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Comment on "Measurements of the temperature dependent diffusion coefficient of nanoparticles in the range of 295–600 K at atmospheric pressure" by V.Y. Rudyak, S.N. Dubtsov, A.M. Baklanov

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ABSTRACT

In a recent paper in this journal, Rudyak, Dubtsov, and Baklanov (2009) presented results of measurements of the penetration of nanoparticles with diameters from 3.5 to 84 nm at temperatures from ~300 to 600 K through a set of wire screens, from which they inferred diffusion coefficients. They argued that the formulation typically used for C, the Cunningham correction that accounts for non-continuum effects on the diffusion of nanoparticles, is not valid for temperatures greater than ~300 K, and they proposed a modification of this formulation which depends on both temperature and particle size. It is shown here that this modification produces unphysical results in that it yields negative values of the momentum accommodation coefficient. A likely reason for their results is that they used a polydisperse size distribution, for which the main contribution to the measured penetration would be from particles at sizes far from those attributed to them.

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1. Introduction

In a recent paper in this journal Rudyak, Dubtsov, and Baklanov (2009) presented results for the diffusion coefficient D of nanoparticles of WO_x (where x is near 2.9) and NaCl in air and of Pt in N_2. Diameters of the particles d_p ranged from 3.5 and 84 nm and temperatures T from ~300 to 600 K; the pressure was near atmospheric pressure. Diffusion coefficients were determined from measured values of the penetration P of particles through a set of wire screens. A total of 76 data were presented (Table 1), with standard errors, determined from the repeatability of measurements, varying mostly between 5% and 20%.

Values of the Knudsen number Kn, defined as the ratio of twice the mean free path λ to d_p ($Kn \equiv 2\lambda/d_p$), ranged from 1.5 to 75, implying that the particles were in the transition and kinetic regimes, and thus that momentum transport between the gas and the particles was partly or predominantly through molecular collisions rather than continuum drag. Values of the C, the Cunningham (1910) correction for non-continuum effects, defined by

$$C \equiv \frac{3\pi\mu d_p D}{kT}, \tag{1}$$

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Table 1
Nanoparticle diameters d_p, temperatures T, and diffusion coefficients D presented by Rudyak et al. (2009), and values of the Cunningham correction C and Knudsen number Kn calculated as $C=3\pi d_p \mu D/(kT)$ and $Kn=2\lambda/d_p$, respectively, where λ is the mean free path and μ the dynamic viscosity of the gas.

Particle	d_p (nm)	T (K)	$10^5 D$ ($cm^2 s^{-1}$)	Kn	C	Used in Fig. 2?
WO_x in air	3.5	294.7	476 ± 107	38	71.0 ± 16	Y
		325.2	814 ± 52.2	43	118 ± 7.6	Y
		367.2	1210 ± 77.3	49	170 ± 11	
		417.2	1530 ± 166	58	207 ± 23	Y
		459.6	1890 ± 130	65	249 ± 17	Y
		517.8	2450 ± 214	75	312 ± 27	Y
	4.4	296	297 ± 24.3	30	55.7 ± 4.6	Y
		313.2	427 ± 32.4	32	78.8 ± 6.0	Y
		338.2	528 ± 47.5	36	95.3 ± 8.6	
		379.3	533 ± 49.1	41	93.2 ± 8.6	
		401.5	594 ± 14.1	44	102 ± 2.3	
		438.1	745 ± 24.2	49	125 ± 4.1	
		483.2	901 ± 70.6	55	147 ± 12	
		514.2	1040 ± 86.3	59	167 ± 14	Y
		573.5	1320 ± 127	68	206 ± 20	Y
	6.2	295.16	141 ± 14.0[a]	21	37.3 ± 3.7	Y
		334.16	195 ± 32.7[a]	25	49.8 ± 8.4	
		384.16	269 ± 87.5[a]	29	66.0 ± 22	
		442.16	355 ± 68.1[a]	35	84.8 ± 16	
		511.16	449 ± 51.5[a]	42	102 ± 12	Y
		565.16	540 ± 83.0[a]	47	119 ± 18	Y
		613.16	734 ± 104[a,b]	52	158 ± 22	Y
	7.6	298	87.0 ± 3.27	18	28.1 ± 1.1	Y
		319.2	99.1 ± 3.33	19	31.4 ± 1.1	Y
		366.2	117 ± 8.11[c]	23	35.7 ± 2.5	
		422.2	157 ± 15.1[c]	27	46.0 ± 4.4	Y
		514.2	255 ± 35.9	34	70.7 ± 10	Y
		566.2	398 ± 26.5	39	107 ± 7.2	Y
		613.2	456 ± 31.0	42	120 ± 8.2	Y
	8.7	293.7	62.1 ± 5.80	15	23.1 ± 2.2	Y
		314.2	73.9 ± 11.1	16	26.9 ± 4.0	Y
		354.7	99.4 ± 2.49	19	35.0 ± 0.88	
		408.2	124 ± 14.9	23	42.0 ± 5.1	Y
		461.2	172 ± 14.0	26	56.3 ± 4.6	Y
		508.2	211 ± 22.8	30	67.2 ± 7.3	Y
	10.0	296.5	56.2 ± 3.90	13	23.9 ± 1.7	Y
		310.4	61.3 ± 2.81	14	25.8 ± 1.2	Y
		335.5	70.7 ± 2.27	15	29.1 ± 1.4	
		367.2	79.2 ± 4.33	17	31.8 ± 1.7	
		416.2	103 ± 13.9	20	39.9 ± 5.4	Y
		467.2	148 ± 3.04	23	55.5 ± 1.1	Y
		508.2	171 ± 18.8	26	62.6 ± 6.9	Y
		546.2	197 ± 12.6	28	70.7 ± 4.5	
		583.2	240 ± 17.0	30	84.5 ± 6.0	Y
		625.2	275 ± 14.7	33	95.0 ± 5.1	Y
Pt in N_2	6.3	297.36	132 ± 4.35	21	33.9 ± 1.1	Y
		334.56	169 ± 18.3	24	42.0 ± 4.6	
		386.16	266 ± 45.8	29	63.5 ± 11	
		438.16	320 ± 27.4	34	73.8 ± 6.3	
		473.16	372 ± 49.5	37	83.9 ± 11	Y
		538.16	459 ± 21.7	43	99.9 ± 4.7	
	18	297.2	18.4 ± 2.06	7.3	13.5 ± 1.5	Y
		327.2	27.1 ± 1.47	8.2	19.4 ± 1.1	Y
		366.7	33.8 ± 1.52	9.4	23.4 ± 1.1	
		418.2	47.9 ± 4.95	11	32.0 ± 3.3	Y
		470.2	60.9 ± 3.67	13	39.3 ± 2.4	Y
		533.9	78.3 ± 4.00	15	48.8 ± 2.5	
		597.6	96.8 ± 3.09	17	58.4 ± 1.9	
	35	297.2	4.67 ± 0.798	3.8	6.67 ± 1.1	Y
		299.2	7.1 ± 0.464	3.8	10.1 ± 0.66	Y
		341.7	9.2 ± 2.05	4.5	12.7 ± 2.8	
		352.5	7.92 ± 1.23	4.6	10.8 ± 1.7	
		385.2	11.7 ± 2.85	5.2	15.5 ± 3.8	
		407.7	11.4 ± 2.54	5.5	14.9 ± 3.3	Y
		453.2	16.6 ± 1.17	6.3	21.1 ± 1.5	Y
		455.2	19.9 ± 5.03	6.3	25.2 ± 6.4	Y
		504.2	21.4 ± 7.20	7.2	26.3 ± 8.9	

Table 1 (*continued*)

Particle	d_p (nm)	T (K)	$10^5 D$ ($cm^2 s^{-1}$)	Kn	C	Used in Fig. 2?
		553.2	25.9 ± 1.46	8.0	31.1 ± 1.8	
NaCl in air	84	289.9	1.03 ± 0.139	1.5	3.71 ± 0.50	Y
		323.2	1.26 ± 0.424	1.8	4.40 ± 1.5	Y
		371.5	1.91 ± 0.114	2.1	6.41 ± 0.38	
		425.9	2.61 ± 0.343	2.5	8.43 ± 1.1	Y
		479	3.09 ± 0.250	2.8	9.66 ± 0.78	
		529.5	3.67 ± 0.316	3.2	11.2 ± 0.96	
		580.1	4.28 ± 1.01	3.6	12.7 ± 3.0	Y
		615.1	4.92 ± 0.819	3.9	14.3 ± 2.4	Y

Some obvious typographic errors were corrected as noted.
[a] Exponent of D changed from -2 to -3.
[b] Exponent of standard deviation of D changed from -2 to -3.
[c] Exponent of D changed from -4 to -3.

where μ is the dynamic viscosity of the gas, ranged from ~4 to ~300, respectively, up to more than 2.5 times those expected according to the expression (Knudsen & Weber, 1911) that is typically used, and from which Rudyak et al. determined particle sizes from diffusivity measurements:

$$C = 1 + A\,Kn + Q\,Kn \exp\left(\frac{-b}{Kn}\right), \tag{2}$$

with A=1.257, Q=0.4, and b=1.1. To account for the temperature dependence of their diffusion coefficients, Rudyak et al. noted that the values of A, Q, and b that are typically used were determined at temperatures near room temperature, and they proposed an *ad hoc* formulation in which A and Q each vary as a power law in T with exponent that depends on particle diameter:

$$(A+Q) = (A+Q)_0 \left(\frac{T}{T_0}\right)^j, \tag{3}$$

with $(A+Q)_0$=1.657 and T_0=295, where j is ~1.6 for particles with diameters less than ~3.5 nm and abruptly decreases to near unity for particles with diameters greater than ~4 nm. Thus, at 600 K, for instance, $(A+Q)$ would equal 5.0 for particles with $d_p < 3.5$ nm and 3.5 for particles with $d_p > 4.5$ nm.

The formulation for C given by Eq. (2) is an empirical one introduced by Knudsen and Weber (1911) as an interpolation formula to merge the correct limits for large and small Kn. This formulation can be rewritten and expanded for values of Kn greater than unity as

$$C = 1 + (A+Q)Kn - Q\,Kn\left[1 - \exp\left(\frac{-b}{Kn}\right)\right] \approx (A+Q)Kn + (1-Qb) + \frac{Qb^2}{2Kn} + \cdots; \tag{4}$$

thus as Kn increases, C approaches a constant times Kn. In this so-called kinetic regime, which contains most of the measurements of Rudyak et al., the diffusion coefficient can be written as

$$D \approx \frac{2\lambda kT(A+Q)}{3\pi\mu d_p^2}, \tag{5}$$

where the mean free path λ is related to the dynamic viscosity μ of the gas by (Willike, 1976)

$$\lambda = \frac{\mu}{\rho\bar{c}\phi}, \tag{6}$$

where ϕ is a constant near 0.5 that depends on the interactions between molecules of the gas (Kennard, 1938), ρ is the mass density of the gas, and $\bar{c}$ is the mean molecular velocity, equal to $[8kT/(\pi m)]^{1/2}$, m being the mass of a gas molecule. The expression for D given above can therefore be written (assuming an ideal gas) as

$$D \approx \frac{(A+Q)}{3\phi} N_{Av} \left(\frac{m}{2\pi}\right)^{1/2} \frac{(kT)^{3/2}}{p} \left(\frac{1}{d_p^2}\right), \tag{7}$$

where N_{Av} is Avogadro's number. Consequently, for fixed $(A+Q)$, D should vary inversely as the square of d_p and directly as the 1.5 power of T. Additionally, for all other factors being the same, diffusion coefficients in N_2 should be nearly the same as those in air, being only ~2% less due to the mass of its molecules being smaller than those of air by ~3.5%.

2. Analysis

To investigate whether the data support this relationship, the 76 diffusion coefficients presented by Rudyak et al. (2009) were sorted by temperature (Fig. 1) and 47 were placed into bins not more than 20 K wide at temperatures near 295 K (11 data), 320 K (7 data), 415 K (7 data), 460 K (7 data), 510 K (6 data), 570 K (5 data), and 620 K (4 data) and plotted against particle diameter (Fig. 2). Dry NaCl particles are probably cubic rather than spherical, and thus the diameters determined from Eq. (2) differ from mobility diameters by a shape factor; however, this factor probably differs from unity by only ~10–15%, and this effect is omitted from further consideration. The graphs in Fig. 2 show that the data are consistent with the expected functional dependence on d_p. All of the diffusion coefficients are graphed against temperature in Fig. 3, in which several features are evident. First, the 6.2 nm WO_x particles and the 6.3 nm Pt particles have very nearly the same diffusion coefficients over the entire range of temperatures considered. This would imply that the interaction of air with WO_x and N_2 with Pt are nearly the same for these particles (i.e., the momentum accommodation coefficients, which are defined below, are the same). Second, the temperature dependence appears to be somewhere between a 1.5 and a 2.0 power, although the value is not constant over the entire temperature range and the scatter in the data make it difficult to argue for a precise value. However, even if the data follow the functional dependence on d_p and T given by Eq. (7), it does not necessarily follow that they yield the value of the coefficient given there.

To investigate whether or not this is the situation, I present the data as $C \equiv 3\pi d_p \mu D/(kT)$, a dimensionless quantity characterizing the diffusion coefficient, vs. $Kn \equiv 2\lambda/d_p$, a dimensionless quantity characterizing particle size, in Fig. 4. (Values of the mean free path in air and N_2 as a function of temperature were determined from viscosity as above, the viscosity being fitted as a power law in T with exponent 0.70 for N_2 and 0.72 for air; for T between 300 and 700 K these fits agree with the data of Matthews, Thomas, Duffy, and Smith (1976) to within ~1.5%, well within the uncertainties of the present data.) Clearly values of C as a function of Kn do not lie on a single curve, which would imply that values of A and Q

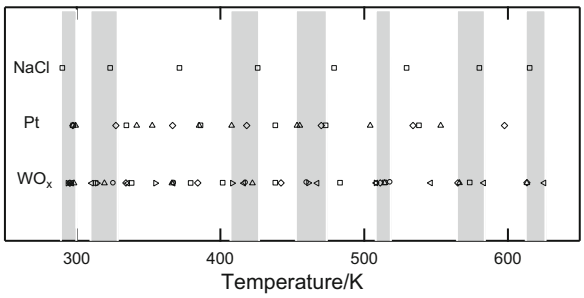

Fig. 1. Temperatures at which measurements of Rudyak et al. (2009) were conducted, and temperatures ranges (shaded regions) into which data were sorted for presentation in Fig. 2.

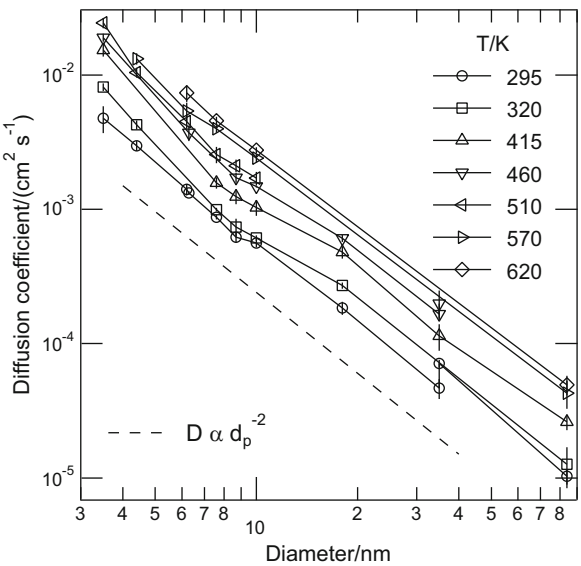

Fig. 2. Diffusion coefficients D measured by Rudyak et al. (2009) sorted into seven temperature ranges not more than 20 K wide as a function of particle diameter d_p. Dashed line shows D inversely proportional to the square of d_p.

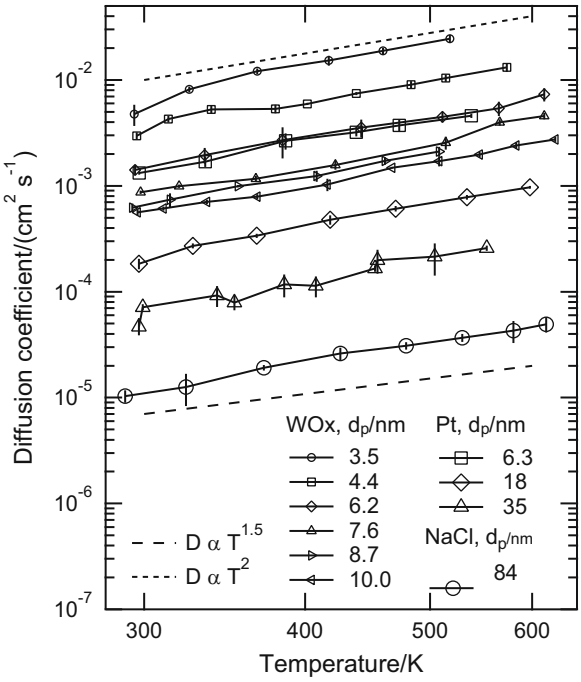

Fig. 3. Diffusion coefficient D as a function of temperature T for data of Rudyak et al. (2009) for particles of various diameters of WO_x (where x is near 2.9) and NaCl in air and of Pt in N_2. Also shown are power law dependencies of D as a function of temperature with exponents 1.5 and 2.

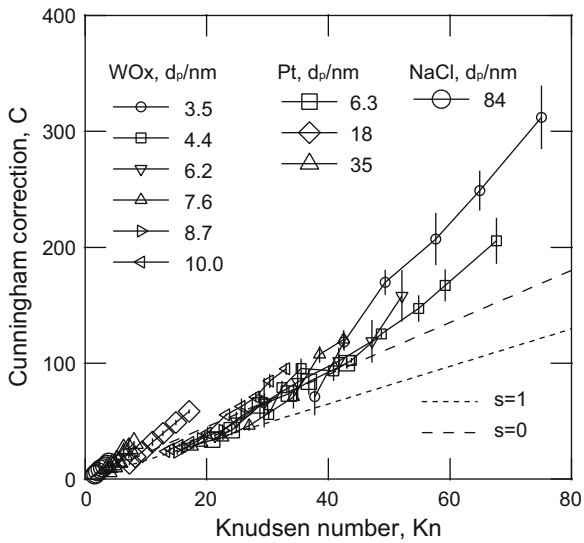

Fig. 4. Cunningham factor C, defined as $C=3\pi d_p \mu D/(kT)$, where D is the diffusion constant of the nanoparticle with diameter d_g in a gas with viscosity μ at temperature T, as a function of Knudsen number Kn, defined by $Kn=2\lambda/d_p$, where λ is the mean free path, both calculated from data of Rudyak et al. (2009) for nanoparticles of various diameters of WO_x (where x is near 2.9) and NaCl in air and of Pt in N_2. Also shown are values of C given by Eq. (2) for accommodation coefficient s equal to 0 and equal to unity.

are not constant over the conditions investigated. Data at higher temperatures exhibit greater deviation from a linear relationship between C and Kn for $Kn \gg 1$ than those at lower temperatures. To account for these discrepancies, Rudyak et al. proposed that $(A+Q)$ depends on temperature according to a power law whose exponent depends on particle size, as discussed above.

According to the conventional paradigm (Epstein, 1924), a certain fraction s of the gas molecules that collide with a surface (e.g., the particle) accommodate to that surface (i.e., remain at the surface for some time) and are later emitted

diffusely with no preferred direction (and thus provides a net transfer of tangential momentum to the surface), with $1-s$ being reflected specularly; s, called the accommodation coefficient for momentum, lies between 0 and 1 inclusive. The value of $(A+Q)$ is equal (Epstein, 1924) to $36\phi/(8+\pi s)$, where ϕ is near 0.5, and thus lies between 1.62 for full accommodation, $s=1$, and 2.25 for no accommodation, $s=0$ (the value 1.657 implies $s\approx 0.9$); these limits are shown in Fig. 4 by dotted and dashed lines, respectively. The formulation proposed by Rudyak et al. would imply that s depends on temperature, but further that s would be <0 over a wide range of temperatures and particle sizes under consideration; e.g., for $T>360$ K for $d_p=3.5$ nm and for $T>400$ K for $d_p>5$ nm. Additionally, the momentum accommodation coefficient in that formulation depends also on particle size; the consequences of this size dependence are discussed below.

3. Discussion

Rudyak et al. disparage the results of Epstein (1924) and others who presented expressions for the Cunningham factor based on gas kinetic arguments, stating that such formulae are "practically semi-empirical because they include accommodation coefficients" which are functions of the material of the particles and the type of gas. They also stated (without justification) that the accommodation coefficients depend on temperature and on the size and form of the particles. Although it is generally accepted that the momentum accommodation coefficient depends on the type of gas and the material of the particles, and that it may depend on temperature, there is no physical basis for the assertion that it depends on the size of the particles, as this would require that the nature of the collision of the gas molecule with the surface of a particle depends on the particle size. For a gas molecule with diameter $\sim$0.3 nm and particles more than an order of magnitude larger, such a dependence seems unlikely, as the interaction of the gas molecule with the particle does not extend to these distances to any appreciable extent. The dependence proposed by Rudyak et al. would require that the curvature of the surface of a particle would influence the interaction of a gas molecule to such an extent that it would behave differently upon interaction with a particle with diameter ten times as large as that of the gas molecule than it would with a particle with diameter $\sim$15 times as great or greater.

The formulation for the relationship between C and Kn presented in Eq. (2) (sometimes with slightly different coefficients) has been widely verified over a wide range of conditions: for values of Kn from 0.029 to 92.378 by Millikan (whose results are summarized in Allen and Raabe (1982), for Kn from 0.5 to 60 by Wahi and Liu (1971), for Kn from 0.06 to 500 by Hutchins, Harper, and Felder (1995), and for Kn from 0.5 to 83 by Kim, Mulholland, Kukuck, and Pui (2005), to name only a few investigations. This expression is universally and routinely used to convert mobility diameters, such as those measured in a differential mobility analyzer, to geometric diameters, and its validity has been well accepted for many years. Although most measurements verifying this relationship between C and Kn have been made at temperatures near 300 K, this relationship has been shown to hold accurately over a wide range of pressures and thus mean free paths (and Knudsen numbers), with no indication of a size-dependent momentum accommodation coefficient. The immense success of this expression, and of the basic paradigm that some fraction of the gas molecules are accommodated with the surface of the particle and the rest reflecting specularly, would strongly support the applicability of the expression at temperatures other than near room temperature.

In view of the problems noted, Rudyak et al. (2009) suggest treating the diffusion of a nanoparticle using the Boltzmann equation applied to a binary mixture, with the nanoparticle considered a sparse gas; however, such an approach raises concerns. The Boltzmann equation implicitly assumes that even a sparse gas is sufficiently dense that properties such as concentration and the like can be treated as continuous variables, an assumption that is questionable for a single nanoparticle. Furthermore the Boltzmann equation explicitly assumes only binary collisions. For a gas at atmospheric pressure there is $>50\%$ probability that there is more than one gas molecule within one molecular diameter (taken as 0.3 nm, characteristic of N_2 and air) of a nanoparticle with diameter greater than $\sim$5.5 nm at 300 K (and $\sim$7.5 nm at 600 K), and if a gas molecule accommodates during a collision, implying it will remain longer at the surface of the particle than if the collision were assumed to be that between two rigid bodies, then these diameters are reduced. Such a situation would imply that the influence of more than one gas molecule would typically be felt by a nanoparticle with diameter larger than that given above, and thus that the Boltzmann equation could not be correctly applied to any but the smallest nanoparticles considered. Finally, this approach might not describe the physics of the situation, as accommodation of a gas molecule with the surface of a nanoparticle is fundamentally different from an elastic binary collision in that the molecule resides at the surface for some time before being emitted back into the gas phase.

What would explain the results of Rudyak et al., and the apparent failure of the diffusion coefficients to follow the expected behavior? One strong possibility is misinterpretation of the data caused by failure to take into account the polydisperse size distribution employed. Rudyak et al. argued that the nanoparticle size distributions were lognormal, and they presented examples in their Fig. 3 for WO_x particles with arithmetic diameters 3.7 and 12.1 nm, Pt particles with arithmetic mean diameters of 34.5 nm, and NaCl particles with arithmetic mean diameters of 84 nm. The graphs they presented of these size distributions could be accurately matched by lognormals having geometric standard deviations σ_g of 1.15, 1.31, 1.18, and 1.20, respectively, and although these may not seem large, their effects can be important.

For a lognormal size distribution with geometric mean diameter $d_{p,g}$ and geometric standard deviation σ_g, the mean value of the diffusion coefficient D, under the assumption that it is inversely proportional to the square of the nanoparticle diameter d_g,

is greater than the diffusion coefficient evaluated at $d_{p,g}$ by a factor of $\exp[4(\ln\sigma_g)^2]$, or by 8, 34, 12, and 14% for the examples shown (Rudyak et al. presented results in terms of the arithmetic mean diameters, which are greater than the geometric mean diameters by a factor of $\exp[(\ln\sigma_g)^2/2]$, although this factor is not much greater than unity for the size distributions under consideration). The mean value of the diffusion coefficient of the size distribution is equal to the diffusion coefficient of a particle with diameter two geometric standard deviations smaller than $d_{p,g}$, at which size the magnitude of the size distribution is $<15\%$ of the maximum. Thus smaller particles overwhelmingly contribute more to the mean diffusion coefficient of the size distribution than larger ones, and in the present example half the contribution to this quantity derives from particles with diameter more than two geometric standard deviations smaller than $d_{p,g}$. This conclusion holds for any lognormal, regardless of the value of σ_g. Typically when size distributions are fitted to lognormals, only particles with diameters near $d_{g,p}$ are considered, and, as was the situation with the fits of Rudyak et al., the actual size distribution for particles with diameter more than two geometric standard deviations smaller than $d_{p,g}$ is not accurately known.

The consequences of treating a polydisperse distribution as monodisperse are even greater when considering penetration, which was the situation for the measurements presented by Rudyak et al. (2009), in which the mean value of the penetration was measured rather than the mean value of the diffusion coefficient. The penetration for a single nanoparticle was assumed to be given by

$$P = \exp(-aD^{2/3}), \tag{8}$$

where a is a constant which depends on the experimental arrangement, and may have differed for different particle sizes and temperatures (as this value was not presented it is not possible to evaluate the mean penetration and relate it to parameters such as $d_{p,g}$ and σ_g). As penetration is a highly nonlinear function of particle diffusion coefficient (Eq. (8)) and thus of particle diameter, the mean penetration of the polydisperse size distribution of nanoparticles is not equal to the penetration evaluated at the geometric mean (or arithmetic mean) particle diameter of this size distribution. In view of the nonlinear relation between P and d_p, it is likely that the dominant contribution comes from particles with diameter even more less than $d_{p,g}$ than was the situation for D, and for these sizes the assumption that the distribution can be treated as lognormal becomes even less certain. Furthermore, the nonlinearity is such that there will be a temperature dependence of the relation between $d_{p,g}$ and P, and this dependence will depend on the constant a which may have differed for different experimental conditions (i.e., particle composition, $d_{p,g}$, and T).

As Rudyak et al. (2009) did not have an independent means of determining particle size during their measurements, they employed Eq. (8) to determine D from P, and then Eqs. (1) and (2) to determine the value of d_p at temperatures near 295 K. Such a procedure ensures that the parameters of the Cunningham relation given by Eq. (2) will match at the lowest temperatures investigated. However, this diameter is not equal to the geometric (or arithmetic) mean diameter of the size distribution, but rather differs from this quantity by a factor that depends on temperature (and may have changed during the measurements as different experimental arrangements were used). Thus the apparent departure of the temperature dependence of the diffusion coefficient from the expected value of a 1.5 power, and the apparent dependence on temperature in Fig. 3, is likely due to the contribution from particles with diameters far from the diameter they chose to characterize the size distribution and to which the diffusion coefficient was assigned. Further, this discrepancy between the diameter inferred at 295 K and the effective diameter of penetration might also account for the anomalous temperature and size dependence of the values of C determined from Eq. (1).

4. Summary

The data presented by Rudyak et al. (2009) for diffusion coefficients of nanoparticles as a function of particle diameter and temperature depart markedly from the expected 1.5 power temperature dependence and from the expected inverse square dependence on particle diameter. To account for these results, Rudyak et al. proposed that the values of A and Q in Eq. (2) have a diameter and temperature dependence given by Eq. (3), a power law in temperature with exponent that depends on particle diameter. This proposal is shown to lead to results that are not physically meaningful, namely that it requires negative values for the momentum accommodation coefficient of gas molecules on the particles. A more likely explanation of their results is that the polydisperse size distributions of the nanoparticles leads to the majority of the contribution to the penetration, and thus to the diffusion coefficient, being from particles with diameters far from those that have been used to characterize the size distribution, and to which they are associated, and for which the assumption that the size distribution behaves as expected may be inaccurate. Their measurements are of mean values of the penetration of a size distribution of particles which, though varying little in size, are nonetheless not monodisperse, and the nonlinear dependence of the penetration with diffusion coefficient and thus particle size implies that the inferred value of the diffusion coefficient will not correspond to that of the mean particle diameter. Furthermore, the inaccuracy of attributing the inferred diffusion coefficient to the mean particle diameter will vary with temperature, depending on the experimental arrangement. It is necessary that these concerns, which apply to all such experiments, be addressed before throwing out one of the basic paradigms of gas-particle interaction, the concept of accommodation, and the associated theory that has worked so well for so long.

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