simultaneously, the horizontal path x of the particle during the same time. Thus $x/\tau = u(z) = u_1$ was measured directly. (By this method the thermophoretic velocity was also measured for those aerosols for which u_1 had previously been found from the graphs $u(z)$, and the results of the two methods agree satisfactorily.) The results obtained by the same method of total sedimentation, but for particles in helium, are given in Table 2. The experimental error is about 15%.

Fig. 3

Results of the measurements and their discussion. Figure 2 gives the graph $u(z)$ for the case of a fog of vaseline oil. A certain asymmetry of the graph is due to gravitational-thermal convection. Table 1 compares the values of u_1 found by graphical averaging for oil fog and MgO smoke in air with theoretical values calculated from formulas (1) and (2), and also from the formulas of Epstein (4) and Derjaguin and Bakanov (6).

Table 1 also gives the values of u_1 found by the same method in a cuvette with an electric field. As is seen from the table, the experimental values of the velocity agree satisfactorily with formula (2). According to formula (1), u_1 for vaseline oil is 2.7 times smaller than according to formula (2), and 2.5 times smaller than the experimental values (see Table 1). The data for NaCl are still more indicative; according to formula (2), $k = 0.50$, which agrees well with the experimental value $k = 0.56$, whereas according to formula (1) $k = 0.22$. Similar experiments were carried out in an He atmosphere at normal pressure. Particles of vaseline oil of radius $R = 0.4 \div 0.6\ \mu$ were studied. The results given in Table 2 agree satisfactorily with formula (2) and contradict formula (1).

Table 2

Dispersing medium—He. $T = 300^{\circ}$K, $\lambda/R = 0.38$.

Aerosol	grad T, deg/cm	u_1, μ/sec	k_{exp}	Theory
Oil fog	1.94	90	1.14	$k_1 = 0.34$
Oil fog	2.34	130	1.19	$k_2 = 1.20$
Oil fog	2.60	150	1.42	$k_3 = 1.55$
Oil fog	2.66	136	1.26	$k_4 = 0.52$
Oil fog	2.80	130	1.14	$k_1 = 0.34$
Oil fog	3.00	140	1.15	$k_2 = 1.20$

Aerosol	grad T, deg/cm	u_1, μ/sec	k_{exp}	Theory
Oil fog	–	–	$\bar{k} = 1.22$	$k_3 = 1.55$
Stearic acid aerosol	2.34	105	1.10	–
Stearic acid aerosol	2.66	132	1.22	–
Stearic acid aerosol	–	–	$\bar{k} = 1.16$	–

In Fig. 3 the curve represents the coefficient k, calculated according to theory (7) (see formula (2)), as a function of $(\varkappa_e/\varkappa_i) : (1 + 2c_t\lambda/R)$. The points taken from Tables 1 and 2 lie well on the curve and contradict formula (1). There is an even greater discrepancy between experiment and Epstein’ s formula. Within the particle-radius range $0.3 \div 0.6\ \mu$, no strong dependence of the thermophoretic velocity on R was found, in agreement with the theory of Derjaguin–Bakanov, according to which the velocity of large particles (6) is close to the velocity of small particles calculated by them earlier (11), and in contradiction to Brock’ s theory. Indeed, for $R \ll \lambda$, with diffuse reflection of molecules (11):

$$u_1 = \frac{6}{8+\pi}\frac{\eta}{\rho T}\,\text{grad}\,T. \tag{3}$$

Hence, for air at normal pressure $u_1 = 2.8$ grad T (μ/sec). In the case of NaCl particles, at $\lambda/R = 0.15$, according to the Derjaguin–Yalamov theory,

$$u_1 = k_2\frac{\eta}{\rho T}\,\text{grad}\,T = 2.6\ \text{grad}\,T\ (\mu/\text{sec}),$$

whereas according to Brock’ s formula

$$u_1 = k_1\frac{\eta}{\rho T}\,\text{grad}\,T = 1.16\ \text{grad}\,T\ (\mu/\text{sec}).$$

It should be noted that the dependence of the thermophoretic velocity on the particle sizes of tricresyl phosphate, paraffin oil, and castor oil for $R = 0.4 \div 2\ \mu$, found in the works of Rosenblatt and La Mer (12) and of Saxton and Ranz (13) with the aid of a Millikan condenser at a pressure of 760 mm Hg, was small.

The thermophoresis velocity of large particles found in works (12-14) agrees well with the velocity calculated from formula (1) for particles with $\lambda/R < 0.25$. For $\lambda/R > 0.25$, the experimental value of the thermophoresis velocity is

Fig. 4. Profile of thermal transpiration velocities grad $T = 4.0$ deg/cm, $2h = 0.5$ mm

Figure 2: Fig. 4. Profile of thermal transpiration velocities grad $T = 4.0$ deg/cm, $2h = 0.5$ mm

one and a half times greater than the theoretical value according to Brock' s formula. In works (12–14) only substances with low thermal conductivity were investigated. In work (15) the thermophoresis velocity of suspended NaCl and mercury particles ($\chi = 2.8 \cdot 10^{-2}$ cal $\cdot$ cm^{-1} $\cdot$ sec^{-1} $\cdot$ deg^{-1}) was studied. Here the discrepancy with Epstein' s theory reaches factors of 30 and 50, respectively. The results of work (15) agree well with formula (1) and differ substantially from ours. At the same time, the velocities of small ($\lambda/R \geqslant 2.5$) particles in work (15) agree with Cawood' s formula (16), and in work (14) with formula (11), i.e., the results differ by almost a factor of 3. This once again emphasizes the contradictory nature of the results obtained in the Millikan condenser.

The disagreement between our results and those of works (12–15) can be explained not only by the neglect, in the latter, of thermostatic convection, but also by the lowering of the results obtained in the Millikan condenser, because, when the particles move repeatedly along one and the same path, they reduce the temperature gradient in the gas as a result of mixing it.

Thus, experiments in which errors due to gas convection are excluded decisively refute formula (1) and confirm the Derjaguin–Yalamov formula.

Fig. 4. Profile of thermal-transpiration velocities grad $T = 4.0$ deg/cm, $2h = 0.5$ mm

Thermo-osmosis (thermal transpiration) of air in wide capillaries. From Fig. 2 (taking gravitational convection into account), in addition to the thermophoresis velocity u_1, one can find the velocity profile of the gas particles:

$$u_0(z) = u(z) - u_1. \tag{4}$$

In our experiments with closed ends of the slit, the stationary velocities u_0 were equal to $u_0 = u_2 + u_3$, where u_3 is the velocity of the thermal-transpiration flow at $\Delta p = 0$, and u_2 is the counterflow velocity caused by the thermomolecular pressure difference Δp that arises. In this case

$$\int_{-h}^{+h} u_2 dz + \int_{-h}^{+h} u_3 dz = 0. \tag{5}$$

We calculated $\overline{u_3}(z)$ on the basis of the theory of one of us (2, 17). The resulting profile $u_3(z)$, shown in Fig. 4 for the case of oil mist in air, demonstrates, in agreement with theory, the volume-distributed character of thermal slip.

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