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Size Effects in Aerosol Particle Interactions:
The van der Waals Potential and Collision Rates

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Abstract

Three effects which are explicitly dependent on aerosol particle size are identified and discussed. They are focussed about the particle collision rate and how it relates to the properties of the gas, the particle, and the particle's interaction potential energy which play roles in particle-particle collision rates. By incorporating the conduction electronic free path effect for conductors into the frequency-dependent dielectric constants of silver and graphite, particle size effects in the Lifshitz-van der Waals potentials for identical pairs of 1 nm and 100 nm particles are evaluated. Water and tetradecane particle interaction potentials for the same size particles are also calculated to illustrate size effects due to the retardation of the interaction. These potentials are then used to calculate the enhancement of the particle collision rates above their values in the absence of any potential at various gas pressures. The roles of the interaction potential in collision among identical pairs of particles of differing compositions is also briefly discussed.

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Size Effects in Aerosol Particle Interactions: the van der Waals Potential and Collision Rates

I. Introduction

A. Aerosols and Aerosol Particle Collision Rates

Aerosols are gas-borne suspensions of particulate matter. Numerous attempts at more specific definitions have been made, but none is satisfactory for the systems which need be considered (see Marlow [1] for further discussion and references). Generally, the role of the gas is central to the description of transport processes involving aerosol particles. To quantify this role, the particle Knudsen number is conventionally defined as $Kn = \lambda/a$ where λ is the gas molecular mean free path and a is the particle radius (Hidy and Brock [2] present an extensive treatment of aerosol transport). In these terms, the kinetic condition $Kn \leq 0.25$ is termed the collision-dominated or continuum regime since the gas can be treated as a fluid or continuum. The condition $Kn \geq 10$ is termed the free molecular regime since particle-gas collisions are isolated allowing the particles to follow primarily collisionless trajectories as is the case for individual molecules in a dilute gas. The transition regime, $0.25 < Kn < 10$, falls between the collision-dominated and free molecular regimes.

Wagner [3] has pointed out that though the above single-particle Knudsen number regime classification is suitable for the description of aerosol processes in which the gas-particle interaction alone is of interest (assuming particle radius is much larger than gas molecular dimensions), it is inadequate for considerations of the collision rates of similar-sized particles. In this situation, the interaction of the particles with each

other must also be considered. At low Knudsen numbers this interaction is usually of secondary importance because of the dominance of gas-particle collisions whereas at high values it must play a central role because of the diminished importance of the gas. Wagner argues that the values of Kn specifying the transition and free molecular regimes in particle Brownian collision rates is ambiguous because these rates become independent of gas molecular mean free path upon approaching the well-understood free molecular regime. As a result, he shows that as Kn increases, for sufficiently large Kn, the dimensionless collision rate (actual collision rate divided by the continuum form of the collision rate) approaches a constant value if particle radius is held constant (i.e. decreasing gas pressure) but decreases if gas pressure is held constant (i.e. decreasing particle radius). However, in both cases the dimensionless collision rate decreases as particle radius decreases. This does not occur in the collision-dominated regime. The consequence of this observation is that a kinetic size effect for aerosol particle collision rates may be identified as the decrease in the dimensionless collision rate with decreasing particle size for sufficiently large values of Kn. Since $\lambda \approx 60$ nm for atmospheric conditions, a ≤ 10 nm is typically the size range for particles in the free-molecular regime.

The importance of quantifying the particle-particle interaction potential for the purpose of estimating collision rates thus becomes coupled to the physics of those particles exactly in that domain of particle size where some physical properties of particulate matter depart from their values for those materials in bulk.

B. Size Effects and Particle Interactions

The kinetic size effect refers to the transport of two particles in a gas and is therefore concerned only with the interactions-at-a-distance of the particles. However, each pair has an interaction potential energy due to the sum over the fluctuation-induced fluctuations of their electrons, the Lifshitz-van der Waals interaction (see Langbein [4], for example). Therefore, the question arises as to whether a size effect pertains in this interaction which is not implicit to the interaction under all (i.e. macroscopic) conditions. Again, a "size effect" may be identified based upon the distance of separation of the particles and their frequency-dependent dielectric susceptibilities, the parameters that specify the physical system in question. This effect is the onset of retardation of the interaction for separations $s > \lambda$, where λ is the wavelength of the field due to an electronic fluctuation. The nonretarded interaction is the limiting interaction as the speed of light approaches infinity much as the assumption that the gas mean free path ℓ is infinite corresponds to the free-molecular limit in kinetic theory. In the Lifshitz-van der Waals interaction, retardation effectively depresses the strength of interaction at a given separation whenever the contributions to the interaction energy are dominated by fluctuations corresponding to wavelengths $\lambda < s$. Thus, at close approach the nonretarded interaction pertains, providing the sizes of the particles are small enough that nonretarded multipole susceptibilities of the particles may be assumed (Marlow [5] discusses this and argues that it is a very good approximation for particles under 100 nm). Using the above properties of the interaction and the fact that the nonretarded interaction energy of spherical particles is known to scale with s/r , the ratio of separation to

radius (see Langbein [6] and below), the size effect for particle interaction energy can be identified. The effect is the convergence of the van der Waals interaction energy to its nonretarded form for a constant value of this ratio as radius decreases. To be meaningful, only nonretarded susceptibilities may apply (meaning $r \lesssim 100$ nm) and only wavelengths from which the principal nonretarded contributions to the energy arise need be included. If the latter are assumed to be no greater than 10 nm, then this size effect should hold for $s/r \gtrsim 0.1$.

The final size effects of relevance to aerosol particle interaction energies and collision rates are those which can manifest themselves in the dielectric susceptibility of the particle. This of course is part of the larger study of the electronic structure of clusters and ultrafine particles which is being investigated at numerous laboratories.

II. Lifshitz-van der Waals Energies between Ultrafine Particles

As mentioned above, the Lifshitz generalization of the van der Waals interaction energy (Lifshitz [7]) is the potential due to the fluctuation-induced fluctuations of the electrons of the interacting bodies. Since these fluctuations are related to the electric and magnetic susceptibilities of the media via the fluctuation-dissipation theorem and the magnetic susceptibilities are negligible the cases discussed below, the energy can be expressed in terms of the particles' frequency-dependent dielectric susceptibilities alone. For this to be the sole source of the interparticle potential, neither particle can carry either a net electrical charge or a permanent multipole moment. In other contexts of colloid science where mobile free charges are present in the intervening medium, such as in

hydrosols, both the double-layer repulsion between the two particles and screening of the static interaction must also be accounted for.

The form of the Lifshitz-van der Waals interaction potential used here is an approximation to Langbein's exact nonretarded form (Langbein [6]) given by Kiefer, Parsegian, and Weiss [9]. Retardation of the interaction is incorporated by assuming a point dipolar retardation factor $F_z(\omega)$ where ω is circular frequency and z is center-to-center distance of the particles. The energy is determined by summing over the first 101 thermal excitation frequencies $\xi_n = (2\pi kT/\hbar) n$, $n = 0, 1, 2, \dots, 100$, and integrating, using the Euler-Maclaurin formula, over the remaining frequencies. Both the retardation factor and the sum over thermal fluctuations were discussed by Marlow [5]. The resultant formula is

$$\Delta E = \frac{kT}{2} g(0, z) + kT \sum_{n=1}^{100} g(i\xi_n, z) F_z(\xi_n) + \frac{\hbar}{2\pi} \int_{\xi_{101}}^{10^{18}} d\xi g(i\xi, z) F_z(\xi) + \frac{kT}{2} g(\xi_{100}, z) F_z(\xi_{100}) \quad (1)$$

where the various functions of ω are evaluated on the imaginary frequency axis for computational convenience giving $\omega = i\xi$. $g(\omega, z)$, as well as the complete expressions from which it is derived, is a function of the ratios s/r_j where s is surface-to-surface separation and r_j ($j = 1, 2$) are particle radii. Thus, the scaling of the energy ΔE with s/r_j in the nonretarded interaction, that is applicable only for the smallest particles as discussed above, is broken by the retardation factor $F_z(\omega)$. The dielectric susceptibilities for the particles, $\epsilon_j(\omega)$, give the frequency dependence of $g(\omega, z)$.

Calculations of the interaction energy (1) for two nonconductors, water and tetradecane ($C_{14}H_{30}$), were performed. The dielectric properties of

water were taken from the fit to experimental data tabulated from the literature by Parsegian [8]. Tetradecane's dielectric properties were modelled by a two-resonance fit to the data of Heller, Birkhoff, and Painter [10]. For frequencies above those for which $\epsilon(\omega)$ was measured, a linear interpolation on the $\log_{10}(\omega)$ axis was made between the highest measured value and the free electron expression (assuming all electrons to be free) at a frequency corresponding to an ionization energy on the order of the most tightly bound electron. The free electron expression for $\epsilon(\omega)$ was used for higher values of ω . The static dielectric constants were taken to be 80 for water and 2.05 for tetradecane. No accounting was made for the possibility of nonrandom ordering of the water molecules. Figure 1 displays the results of these calculations for 1 nm and 100 nm particles as a function of s/r , surface-surface separation divided by particle radius. The similarity of the interaction energies for the 1 nm particles is evident while a splitting occurs in the 100 nm case due to retardation. Since the static and long wavelength dielectric susceptibilities of water are considerably higher than those of tetradecane, retardation of the shorter wavelength fluctuations has a greater effect on tetradecane's interaction energy than on water's as is manifest for the 100 nm particles. This has the further curious effect of reversing the relative attractive energies: the smaller pair of tetradecane particles has a stronger attractive interaction than the correspondingly sized water droplets while the attractive interaction between the larger sized water droplets is somewhat greater than for the correspondingly sized alkane droplet pair. Had retardation not been included in the interaction, the 1 nm and 100 nm curves would be identical and the order of strengths therefore preserved.

The interaction energies for two conductors, graphite and silver, were also computed. The interest in these cases is that silver is a good electronic conductor in which a size-related alteration of the optical properties has been measured for particles and identified as being due to conduction electron scattering from the particles' surfaces (Kreibig [11]), the "free-path effect" (f.p.e.). Due to the dominance of $\epsilon(\omega)$ for silver by its conduction electrons, interband contributions were ignored and $\epsilon(\omega)$ is taken to have the form given by Kreibig [11] as a function of size, assuming isotropic scattering of the electrons from the surface. Graphite has somewhat different properties whose effects may be expected to contrast with silver. Philipp [12] has shown that his graphite infrared optical data can be described by using a Drude free electron description plus a resonance while his earlier optical data (Taft and Philipp [13]) has a two-resonance structure. In the present work, graphite's dielectric susceptibility has therefore been modelled by three resonance terms and one free electron term which is now modified to account for the free path effect as described for silver by Kreibig [11]. All the graphite data used here were derived from reflectance measurements taken at near-normal incidence to the carbon-layer planes. Interpolations between the measured and asymptotic values of $\epsilon(\omega)$ for both silver and graphite were done as described above for the nonconductors.

Figure 2 presents results of the energy computations on a plot similar to Figure 1. Silver's attractive potentials are plotted for pairs of 1 nm particles both including and omitting the free path effect. In this case the f.p.e. clearly plays a role in diminishing the attractive interaction energy while it plays no significant role for 100 nm silver particles nor for either 1 nm or 100 nm graphite particles.

Comparison of the attractive energies in Figures 1 and 2 indicate that the presence of conducting electrons enhances the strength of the van der Waals interaction relative to materials with only bound electrons. For the cases computed here, the interaction energies are ~5-12 times larger for the conductors than for the nonconductors.

III. Collision Rates

Recently, a physically rigorous extension of Fuchs' method of interpolation of aerosol particle collision rates between the free molecular and collision-dominated regimes has been given (Marlow [14]). This extension is based upon a new formulation for the collision rate of free molecular regime particles which affords the rigorous incorporation of particle interaction potentials that are attractive and singular at particle contact as is the Lifshitz-van der Waals potential. Evidence exists from various sources (see Marlow [5, 14] and references therein) that nonelectrostatic interactions enhance transition and free molecular regime aerosol particle collision rates. Consequently, estimates of the collision rate enhancement factors for representative conducting and nonconducting particles are of interest as not only a somewhat macroscopic manifestation of the electronic properties of small particles but also for the interpretation of experimental data.

Table I lists the collision rate enhancements for the particles whose interaction energies are given in Figures 1 and 2. These enhancements are the ratios of the calculated collision rates with an attractive interaction to the collision rates with no interaction potential in a gas of atmospheric composition at a temperature of 298°K. As is expected, the enhancement is related to the energy, but only in order, not in degree. For example,

the order of magnitude difference in energy between 1 nm water and silver particles corresponds to less than a factor of 2 difference in their collision rates. The 1 nm conductors both have somewhat larger enhancements than the nonconductors. However, the difference between the graphite and silver cases is much larger than the tetradecane-water difference suggesting that the absolute values of the differences in the interaction energies, rather than the ratios, plays an important role. This is to be expected as the attractive energy becomes larger than the mean thermal energy. In the case of silver, the free path effect plays a role, though small, in lowering the collision rate from that to be expected based solely on bulk dielectric data. The difference in the collision rate enhancements between the 1 nm and 100 nm cases is due both to retardation of the interaction (see results at zero pressure in Table I) and to the importance of gas molecular collisions in the particle collision process as is discussed in Marlow [5].

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Table 1

Collision Rate Enhancements

		Pressure (atm.)		
	<u>f.p.e.</u>	<u>0</u>	<u>0.1</u>	<u>1.0</u>
H ₂ O				
1 nm	n.a.	2.45	2.45	2.45
100 nm	n.a.	1.77	1.30	1.07
C ₁₄ H ₃₀				
1 nm	n.a.	2.47	2.47	2.47
100 nm	n.a.	1.67	1.24	1.05
C (graphite)				
1 nm	yes	4.00	4.00	4.00
	no	4.01	4.01	4.00
100 nm	yes	2.43	1.62	1.16
	no	2.43	1.62	1.16
Ag				
1 nm	yes	4.67	4.67	4.67
	no	4.86	4.86	4.86
100 nm	yes	2.82	2.25	1.25
	no	2.82	2.25	1.25

Figure Captions

Figure 1. Lifshitz-van der Waals potential energies of nonconductors.

Computations of eq. (1) for temperature of 298°K for identical pairs of 1 nm and 100 nm particles of water and tetradecane.

Energy (ΔE) in ergs vs. ratio of surface separation, s , to particle radius, r .

Figure 2. Lifshitz-van der Waals potential energies of conductors.

Computations of eq. (1) for temperature of 298°K for identical pairs of 1 nm and 100 nm particles of graphite and silver.

Energy (ΔE) in ergs vs. ratio of surface separation, s , to particle radius, r .

Figure 1

Figure 2