Van der Waals attraction and coalescence of aqueous salt nanodroplets

Pavel Jungwirth[a] and Victoria Buch[b]

a) J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, and Center for Complex Molecular Systems and Biomolecules, Dolejškova 3, 18223 Prague 8, Czech Republic

b) Department of Physical Chemistry and Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract

Collisions of aqueous salt nanodroplets at zero initial relative velocity are investigated by means of molecular dynamics simulations. The character of the van der Waals interactions, which bring the droplets together and cause coalescence, is described in detail, and the parameters of the droplet–droplet potential are extracted from the collisional trajectories. Concentration and size effects, together with implications for cloud and precipitation modeling are discussed.

Keywords: van der Waals interaction, aqueous droplets, coalescence, molecular dynamics

Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

A. Introduction

Collisions and coalescence of aqueous nanodroplets play a key role in the natural process of formation of precipitation (the so called warm rain) [1]. Consequently, a number of experimental studies has been performed with the aim to obtain collision and coalescence probabilities of freely falling droplets of varying sizes [2–4]. Data extracted from these experiments are then fed as parameters to computer cloud and precipitation models. Despite the increasing sophistication of such models they typically fail to quantitatively reproduce observed droplet size distributions and time scales pertinent to the early collisional growth regime characterized by droplet sizes between 10 and 20 μm [5]. Several possible physical mechanisms responsible for this flaw have been invoked, including turbulences [5], wake capture [6], and attractive van der Waals forces [6,7]. While the former two can at least in principle be described within macroscopic hydrodynamics, the latter clearly refers to the microscopic, molecular structure of the aqueous nanodroplets.

Van der Waals interactions between microscopic bodies can be divided into three types: London *induced dipole–induced dipole* dispersion forces present in all atomic and molecular systems, Debye polarization forces of the *permanent dipole–induced dipole* type, and Keesom forces, which arise in polar systems from thermally averaged *permanent dipole–permanent dipole* interactions [9,10]. Since water molecules possess a large dipole and at the same time are not very polarizable, the last term will dominate the interactions between aqueous nanodroplets. Interestingly, however, previous studies of water droplet collisions and coalescence considered solely the London dispersion forces [6–8]. Despite having a different microphysical origin, London and Keesom forces have the same dependence on the interparticle distance R, with the limits of R^{-6} for large separations and small particles, and R^{-2} at close contact of very large particles [10,11]. However, for very large distances there is one significant difference between these two types of interaction, namely the importance of the retardation effect [12]. London forces are subject to retardation already at separations larger than 0.1–1 μm, while Keesom forces become retarded only above ≈1 mm [13]. Therefore, for nano- to micrometer sizes of aqueous droplets the effect of retardation, which changes the distance dependence from R^{-6} to R^{-7} [12], and thus significantly reduces the intermolecular interactions at relevant interparticle separations, would play a significant role if dispersion London forces dominate, but it can be safely neglected for Keesom forces.

Recently, pair collisions of aqueous nanodroplets with sizes ranging from 125 to 1000 water molecules have been modeled by means of classical molecular dynamics (MD) simulations [14]. Depending on the impact parameter and the collision velocity, varied in the range of 600–3000 ms^{-1}, three main scattering channels have been observed: coalescence, stretching separation, and shattering collisions. Interestingly, it has been found that the results are rather insensitive to the water cluster size and extrapolate well to experimental data for micrometer size aqueous droplets [15]. In the present study we have performed MD simulations of collisions of aqueous nanodroplets with *zero* initial relative velocity. To the best of our knowledge, these are the first simulations in which two aqueous nanodroplets are placed at a relatively large distance from each other, leaving it solely to the long range attractive interactions to eventually bring them together. The principal goals of the present simulations with zero initial collision velocity are to describe in detail such untypical collisions and to extract from the collisional trajectory the macroscopic interaction potential between the droplets.

B. Method

The MD simulations have been performed as follows. First, we have separately equilibrated two aqueous nanodroplets at 280 K. Each of them contained 144 water molecules and a fixed amount (one or sixteen) of Na^+Cl^- ion pairs. This corresponds to a droplet diameter of roughly 15 Å in the former case and 18 Å in the latter case. The inclusion of salt is partly motivated by the atmospheric reality. In clouds, droplets grow on condensation nuclei, typically formed by soluble salts. Our simulation of droplets with low salt content roughly corresponds to ionic impurity concentrations in micrometer droplets, while the concentrated nanodroplets correlate with concentrations pertinent to early stages of atmospheric droplet growth.

After equilibration (typically 200 ps) we have removed the centers of masses (cms) velocities of the droplets and have placed them approximately 50 Å from each other (distance between cms of the two droplets). We have then performed constant energy MD simulations following the trajectories of the two droplets until they collided and coalesced. MD runs have been performed with a time step of 1 fs and all intramolecular interactions have been included explicitely. For water we have adopted the polarizable SPC/POL potential model [16]. Parameters for the polarizable sodium and chloride ions were taken from Ref. [17]. All MD simulations have been performed using the Amber program package [18].

C. Results and Discussion

A first view of the collision and coalescence process is obtained by simply examining snapshots from the MD simulations. Figures 1 and 2 display a series of such representative snapshots for a pair of diluted and a pair of highly concentrated aqueous salt nanodroplets. In both cases the snapshots cover a 250 ps time interval: roughly 170 ps before and 80 ps after the point when the droplets begin to coalesce. The first snapshot in both figures corresponds to well separated nanodroplets, the second snapshot covers the onset of coalescence, while the third displays merged droplets. Probably the most interesting point is that the droplets, placed initially relatively far from each other with zero collision velocity, do collide and coalesce at all and, as a matter of fact, on a very fast time scale of hundreds of picoseconds. Clearly, the inter–droplet attractive van der Waals interactions are strong enough, even at cms separations exceeding twice the droplet diameter, to bring the droplets together. As a consequence, the collisional cross sections at small collision velocities (atmospheric microdroplets typically collide at 0–10 ms^{-1}) can be significantly larger than those corresponding to the droplet diameter.

In order to quantify the collision and coalescence process, we have extracted from the simulations the time evolution of the distance R between the cms of the two droplets. Thick full lines in Fig. 3 display such collisional trajectories for both diluted and concentrated pairs of droplets. The two trajectories are qualitatively similar displaying a gradually increasing negative curvature, followed by a very rapid approach of the two droplets just before and at the onset of the collision (in Fig. 3, the contact distance is marked by the thin full line). Finally, the curve almost levels off marking the early stages of droplet coalescence. Within the interval of less than 100 ps after the collision, covered in Fig. 3, the curve does not reach zero yet, indicating that the two droplets, although coalesced, still pertain a certain degree of individuality at the molecular level.

The fact, that the collisional trajectories are relatively smooth curves (at least before the actual droplet collisions) invokes the possibility of extracting from them the droplet–droplet interaction potentials. We know that at large inter-droplet separations the Keesom potential, which dominates the attractive interaction, should be proportional to R^{-6}. Using the Newton's law it is easy to show that for an inter-droplet potential of the form $-CR^{-6}$ the collision trajectory is given (for times smaller than the time of collision) by an analytic expression

$$R = R_0 t_c^{-\frac{1}{4}} (t_c - t)^{\frac{1}{4}}. \tag{1}$$

Here, t_c is the collision time corresponding to the Keesom potential (t_c is taken as a fitting parameter) and R_0 is the initial value of the inter-droplet separation R. The potential constant C is then given as

$$C = \frac{M_r R_0^8}{32 t_c^2}, \tag{2}$$

where M_r is the reduced mass, equal to one half of the mass of the single droplet.

The thick dashed lines in Fig. 3 represent best fits of the collision trajectories to those resulting from the Keesom potential. We see that for both diluted and concentrated droplet pairs the fit is almost perfect for cms separations between 45 and 25 Å. Only at shorter separations, just before the collision, the $-CR^{-6}$ potential form appropriate for large values of R ceases to be adequate and, of course, after the collision it no more make sense to speak about an effective droplet–droplet potential. From the fits, we have extracted the following values of the potential parameter: $C = 2.8\times10^6$ eVÅ^6 for the diluted and $C = 4.1\times10^6$ eVÅ^6 for the concentrated pair of aqueous salt nanodroplets. For example, this means that at a cms separation of twice the droplet diameter the attractive inter–droplet interaction still amounts to 3.7 meV in the former case and to 1.9 meV in the latter case. Note that the concentrated droplets are bigger which explains why the interaction at twice the droplet diameter is smaller even though the constant C is larger.

Strictly speaking, the polarizable potential model employed in the simulations includes both Keesom as well as Debye polarization interactions. In order to evaluate the relative importance of these two types of interactions we have also performed test simulations with switched off polarization interactions. As expected, qualitatively the same behavior as before is observed, confirming that the Keesom interactions dominate for aqueous droplets, the effect of polarization being only minor. Quantitatively, inclusion of electronic polarization increases the strength of the droplet–droplet interaction by about 10–20 %. The present simulations also allow to elucidate the effect of salt concentration on the attractive interaction between aqueous salt nanodroplets. As seen above, the salt concentration effect is rather week and its sign depends on the particular way of its quantification. Adding salt to a droplet containing a fixed amount of water molecules leads to an increase of the attractive droplet–droplet potential. However, this also leads to an increase of droplet size. As a results the strength of the interaction at a separation equal to a fixed multiple of the droplet diameter decreases slightly upon adding salt.

Finally, we address the question of the relevance of the present simulations of droplets with a diameter of 15–20 nm to the atmospheric reality with droplets of micrometer sizes. First, earlier simulations of highly energetic nanodroplet collisions showed that the results extrapolate quantitatively to experiments on micrometer droplets, indicating that the effects of surface curvature and tension are relatively minor [14]. Second, potentials decaying with separation as R^{-6}, such as the unretarded Keesom interaction, have in a certain sense a constant scaling with system size. Namely, the strength of the inter-droplet interaction is proportional to the product of the volumes of the two droplets, i.e., to R^6. Consequently, for (and only for) this type of interaction the scaling with volume cancels the decay with inter-droplet separation. As a result, the strength of the inter-droplet Keesom interaction at a given multiple of droplet diameter is independent on this diameter. Therefore, the principal conclusions of the present study, i.e., that aqueous droplets exhibit coalescence even if placed initially at a non-zero separation and not only at close contact, and that the attractive inter-droplet potential can be extracted from the collision trajectory, may help to overcome some of the present problems pertinent to cloud and precipitation modeling.

Acknowledgment

The Center for Complex Molecular Systems and Biomolecules is supported by the Czech Ministry of Education via a grant No. LN00A032.

REFERENCES

[1] Pruppacher H. R., Klett J. D., *Microphysics of Clouds and Precipitation* Kluwer, Dordrecht 1997.

[2] Orme M., *Prog. Energy Combustions Sci.* **1997**, *23*, 65.

[3] Low T. B., List R., *J. Atmos. Sci.* **1982**, *39*, 1591.

[4] Abbott C. E., *J. Atmos. Sci.* **1982**, *39*, 1591.

[5] Khain A., Ovtchinnikov M., Pinsky M., Pokrovsky A., Krugliak H., *Atmos. Res.* **2000**, *55*, 159.

[6] Hu Z., Bruintjes R. T., Betterton E. A., *J. Atmos. Sci.* **1998**, *55*, 2502.

[7] Rogers J. R., Davis R. H., *J. Atmos. Sci.* **1990**, *47*, 1075.

[8] Davis R. H., *J. Fluid Mech.* **1984**, *145*, 179.

[9] Hobza P., Zahradnik R. *Intermlecular Complexes* Elsevier, Amsterdam 1988.

[10] French R. H., *J. Am. Ceram. Soc.* **2000**, *83*, 2117.

[11] Hamaker H. C., *Physica* **1937**, *4*, 1058.

[12] Casimir H. B. G., Polder D., *Phys. Rev.* **1948**, *73*, 360.

[13] Buckingham A. D., *Adv. Chem. Phys.* **1977**, *12*, 107.

[14] Svanberg M., Ming L., Markovic N., Pettersson B. C., *J. Chem. Phys.* **1998**, *108*, 5888.

[15] Ashgriz N., Poo J. Y., *J. Fluid Mech.* **1990**, *221*, 183.

[16] Caldwell J., Dang L. X., Kollman P. A., *J. Am. Chem. Soc.* **1990**, *112*, 9144.

[17] Perera L., Berkowitz M. L., *J. Chem. Phys.* **1991**, *95*, 1954.

[18] Case D. A., Pearlman D. A., Caldwell J. A., Cheatham T. E., Ross W. S., Simmerling C. L., Darden T. A., Merz K. M., Stanton R. V., Cheng A. L., Vincent J. J., Crowley

M., Ferguson D. M., Radmer R. J., Seibel G. L., Singh U. C., Weiner P. K., Kollman P. A., *Amber 5.* University of California, San Francisco 1997.

FIGURES

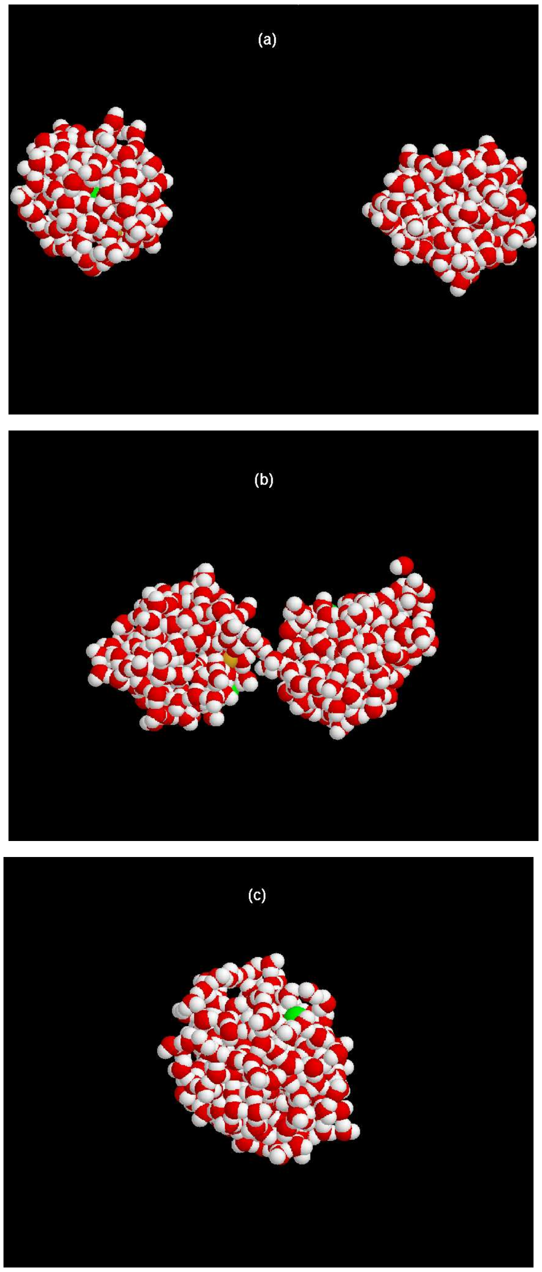

FIG. 1. Collision of two nanodroplets (each containing 144 water molecules and a single $Na^{+}Cl^{-}$ ion pair) at zero initial relative velocity. (a) t=0 ps, (b) t=160 ps, and (c) t=250 ps.

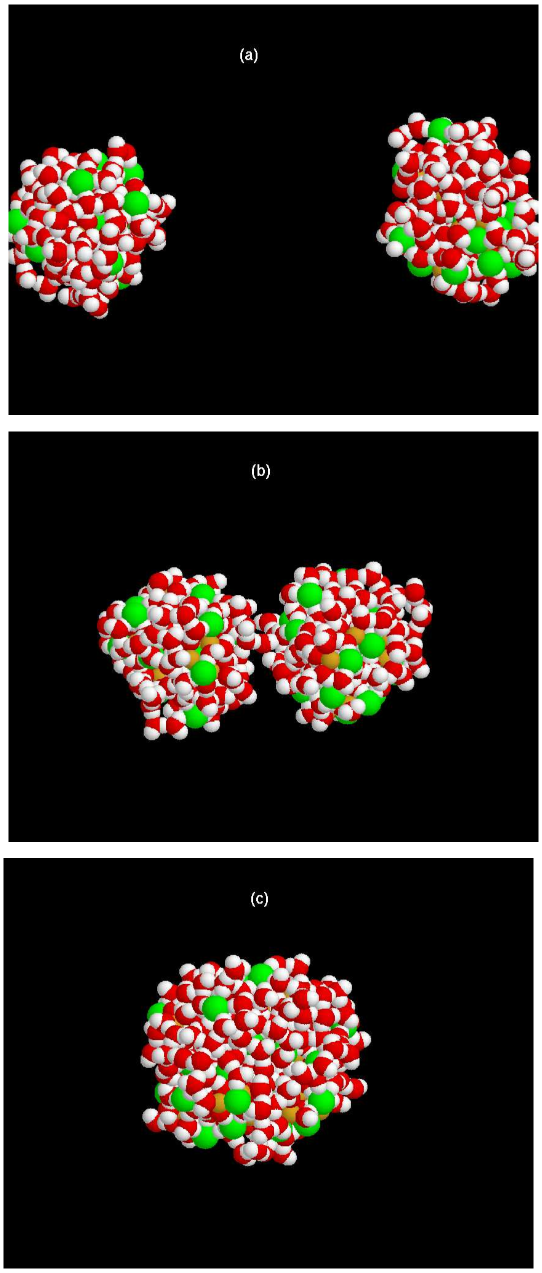

FIG. 2. Collision of two nanodroplets (each containing 144 water molecules and sixteen $Na^{+}Cl^{-}$ ion pairs) at zero initial relative velocity. (a) t=0 ps, (b) t=173 ps, and (c) t=250 ps.

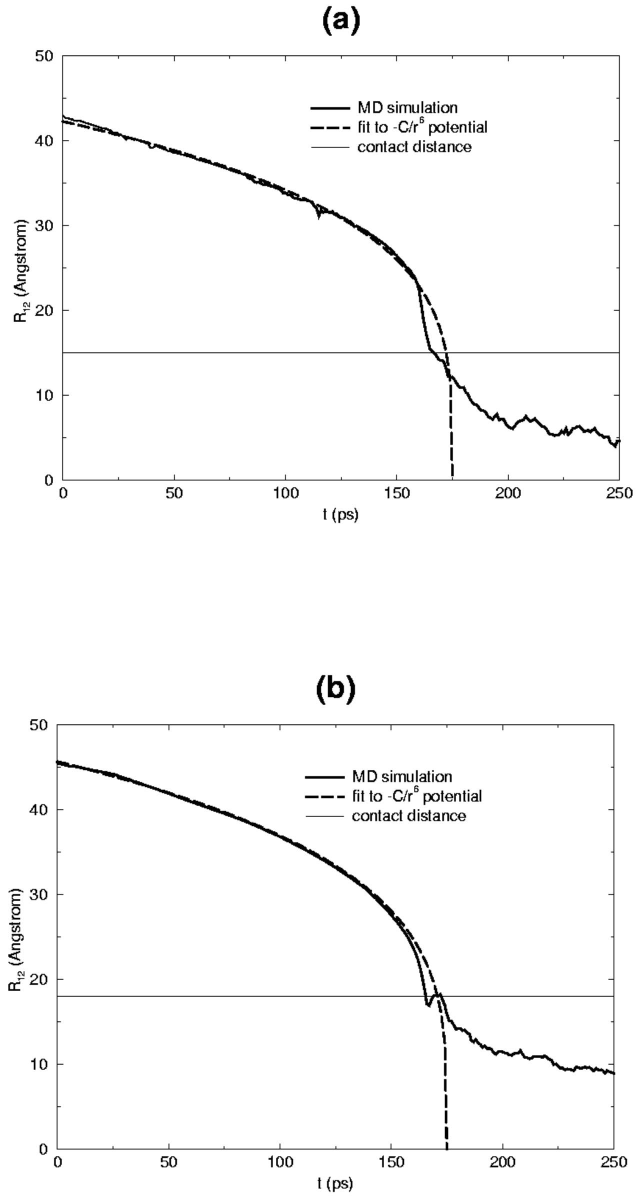

FIG. 3. Time dependence of the separation of the centers of mass of the two nanodroplets. Full thick lines show the results of MD simulations, dashed thick lines represent the best fit assuming the Keesom potential, and thin full line denots the droplet contact distance. (a) Diluted and (b) concentrated aqueous salt nanodroplets.