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Motion of a Particle in a Temperature Gradient; Thermal Repulsion as a Radiometer Phenomenon*

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The dependence of the velocity of thermal repulsion of tricresyl phosphate droplets suspended in air on temperature gradient, pressure, and particle radius, a, was measured and compared with the velocities calculated from radiometer theory. Thermal repulsion is shown to be a radiometer effect. The velocity of thermal repulsion is directly proportional to the temperature gradient. The velocity of thermal repulsion at constant pressure increases with decreasing particle radius to a maximum when the mean free path, L, is about 1.5 times the radius, and then decreases. The velocity of thermal repulsion is approximately proportional to $1/P$ when $L/a<0.5$. The dependence of the force of thermal repulsion on temperature gradient, pressure, and particle radius are in agreement with the requirements of radiometer theory at high pressures. The resistance of air to the motion of tricresyl phosphate droplets is accurately given by Millikan's equation. The coefficient of slip on these droplets is 8.25×10^{-6} cm at 76-cm pressure and 30°C. The measured velocities of thermal repulsion have been compared with the theoretical values calculated from the resistance of the medium and the radiometer forces as given by Albert Einstein and by Paul S. Epstein. The numerical agreement is satisfactory in view of the approximations in the theoretical derivations and the uncertainty in the heat conductivity of the tricresyl phosphate. Thermal repulsion can be used to determine the radius of particles too small to be measured by sedimentation velocity.

INTRODUCTION

THE dust-free region or dark space which extends above a hot body in a suitably illuminated dust-filled chamber was observed by Tyndall[1] and Rayleigh.[2] Particles were carried around the chamber by convection currents, but they did not penetrate into the dark space. The dust-free region was shown to extend completely around the hot body by Aitken,[3] who attributed the repulsion of the dust particles to a greater molecular bombardment from the direction of higher temperature. The movement of the particles away from the hot body has been termed thermal repulsion.

The width of the dark space has been studied by Aitken,[3] and by Lodge and Clark.[4] Miyake[5] and Watson[6] have found empirical formulas for the dependence of the width on the pressure of the gas, the excess in temperature of the hot body over the surrounding air, the shape of the body, and the convective heat loss.

No quantitative explanation of the phenomenon exists. An approximate, but incorrect, calculation of the velocity with which particles recede from a hot body to reform the dark space after the dark space is destroyed by an air blast was made by Cawood.[7] Measurement of the velocity was possible only to order of magnitude, because of the uncertainties in the temperature gradient involved, and to the presence of convection currents. Paranjpe[8] has shown that the rate of settling of the top of a cloud of tobacco smoke was proportional to the temperature gradient in the gas.

The dark space results from a steady state in which the force of thermal repulsion is balanced against Brownian motion and the effect of convection currents, both of which tend to destroy the dark space. For a theoretical solution, it would be necessary to evaluate the force of thermal repulsion in the absence of convection, and then to calculate the flow of air using the hydrodynamic laws of motion of a viscous fluid

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[1] J. Tyndall, Proc. Roy. Inst. 6, 3 (1870).
[2] Rayleigh, Proc. Roy. Soc. 34, 414 (1882); Nature 28, 139 (1882).
[3] J. Aitken, Trans. R.S.E. 32, 293 (1884); Nature 28, 139 (1884).
[4] O. J. Lodge and J. W. Clark, Phil. Mag. 17, 214 (1884).
[5] S. Miyake, Aero. Res. Inst. (Tokyo) 10, 85 (1935).
[6] H. H. Watson, Trans. Faraday Soc. 32, 1037 (1936).
[7] W. Cawood, Trans. Faraday Soc. 32, 1068 (1936).
[8] M. K. Paranjpe, Proc. Ind. Acad. Sci. 4a, 423 (1936).

and Fourier's laws of heat conduction. The mathematical difficulties in the calculation of convective flow have been too great to allow a complete solution. Boussinesq[9] and Russel[10] have applied these laws to the calculation of convective heat transfer in the idealized case of the laminar flow of a non-viscous fluid. Their results do not agree with experiment.

The objectives of this investigation are the measurement of thermal repulsion of small particles in the absence of convection, and its identification and quantitative comparison with the theory of radiometer action.

1. RADIOMETER THEORY

A radiometer force is a force, other than that caused by convection, which acts on a body suspended in a gas which is not in thermal equilibrium. In the usual form of radiometer, the suspended body is a vane, and temperature differences are produced by radiation falling on the vane, or by conduction of heat through the gas from unequally heated boundaries.

The effect of radiation on a body suspended in a gas was first observed by Fresnel.[11] Crookes[12] showed that the force on a vane radiometer was a function of gas pressure and Reynolds,[13] that there was an optimum value of the pressure, depending on the apparatus, for which the force was a maximum.

The pressure of the gas is defined as high or low, according as the mean free path of the gas molecules is small or large compared with the radius of the particle experiencing the radiometer force.

The mechanism by which radiometric forces are produced is different at high and at low pressures, and the theoretical treatment is simplified by considering each region separately.

Knudsen[14,15] has shown theoretically and experimentally that the relations for a vane radiometer at low pressures are particularly simple. The force is directly proportional to the pressure, and is independent of the nature of the gas and of the size or shape of the radiometer vane.

The high pressure phenomenon, with which we shall be concerned, is more complicated. Early theories[16–19] led to equations which were in some cases not even in qualitative agreement with the experimental data. A result for vane radiometers, correct in order of magnitude, was first obtained by A. Einstein[20] on the basis of a simplified development in which the force resulted from a flow of heat.

He regarded the force as exerted at the edge of the vane and found the force per unit length of edge, F', on a disk at right angles to a temperature gradient, dT/dx, in the gas to be

$$F' = -\tfrac{1}{2}(PL^2/T)(dT/dx); \qquad (1)$$

L is the mean free path, P the pressure of the gas, and T, the absolute temperature. The equation predicts the experimentally found dependence of the force on the temperature gradient and the pressure, and indicates that the size or shape[21–23] of the vane influences the force. The negative sign is used because the force is in the direction of decreasing gradient; i.e., away from the hotter regions.

More rigorous derivations[24–26] have been based on Maxwell's calculation[17] of the stresses set up in an unequally heated stationary mass of gas. The calculations made for Maxwell's special type of molecule, where the force of repulsion varies inversely as the fifth power of the distance, have now been extended[27–30] to any type of molecule. Maxwell found that no stresses which depend upon the first power of the temperature gradient were set up in the body of the gas. At an unequally

[9] Boussinesq, Comptes rendus **132**, 1383 (1901).
[10] A. Russel, Phil. Mag. **20**, 591 (1914).
[11] A. Fresnel, Ann. Chim. Phys. **29**, 57, 107 (1825).
[12] W. Crookes, Phil. Trans. **164**, 501 (1874); **166**, 340 (1876); **170**, 132 (1880).
[13] O. Reynolds, Phil. Trans. **166**, 727 (1880).
[14] M. Knudsen, Ann. d. Physik **32**, 809 (1910); **34**, 823 (1911).
[15] M. v. Smoluchowski, Ann. d. Physik **34**, 182 (1911); **35**, 983 (1911).
[16] O. Reynolds, Phil. Trans. **170**, 727 (1880).
[17] C. Maxwell, Phil. Trans. **170**, 231 (1880).
[18] G. Laski and F. Zerner, Zeits. f. Physik **3**, 224 (1920); 6, 411 (1921).
[19] E. Einstein, Ann. d. Physik **69**, 241 (1922).
[20] A. Einstein, Zeits. f. Physik **27**, 1 (1924).
[21] G. J. Stoney, Sci. Trans. Roy. Soc. Dublin **1** (2), 39 (1878).
[22] Fitzgerald, Phil. Mag. **7**, 15 (1879).
[23] H. E. Marsh, J. Opt. Soc. Am. **12**, 135 (1926).
[24] P. S. Epstein, Zeits. f. Physik **54**, 537 (1929).
[25] G. Hettner and Czerny, Zeits. f. Physik **30**, 258 (1924); G. Hettner, Zeits. f. Physik **37**, 179 (1926).
[26] T. Sexl, Zeits. f. Physik **52**, 261 (1928).
[27] D. Enskog, Physik. Zeits. **12**, 58 (1911).
[28] Pidduck, Proc. Math. Soc. London **15**, 279 (1916).
[29] S. Chapman, Phil. Trans. **216**, 279 (1916); **217**, 115 (1918).
[30] J. E. Jones, Phil. Trans. **223**, 1 (1922).

heated boundary, however, there resulted a steady creep of the gas from colder to hotter regions. The velocity of thermal creep, U_s, over a body with a tangential temperature gradient, $\partial T/\partial S$, was given by

$$U_s = \frac{3}{4}\frac{\eta}{\rho T}\frac{\partial T}{\partial S}, \tag{2}$$

where ρ is the density of the gas and η its viscosity. The existence of such flow streams in the gas has been experimentally demonstrated by Gerlach and Schutz.[31] The thermal creep of the gas builds up an excess pressure over the hotter regions of the body, which pressure produces the radiometric force.

Epstein,[24] in order to calculate the force, first determined the temperature distribution resulting from the flow of heat and the boundary conditions. The hydrodynamic problem of the streaming of a gas with the creep velocity as a boundary condition was then solved for the shearing stress over the surface, and the total force found by integration. The equation found for the force, F, on a sphere of radius, a, in a gas in which a homogeneous temperature gradient exists at a large distance from the sphere was

$$F = -\frac{9\pi a H_a}{2H_a + H_i}\frac{\eta^2}{\rho T}\frac{dT}{dx}, \tag{3}$$

where H_a and H_i are the heat conductivities of the gas and the material, respectively. This equation for a sphere was derived as a preliminary to what Epstein regarded as the experimentally important case of a flat disk, which he approximated by a thin ellipsoid of revolution. By means of the relations[32] $\eta = 0.499\rho\bar{v}L$* and $\rho\bar{v}^2 = (8/\pi)P$, Eq. (3) can be brought to the form:

$$F = -17.9\frac{aH_a}{2H_a + H_i}P\frac{L^2}{T}\frac{dT}{dx}. \tag{4}$$

The derivation of the equation indicates that the force is distributed over the surface and is not an edge effect.

Epstein points out that Eq. (1) contains the implicit assumption that $H_i = 0$ for the vane. The equations can be compared if H_i is set $=0$ in (4) and the length of vane edge to $2\pi a$ in (1).

$$F = -8.95aP\frac{L^2}{T}\frac{dT}{dx}, \quad \text{Epstein;} \tag{5}$$

$$F = -3.14aP\frac{L^2}{T}\frac{dT}{dx}, \quad \text{Einstein.} \tag{6}$$

The numerical coefficient for $H_i = 0$ in Epstein's approximation for a disk becomes 8.48.

For a given gas, the product PL is independent of P. The radiometer force is, therefore, inversely proportional to P where L/a is small but directly proportional to the pressure when L/a is large.[14] Where L and a are approximately the same magnitude, the force rises to a maximum. Hettner[25] has investigated the region of intermediate pressure and shown that the force is given by the empirical equation $(1/F) = (a/P) + (P/b)$, where a and b are constants depending on the nature of the gas, the temperature, and the design of the radiometer. The first term is important at low pressures and the second at high pressures. Measurements on vane radiometers[33,34] are in qualitative agreement with Hettner's equation.

Photophoresis is a phenomenon analogous to thermal repulsion. It was first observed by Ehrenhaft.[35] Particles of the order 10^{-6} to 10^{-4} cm. in diameter floating in air were set into motion by an intense beam of light toward (negative photophoresis) or away from (positive photophoresis) the light source. Photophoresis was shown to be a radiometer phenomenon, and the theory for photophoresis at low pressures was developed by Rubinowicz,[36] Zerner,[18] and others. At high pressures, Sexl[26] and Hettner[25] derived equations which can be written

$$F = -\text{const}\,(PL^2/T)\Delta T, \tag{7}$$

where ΔT is the difference in temperature at the poles of the sphere. The values of the constant differ, that of Sexl including a factor which

[31] W. Gerlach and W. Schutz, Zeits. f. Physik **78**, 43, 418 (1932); **79**, 700 (1932).

[32] H. S. Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Company, New York, 1931), second edition, pp. 157, 102.

* Values of L in this paper were calculated from $\eta = 0.499\rho\bar{v}L$. $\bar{v}$ is the average molecular velocity.

[33] E. Bruche and W. Littwin, Zeits. f. Physik **52**, 318, 334 (1928).

[34] P. Schmudde, Zeits. f. Physik **53**, 331 (1929).

[35] F. Ehrenhaft, Ann. d. Physik **56**, 81 (1918).

[36] A. Rubinowicz, Ann. d. Physik **62**, 691 (1920); Zeits. f. Physik **6**, 405 (1921).

depends on the complexity of the gas molecules. The temperature difference ΔT is calculated from the measurements of the force.

2. RESISTANCE OF THE MEDIUM

A particle in a viscous medium moving under the influence of a constant force attains a steady

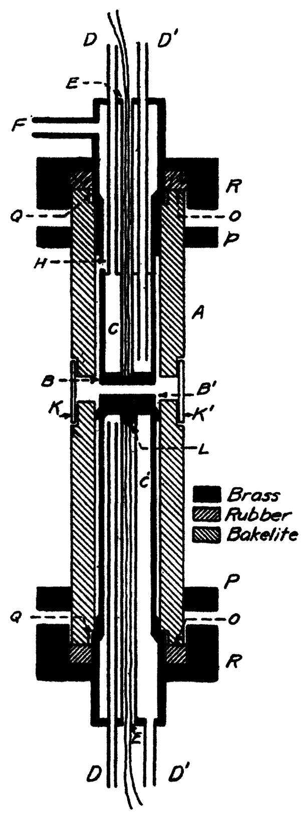

FIG. 1. Apparatus for studying velocity of aerosol particles under a thermal gradient.

velocity which is a measure of the force. We can write

$$v = ZF. \tag{8}$$

The mobility,[37] Z, of the particle depends on the material and shape of the particle, and on the medium. For a sphere in a homogeneous medium, under certain limiting conditions,[38] $Z = 1/6\pi\eta a$ and (8) is Stokes' law.[39] As the inhomogeneity of the medium becomes comparable in size with the particle,

$$Z = (1 + AL/a)/6\pi\eta a, \tag{9}$$

where A is a constant related to the coefficient of slip.[40, 41] When L/a is large, Epstein[42] has shown that

$$Z = (A + B)L/6\pi\eta a^2 \tag{10}$$

and the force is proportional to a^2. The values of the constants $(A + B)$ depend on the law of reflection for the gas molecules from the surface of the sphere. The difficult intermediate region is here again handled by an empirical formula. Thus Knudsen and Weber[43] found from the rate of damping of vibrations of glass spheres in air that

$$Z = \frac{1 + L/a(A + Be^{-Ca/L})}{6\pi\eta a}. \tag{11}$$

A similar equation was found by Millikan[41] to hold for oil drops falling through air for values of L/a from 0.1 to 134. The constants in Millikan's equation, corrected in terms of the modern value of the mean free path,[44] are $A = 1.23$, $B = 0.41$, $C = 0.88$. The equation reduces to (10) for large values of L/a and to (9) for small L/a.

From Eqs. (4) and (11), the velocity which is a measure of the radiometer force F becomes

$$v = -17.9 \frac{1}{2 + H_i/H_a} P \frac{L^2}{T} \frac{dT}{dx} \times \frac{1 + L/a(A + Be^{-Ca/L})}{6\pi\eta}. \tag{12}$$

Equation (12) should accordingly give the velocity of thermal repulsion at high pressures.

3. OUTLINE OF METHOD

Previous investigations of thermal repulsion[1–8] dealt with clouds of particles. In this research, measurements were made upon individual liquid droplets.

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[37] I. Mattauch, Zeits. f. Physik **32**, 439 (1925); Physik. Zeits. **25**, 620 (1924); Ann. d. Physik **85**, 967 (1928).
[38] R. A. Millikan, *Electrons* (+ *and* −) (University of Chicago Press, Chicago, 1935), p. 95.
[39] G. Stokes, Camb. Phil. Soc. Trans. **9**, 5 (1856).

[40] E. Cunningham, Proc. Roy. Soc. **83A**, 357 (1910).
[41] R. A. Millikan, Phys. Rev. **32**, 382 (1911); **21**, 217 (1923).
[42] P. S. Epstein, Phys. Rev. **23**, 710 (1924).
[43] M. Knudsen and S. Weber, Ann. d. Physik **36**, 981 (1911).
[44] D. Enskog, "Kinetische Theorie der Vorgange in Massig Verdonnten Gasen. Dissertation," Upsala (1917).

The dependence of the velocity of thermal repulsion upon thermal gradient, gas pressure, and droplet radius was determined by measuring the velocity with which a droplet fell under the influence of gravity in the presence and absence of a thermal gradient for a range of pressures of the surrounding gas.

In a typical experiment, droplets were produced by spraying tricresyl phosphate through an atomizer. Air containing a number of droplets was drawn into the previously evacuated observation cell. The droplets were electrically charged, and by proper manipulation of the sign and magnitude of an electrostatic potential which could be established between the end plates of the cell, the motion of a particular droplet as it settled could be slowed, stopped, or reversed.

The velocity of the droplet was calculated from 10 to 20 measurements of the time of transit of the droplet between cross hairs in the observing microscope. The droplet was returned to the starting position above the top cross hair by the electrostatic field between each measurement of the time of transit.

Observations were made first of the velocity of fall of the particle under the influence of gravity alone (sedimentation velocity, v_0), and of the velocity of fall, v_m, with several different temperature gradients established in the surrounding air at atmospheric pressure. The pressure in the observation cell was then reduced by pumping the air out slowly through a fine capillary, and the measurements repeated at a series of pressures.

From the force (mass$\times$acceleration) of gravity and v_0, the mobility Z of the droplet can be evaluated at each pressure (Eq. (8)). Since Z is a function of the droplet radius, a, the applicability of (11) was confirmed from the constancy of the a values calculated from Z at each pressure (see Table I).

At each pressure, the dependence of the excess velocity V_T caused by the temperature gradient, dT/dx, on the magnitude of the gradient was investigated. From the velocity at a standard temperature gradient at each pressure, the dependence of the velocity on pressure was determined. Finally, from a similar series of measurements on droplets of different radii, the effect of particle radius on the velocity of thermal repulsion was found.

4. EXPERIMENTAL

The observation cell consisted of two horizontal metal plates spaced 0.2351 cm apart, between which electrical and thermal gradients could be established. A beam of light illuminated the particle, the motion of which was observed with a microscope.

The cell is shown in detail in Fig. 1. The brass pole pieces, B and B', inserted in the Bakelite cylinder A, are 12 mm in diameter. The particles entered between the plates through F, the opening, H, and the annular space, 1 mm wide, between B and A. Water was circulated through the chambers C and C' through the tubes D and D'. The temperatures of the surfaces of the plates were measured[45,46] by the Cu-constantin thermocouples passing through E and soldered flush with the surfaces.

In the bottom plate, L is a brass rod 2.5 mm in diameter electrically insulated from B' by a sleeve

TABLE I. Calculation of particle radius from sedimentation velocity.

Pressure cm Hg	$10^3 v_0$	L/a	A'	$10^4 a$	Δ
		Particle 45			
76.2	35.79	0.0408	1.050	1.610	−0.008
38.8	37.59	0.0801	1.098	1.608	−0.010
16.7	43.02	0.1851	1.228	1.625	+0.007
10.3	48.93	0.303	1.378	1.635	+0.017
7.01	54.94	0.456	1.588	1.622	+0.004
75.9	35.55	0.0408	1.050	1.607	−0.011
			Average =	1.618	±0.009
		Particle 43			
76.3	16.08	0.0625	1.076	1.061	+0.002
52.0	16.69	0.0922	1.133	1.066	+0.007
23.2	18.47	0.207	1.255	1.058	−0.001
8.18	26.04	0.588	1.776	1.056	−0.003
4.45	36.91	1.080	2.523	1.054	−0.005
			Average =	1.059	±0.004
		Particle 37			
76.2	4.217	0.127	1.156	0.5257	−0.0010
39.8	4.661	0.243	1.301	0.5208	−0.0059
16.0	6.616	0.603	1.796	0.5291	+0.0024
9.50	8.979	1.02	2.421	0.5312	+0.0045
			Average =	0.5267	±0.0035

[45] A. P. Kratz and E. L. Broderick, *Heating, Piping and Air Conditioning* (1932), p. 635.
[46] W. F. Roeser and E. F. Mueller, Nat. Bur. Stand. J. Research **5**, 793 (1930).

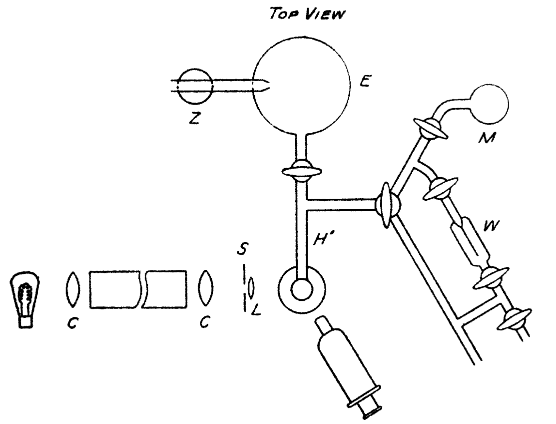

FIG. 2. Schematic view of optical components of apparatus.

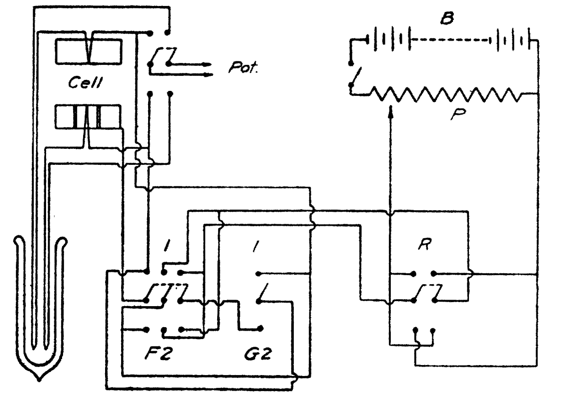

FIG. 3. Electrical components of apparatus.

of Bakelite of 0.5-mm wall thickness. This arrangement due to Fletcher[47] creates an inhomogeneous electrostatic field by means of which the particle could be centered over L whenever it drifted out of the field of view.

The light beam passed through the diametrically opposite windows, K, K'. A third window (not shown) through which the particle was observed was placed at an angle of 35° with the direction of propagation of the beam. The gum rubber washers, O, compressed in the cups, R, by screwing the latter down on the rings, P, were extruded into an annular opening Q between B and A to make a vacuum-tight seal.

The average separation of the plates, 0.2351 cm, was measured with a micrometer microscope through each of the three windows of the cell with the glass removed. The variation in separation on reassembly after cleaning the cell did not exceed 0.0005 cm.

A schematic view of the rest of the apparatus is shown in Figs. 2 and 3. The light source was a 50-cp automobile headlight bulb operated on an 8-volt transformer. An image of the filament was focused on the horizontal slit S by the condensing lens C and C', and the parallel beam formed by the lens L directed through the cell. A 55-cm long column of 1 percent $CuCl_2$ was used to filter out the longer wave-lengths.

The microscope lenses were apochromatic objective of 25-mm focal length and a $10\times$ compensated eyepiece. There were three parallel horizontal crosshairs in the focal plane of the eyepiece. The apparent separation of the outer pair at the focus of the microscope was found with a Leitz 1/100-mm stage micrometer to be 0.1390 ± 0.0005 cm. Cell and microscope were rigidly clamped together and fastened to an optical bench.

The temperature of the plates was controlled by circulating water independently through each from a large reservoir at room temperature or from any one of three thermostat-controlled baths. To avoid convection currents, the upper plate was always made the warmer one when a temperature gradient was established.[8] Ramdas and Paranjpe[48] showed by an interferometric method that the gradient in such an arrangement is linear.

The reference junctions of the thermocouples were kept at 0°C. The thermocouple e.m.f.'s, V, were measured on a L & N type K2 potentiometer to 2×10^{-7} volt, which corresponded to 0.005°C. The pole pieces were immersed in a water bath and the thermocouples calibrated at approximately one-degree intervals against a Bureau of Standards calibrated Beckman thermometer. The differences, ΔT, between each calibration temperature and the temperature T_c calculated from the equation $T_c = 2.6\times10^4$ V were plotted against V and used as a correction curve. Measured voltages were converted to temperatures by the use of the same equation and the curve. Temperature differences were precise to $\pm0.01°$ and the temperature to ±0.1°C.

The sign and magnitude of the potential differ-

[47] H. Fletcher, Phys. Rev. 4, 442 (1914).

[48] L. A. Ramdas and M. K. Paranjpe, Current Sci. 4, 642 (1936).

ence applied to the plates from the B-batteries, B, were controlled by the reversing switch R and the 1 megohm potentiometer P. The motion of the particle in the electric field[47] was controlled by the action of the switches F and G. The table below shows the electrical fields used for a negative particle; for a positive particle the signs of all potentials were reversed by R.

	Switch position		Sign of charge on		
Field	F	G	B	B'	L
(a)	1	1	0	0	0
(b)	1	2	+	−	−
(c)	2	2	−	−	+
(d)	2	1	0	0	0

The fall of a droplet was timed with the plates shorted (field (a)). The droplet was raised vertically against gravity by the application of field (b). Alternate application of field (c), which moved the particle down and sidewise toward L, and field (b) moved the particle in zigzag fashion from any point between the plates to center it over L.

The time of transit of a particle between the crosshairs was measured to the nearest 1/100 second with a Meylan Model E electric stoptimer.

Droplets were produced by spraying tricresyl phosphate from atomizer Z into bulb E with dry air filtered through glass wool, and drawn into the partially evacuated cell through H'. A droplet of the proper size was selected and an electrostatic field which just balanced it against gravity applied. This cleared the field of view of all but a few particles with the proper ratio of charge to mass for balance. The stopcocks between the manometer, M, and the cell were adjusted so that M and the cell remained connected throughout an experiment.

The time of transit of the particle selected was measured from 10 to 20 times under the action of gravity and of one or more temperature gradients. Pressure and temperature measurements were made before and after each set of time readings. The pressure in the system was reduced by evacuating the air slowly through the capillary leak W until the desired pressure was reached. During this time, it was necessary to apply fields (b) and (c) alternately with a period of approximately three seconds to prevent the particle from being swept out with the air.

An experiment on a single droplet required about six hours of continuous observation. All data and supplementary measurements were recorded by an assistant.

Each reduction of pressure took approximately 20 minutes. A steady state of the system, which was indicated by the behavior of the particle, was reached in an additional 10 minutes.

Sidewise motion of the particle when suspended with the aid of the proper electric field served to indicate when pressure equilibrium had not been attained. The same method was used to detect convection currents or leaks.

The tricresyl phosphate was a Monsanto product; $d_{30}=1.1162$, $n_d=1.5538$ at 25°C. The vapor pressure of tricresyl phosphate is less than 0.1 micron at 100°C.[49] This was the principal reason for its selection.

5. RESULTS AND DISCUSSION

Increasing Brownian motion of the small particles and high velocities of the large particles limited observations to the particle radius range 0.4×10^{-4} to 1.6×10^{-4} cm. Measurements were made over the pressure range 760 to 45 mm Hg, corresponding to values of L/a from 0.04 to 1.5. The precision of the time measurements can be estimated from the data of Table II for the times of fall of a particle of 0.82-μ radius under the influence of gravity at various pressures.

TABLE II. Time of fall under gravity at various pressures. Particle No. 48, radius 0.820×10^{-4} cm.

Pressure (cm Hg)	76.0	49.8	29.6	16.5
Time (sec.)	14.01	13.66	12.68	10.60
	.05	.55	.11	.46
	.35	.92	.27	.66
	.14	.70	.63	.67
	.25	.56	.63	.45
	.09	.89	.42	.87
	.25	.40	.44	.40
	.13	.74	.53	.57
	.53	.65	.36	.75
	.39	.53	.56	.36
	.28	.91	.05	.69
	.46	.62	.45	.46
	.18	.44	.13	.64
	.15	.71	.13	.67
Average	14.23	13.66	12.38	10.59
a.d.	0.13	0.13	0.18	0.12
A.D. %	0.24	0.25	0.39	0.30

[49] F. H. Verhoek and A. L. Marshall, J. Am. Chem. Soc. 61, 2737 (1930).

The dependence of v_0, the velocity of fall in a gravitational field, upon the pressure provides a test of the applicability of Eq. (11). If we substitute for the force, F,

$$F = mg = (4/3)\pi a^3(\rho' - \rho), \quad (13)$$

Eq. (11) can be written

$$a^2 = 9v\eta/2(\rho' - \rho)gA', \quad (14)$$

where

$$A' = 1 + (L/a)(A + Be^{-Ca/L}). \quad (15)$$

Here m and ρ' are the mass and density of the particle, and g is the acceleration of gravity.

TABLE III.

Pressure cm Hg	L/a	A'	$\frac{300}{T}\frac{dT}{dx}$ °C/cm	v_s/A' cm/sec. $\times 10^3$	Force $=6\pi\eta a v_s/A'$ dynes $\times 10^{10}$
Particle 37, radius 0.527 μ					
76.2	0.126	1.156	13.5	1.12	2.04
39.8	0.243	1.301	12.4	2.48	4.53
16.0	0.603	1.796	14.7	5.97	10.9
9.50	1.015	2.421	12.2	8.68	15.9
Particle 43, radius 1.059 μ					
76.3	0.0621	1.076	12.3	1.12	4.14
52.0	0.0922	1.113	12.6	1.68	6.22
23.2	0.207	1.255	10.0	3.98	14.7
8.18	0.588	1.776	9.74	12.8	47.4
4.45	1.08	2.523	9.62	18.5	68.5
Particle 45, radius 1.620 μ					
76.2	0.0408	1.050		1.16	6.55
38.8	0.0801	1.098	8.14	2.18	12.3
16.7	0.185	1.228	10.9	5.72	32.3
10.3	0.303	1.378	9.11	10.2	57.6
7.01	0.456	1.588	9.45	16.0	90.5
Particle 48, radius 0.819 μ					
76.0	0.0821	1.101	8.61	1.14	3.26
49.8	0.126	1.154	9.74	1.71	4.88
29.6	0.211	1.260	9.56	2.94	8.39
16.5	0.378	1.480	6.40	6.89	19.6
7.73	0.807	2.105	8.61	11.8	33.7
Particle 49, radius 0.408 μ					
76.3	0.162	1.199	13.3	1.15	1.64
			19.4	1.15	1.64
15.3	0.817	2.119	12.0	5.94	8.45
			18.4	6.07	8.65
8.18	1.53	3.232	15.2	8.32	11.9
Particle 50, radius 1.306 μ					
76.3	0.0515	1.063	9.49	1.15	5.21
			15.0	1.13	5.12
33.3	0.118	1.145	9.03	2.41	10.9
			17.4	2.42	11.0
20.1	0.196	1.241	8.56	4.18	18.9
			16.4	4.27	19.3
12.7	0.311	1.389	8.65	7.92	35.8
			18.1	8.38	37.8
8.21	0.481	1.611	7.08	13.0	58.8
			15.4	13.4	60.7

The velocities v_{01}, v_{02} at the different pressures were plotted against the mean free path, L, and the velocity v_{00} at $L=0$ found by a short and almost linear extrapolation. To obtain a preliminary value of the radius, a_1, A' was set equal to unity and $v=v_{00}$ in Eq. (14). This value of a_1 was then used in A' and a better value, a_2, calculated at $v=v_{01}$ and substituted in turn in A'. The process was repeated until a constant value of the radius was obtained. The magnitude of the difference between a_1 and the final value of the radius can be estimated from the values of A' at atmospheric pressure (Table III). In general, no more than two repetitions were required. Typical results of this calculation for the same particle at various pressures are shown in Table I.

The calculated radii were constant within the limits of precision of the time measurements (see Tables I, II). Equation (11) with the constants of Millikan[41] is, therefore, considered to apply to these measurements. It follows from the equality of A values that the coefficient of slip on tricresyl phosphate is the same as for Millikan's oil drops. The coefficient of slip, ζ, is given by $\zeta = AL$ and equals 8.25×10^{-6} cm at atmospheric pressure at 30°C.

Particle No. 45 was one of those for which v_0 was remeasured at atmospheric pressure and room temperature as a check on evaporation. After six hours of observation, the radius remained unchanged within the experimental error.

Velocity in a Temperature Gradient

Most measurements were made with temperature gradients of 8° to 20° per cm; a few were as high as 50° per cm. The absolute temperature of the system, T, was taken as the average temperature between the plates.

The gravitational and thermal forces acted in the same direction. The velocity, v_T, which measures the effect of the thermal gradient is the difference between the measured velocity, v_m, and v_0. The velocity of thermal repulsion, v_T, was found to be proportional to $(1/T)(dT/dx)$ for a given particle at constant pressure.

$$v_T = v_m - v_0 = (K/T)(dT/dx). \quad (16)$$

The slope, K, was found to be a function of particle size (Fig. 4) and pressure (Fig. 5). The figures are a plot of v_T against dT/dx corrected to

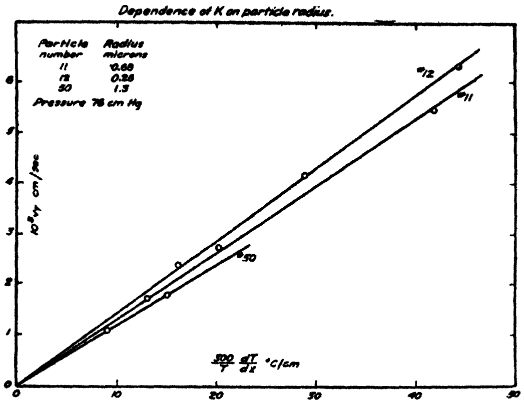

FIG. 4. Dependence of thermal velocity upon temperature gradient and particle size.

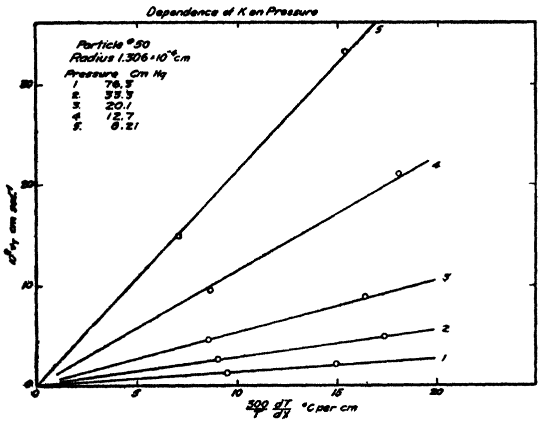

FIG. 5. Dependence of thermal velocity for a fixed size upon pressure and thermal gradient.

a standard temperature of 300°K. The dependence of v_T on T at constant dT/dx was not investigated over large variations in T. Over a range of 10° (25°–35°C) the change in v_T was in the direction demanded by (1) and (3). If the velocity, v_m, of a droplet is measured in two different temperature gradients, the velocity, v_0, can be calculated from (16). The calculated v_0 can be compared with the measured sedimentation velocity of droplets large enough to settle with a measurable rate of fall. This has been done for particle No. 50 (0.8μ) shown in Fig. 5.

Pressure cm Hg	v_0 cm/sec.$\times 10^3$ calculated	observed
76.3	23.55	23.53
33.3	25.55	25.59
20.1	27.64	27.64
12.7	30.28	31.33
8.21	36.16	36.58

Brownian motion obscures the sedimentation of droplets of density $\simeq 1$ when the radius is 0.3μ or less, and the droplets apparently do not settle. It was found, however, that a value of v_0 could be calculated from measured velocities under different temperature gradients from (16), even when the droplets were less than 0.3μ in radius. In one case, the droplet radius calculated by using such a value of v_0 in (14) was 0.05μ.

An important application of (16), therefore, is the determination of radii of droplets too small to be measured by sedimentation velocity.

The lower limit of size and the precision of the suggested method have not been investigated. Since v_0 is calculated from a small difference between two large measured velocities, its precision decreases rapidly with decreasing droplet radius.

The pressure range in which this application is valid will be discussed below.

Dependence of Velocity on Pressure

At constant radius and constant dT/dx, the velocity with which a particle moves in a temperature gradient is a function of the pressure, increasing with decreasing pressure in the range of these measurements. We define a velocity v_s by the equation

$$v_s = \frac{1/300}{(1/T)(dT/dx)} v_T, \tag{17}$$

in order to compare velocities under conditions of constant gradient. The velocity v_s is then equivalent to the velocity with which a particle moves in a temperature gradient of 1° per cm at a temperature of 300°K.

In Fig. 6, v_s/A' is plotted against $1/P$ from the data in Table III. The values of v_s/A' for all the particles at $1/P = 0.013$ (atmospheric pressure) are represented by a single circle on the diagram.

The lines I and II are slopes calculated from Eqs. (4) and (6). The thermal conductivities used in (5) were $H_a = 0.000059$ for air,[50] and $H_i = 0.00048$ cal./cm^2/sec. for a temperature gradient of 1°C per cm for the particle. H_i was calculated from the empirical equation obtained

[50] E. O. Hercus and D. M. Sutherland, Proc. Roy. Soc. **145**, 599 (1934).

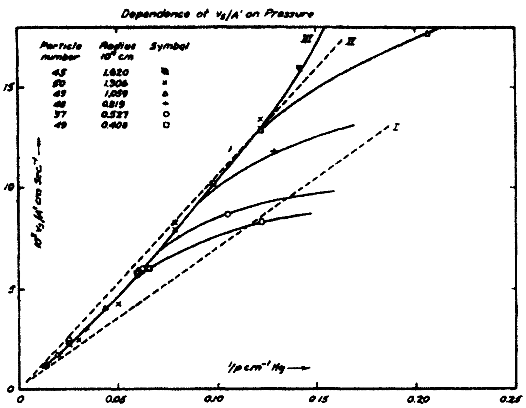

FIG. 6. Dependence of thermal velocity function Vs/A' upon reciprocal of total pressure.

by Smith.[51] The accuracy of the value is probably not better than ± 20 percent; it introduces an uncertainty in the slope of I of approximately the same magnitude. In addition, the applicability of a bulk value of H_i to small droplets is questionable.

Epstein,[42] in the derivation of (10), examines the possible types of reflection of gas molecules from a small sphere. He finds that the value of $(A+B)$ depends on the heat conductivity of the sphere and concludes that oil drops act like perfect non-conductors when $L/a \ll 1/35$ and like perfect thermal conductors when $L/a \gg 1/35$. The constants found by Millikan for (11) are in agreement with this conclusion.

The experimental slope, and therefore the force, differs from I (Epstein) by a factor of about 2. Differences of the same magnitude were found by Gerlach and Schutz.[31] Their experimentally measured forces on a vane radiometer are about half as large as the theoretical forces calculated from Epstein's equation. The agreement with II (Einstein) should be regarded as fortuitous, since the derivation of the equation results from a highly simplified model.

The experimental points do not fall on a straight line as required by (4) and (6), but exhibit a slight upward curvature. Curves similar to III for a vane radiometer in a temperature gradient have been found by Bruch and Littwin[52] and by Fredlund.[53]

[51] J. F. D. Smith, Ind. Eng. Chem. 22, 1246 (1930).
[52] E. Bruch and W. Littwin, Zeits. f. Physik 67, 333 (1931).
[53] E. Fredlund, Phil. Mag. 26, 987 (1938).

In view of the uncertainty in H_i and the assumptions and approximations made in the derivation of (1) and (3), the agreement between these equations of radiometer theory and the present experiments on thermal repulsion is satisfactory.

The curves for small particles deviate from III at higher pressures than do the curves for large particles. The nature of the deviations can be more clearly seen from Fig. 7 where v_s/A' is plotted against L/a for the same particles. The slopes of the curves in Fig. 7 begin to decrease rapidly at values of $L/a \simeq 0.5$.

The transition from the high pressure to the low pressure type of radiometer force occurs in this region, and the velocity of thermal repulsion approaches a maximum. The velocities of the particles used in these experiments became too high to measure in this apparatus before the maximum was reached.

It should be noted that v_T is proportional to dT/dx in the intermediate as well as in the high and low pressure regions, so that the change in slope with pressure shown in Fig. 6 constitutes no limitation on the applicability of (16) to the measurement of particle size at any particular pressure.

Dependence of v_s on Particle Radius a

Case I. $L/a<0.5$: Equation (5) shows that the radiometer force, F, is proportional to the particle radius. The mobility, Z, contains the factor a in the denominator. The velocity, which is given by $v=ZF$, is, therefore, independent of a, except

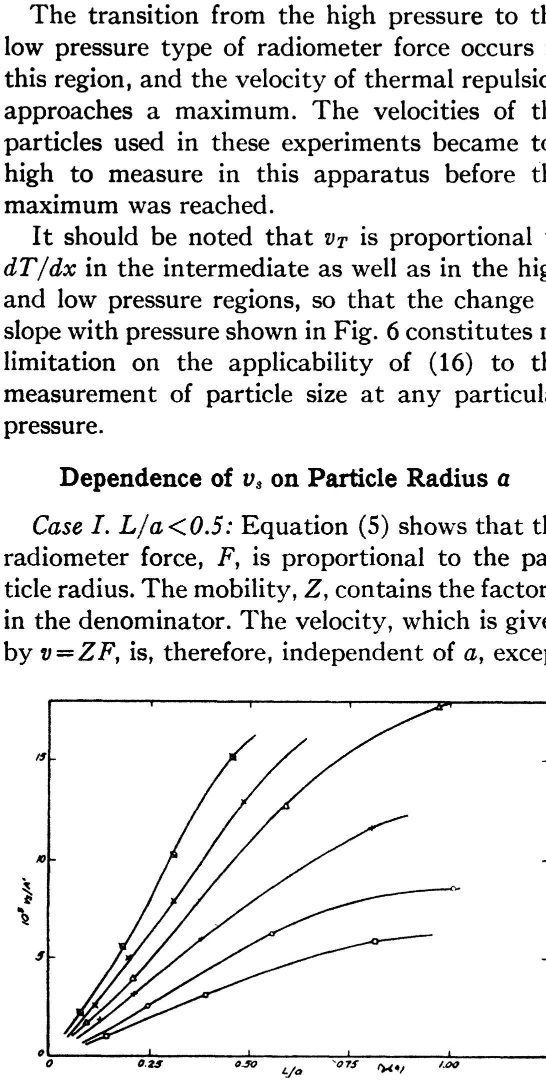

FIG. 7. Dependence of thermal velocity function Vs/A' upon L/a the ratio of the mean free path of gas molecule to radius of aerosol particle.

insofar as a enters in the A' factor of Z. At a given pressure (12) can be written $v_s = c_1 A'$, where the value of c_1 changes with pressure but is independent of a. This is the range[14] in which (9) is valid, and $A' = 1 + AL/a$. Then

$$v_s = c_1 + c_1 LA/a \tag{18}$$

and v_s should be a linear function of $1/a$. This is confirmed experimentally by the constancy of v_s/A' at atmospheric pressure (Table III).

Under the same conditions of pressure and temperature gradient, the velocity of thermal repulsion is greater for smaller particles. A' and, therefore, v_s, increased 15 percent as the radius decreased from 1.6 μ to 0.4 μ at atmospheric pressure.

Case II. $L/a > 0.5$: For particles less than 1.3 μ in radius at atmospheric pressure, or for larger particles at reduced pressures, L/a becomes greater than 0.5. In this range c_1 is no longer independent of a. It can be seen from Fig. 6 that, at pressures where $1/P > 0.06$ ($P < 15$ cm), the values of v_s/A' at a given pressure are greater for large particles than for small ones, i.e., c_1 decreases with decreasing particle size. The velocity of thermal repulsion now depends on the relative rates at which c_1 and A' change with pressure for each particle size.

The effect of reducing the pressure to values where $L/a > 0.5$ is shown in Fig. 8. Curves II to V were calculated from v_s/A' values taken from Fig. 6. The circles in Fig. 8 are measured points, the triangles are interpolated and the crosses are extrapolated points on the curves of Fig. 6. From Fig. 8, the maximum velocity of thermal repulsion is attained at any given pressure when the radius of the particle is approximately one and one-half times the mean free path of the impinging gas molecules at that pressure ($L/a \simeq 1.5$). By the same token, the pressure which yields the maximum repulsive velocity for a given particle radius is that pressure for which the mean free path is one and one-half times the particle radius.

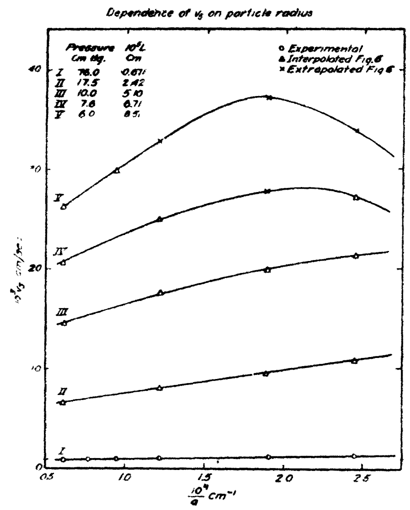

FIG. 8. Dependence of thermal velocity of aerosol particle upon the reciprocal of the radius of the particle for different total pressure or mean free paths of gas molecules.

6. APPLICATIONS OF THERMAL REPULSION

Aitken[3] produced a dust-free atmosphere by drawing air slowly through a channel across which a temperature gradient existed. Watson[6] placed microscope cover slips on the sides of a narrow channel, and deposited dust particles for microscopic and chemical analysis upon them by thermal repulsion.

An arrangement in which air was drawn through the annular space between two concentric pipes, the inner one of which was heated by steam, was employed by Bancroft.[54] He found that the air was effectively cleared of suspended particles, but at rates of flow too small for his purpose. Blacktin[55] has invented an apparatus permitting larger rates of air flow.

The determination of the size of small particles from the velocity of thermal repulsion has been suggested above.

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[54] W. D. Bancroft, J. Phys. Chem. **24**, 421 (1920).
[55] S. C. Blacktin, J. Soc. Chem. Ind. **58**, 334 (1940); **59**, 153 (1940).