Nanoparticle interaction potentials constructed by multiscale computation

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The van der Waals (vdW) potentials governing macroscopic objects have long been formulated in the context of classical theories, such as Hamaker’s microscopic theory and Lifshitz’s continuum theory. This work addresses the possibility of constructing the vdW interaction potentials of nanoparticle species using multiscale simulation schemes. Amorphous silica nanoparticles were considered as a benchmark example for which a series of $(SiO_2)_n$ ($n$ being an integer) has been systematically surveyed as the potential candidates of the packing units that reproduce known bulk material properties in atomistic molecular dynamics simulations. This strategy led to the identification of spherical $Si_6O_{12}$ molecules, later utilized as the elementary coarse-grained (CG) particles to compute the pair interaction potentials of silica nanoparticles ranging from 0.62 to 100 nm in diameter. The model nanoparticles so built may, in turn, serve as the children CG particles to construct nanoparticles assuming arbitrary sizes and shapes. Major observations are as follows. The pair interaction potentials for all the investigated spherical silica nanoparticles can be cast into a semiempirical, generalized Lennard-Jones $2\alpha-\alpha$ potential ($\alpha$ being a size-dependent, large integral number). In its reduced form, we discuss the implied universalities for the vdW potentials governing a certain range of amorphous nanoparticle species as well as how thermodynamic transferability can be fulfilled automatically. In view of future applications with colloidal suspensions, we briefly evaluated the vdW potential in the presence of a “screening” medium mimicking the effects of electrical double layers or grafting materials atop the nanoparticle core. The general observations shed new light on strategies to attain a microscopic control over interparticle attractions. In future perspectives, the proposed multiscale computation scheme shall help bridge the current gap between the modeling of polymer chains and macroscopic objects by introducing molecular models coarse-grained at a similar level so that the interactions between these two can be treated in a consistent and faithful way. © 2010 American Institute of Physics. [doi:10.1063/1.3447890]

I. INTRODUCTION

Substances exhibiting solid-liquid-vapor phase transitions are among the most fascinating natural phenomena known as a consequence of the mutual competition between particle attractions and thermal agitations. The famous van der Waals (vdW) equation of state and the correspondence theory established in 1880s have long laid the foundation of understanding the above phase phenomena. Especially, particles possessing no charges or permanent dipoles are known to be governed by the so-called vdW force. In that case, a celebrated force law had been deduced by Wang during 1920s in an attempt to explain (as prompted by a suggestion of Debye) the net attractions arising from instantaneous electron density fluctuations in one molecule and the subsequently induced dipole on the other.\(^1\) Wang’s result, derived using first-principles calculations, gave rise to the first dispersion potential of the form $C/r^6$ ($C$ is a constant related to the polarizability of the molecule and $r$ is the intermolecular separation)—generally known as the London theory. Supplemeting a heuristic excluded-volume potential of form $B/r^{12}$ ($B$ being a similar material constant) to the previous expression amounted to a widely employed Lennard-Jones (LJ) 12-6 potential, which has extensively been parameterized to characterize the transport coefficients of simple fluid systems.\(^2\)

In contrast, understanding the vdW force laws governing macroscopic objects has relied on Hamaker’s microscopic theory and Lifshitz’s continuum theory.\(^3\)–\(^6\) These classical theories have found ubiquitous applications for macroscopic objects yet are not specific to nanoparticle species. For colloidal nanoparticles, for instance, semiempirical models such as the Baxter’s sticky model\(^7\) and a later refined square-well model\(^8\) have often been used instead, especially in describing the structure factor in neutron or x-ray scattering experiments. Inspired by the success of rapidly advancing multiscale coarse-grained (CG) simulations for long-chain molecules\(^9\)–\(^31\) as well as a few small-sized nanoparticles,\(^32\) we elaborate in this paper the possibility and apparent advantages of utilizing multiscale simulation schemes to systematically construct molecule-based vdW potentials for specific nanoparticle species assuming arbitrary sizes and shapes, as well as how essential new insights complementary to classical theories can thus be gained.

The primary observations of this multiscale simulation for amorphous silica nanoparticles are as follows. Among a series of potential candidates, we first identified in atomistic molecular dynamics (AMD) simulations an ideal packing...
molecule—$\text{Si}_4\text{O}_{12}$—that allows the simulation to well reproduce two distinct bulk material properties known for amorphous silica. The packing molecules were later treated as the elementary CG particles, the interaction potential of which was established through the corresponding coarse-grained molecular dynamics (CGMD) simulation to be well mimicked by the usual LJ 12-6 potential. Afterward, analogous to the Hamaker’s theory summing up all the interacting CG pairs each governed by the fundamental potential law of $C/r^6$, the pair interaction potentials of bulk silica nanoparticles with diameters ranging from 0.62 to 100 nm have been systematically computed and the results cast into a semi-empirical, generalized LJ $2\alpha - \alpha$ potential. A reduced form of this generalized potential was suggested, for which we discussed the implied universalities and thermodynamic transferability. An effect of interfacial properties was also briefly examined so as to shed light on the impact of a tiny shell of “screening” media mimicking polymer brushes or electrical double layers in applications with colloidal suspensions.

This paper is organized as follows. Section II describes the AMD simulations for surveying candidate packing molecules (or CG particles) of amorphous silica and, afterward, the corresponding CGMD simulation for establishing the interaction potential of the entire CG particle. Section III A presents the simulation results and verifications on the bare interaction potentials of silica nanoparticles for a wide range of particle diameters, as well as fits to a generalized LJ potential function and a reduced form suggested for it. Section III B comments on the thermodynamic transferability of the potential functions currently reached. Section III C briefly examines an effect of interfacial properties for applications with colloidal suspensions. Section IV summarizes this first multiscale modeling of an amorphous nanoparticle species along with several future perspectives.

II. SIMULATION PROTOCOLS

Contemporary CG simulation schemes for large molecules identifiably identify plausible molecular units as the mapping centers of the so-called CG particles, and statistical trajectories essential for constructing the interaction potentials between two such CG particles are later collected from AMD simulations or, if necessary, first-principles computations of a miniature ensemble system. Thus, quantitative force expressions can, in principle, be deduced for the computationally more efficient molecular or Langevin dynamics simulations based on the CG representation of the ensemble system. By simultaneously reducing the total number of particles and enlarging the simulation time step size, the promotion in the computational efficiency is usually enormous for the corresponding CG simulations. A great enhancement in computational efficiency, in turn, permits the exploration of larger ensemble sizes and longer real times for capturing practically interested material properties.

In contrast with the case of chain molecules having definite repeating units, however, the way of identifying plausible CG particles for nanoparticle species remains elusive, especially for amorphous nanoparticles. This prime challenge, in fact, has somewhat impeded the development of similar CG simulations for nanoparticle species lacking a well-defined structure. Using amorphous silica nanoparticles as a benchmark example, we elaborate a potential pathway of identifying the elementary CG particles for constructing the simplest model nanoparticles and remark on how the proposed protocols and major simulation results might, in principle, be generalized to a certain range of nanoparticle species assuming arbitrary sizes and shapes. To that end, several special advantages and potential future applications of such a multiscale modeling for nanoparticle species will become readily apparent.

For dense or condensed amorphous materials, we note that many bulk material properties are virtually dictated by the cluster interactions of representing “packing units.” For instance, the clusters could be the polymer “blobs” introduced by de Gennes in describing the universal properties of polymer molecules. In this case, some molecular details (both structural and dynamic) become unimportant, and hence, more coarse-grained views may be adopted. A similar thinking, in fact, has underscored the prevailing CG simulations of large molecules. Below, using amorphous silica as a concrete example, we discuss guidelines for identifying plausible packing units or CG particles for a model nanoparticle species that can be systematically tested in AMD simulations against known bulk material properties. The basic assumption has been that for each amorphous material, there exist fundamental packing units assuming certain supramolecular forms that can be exploited to reproduce representative bulk material properties and, subsequently, form the basis of evaluating the pair interaction potentials of the particulate
species packed by them. The possibility of exploiting perhaps more realistic, hybrid building molecular units—which shall make the subsequent modeling and computation substantially more complex—is not considered at the present stage.

A. AMD simulations

Following the basic assumptions noted above in search of plausible packing molecules for amorphous silica, it appears that any combinations of \((\text{SiO}_2)_n\) (\(n\) being an integer) might be the potential candidates, as listed in Table I for various sizes and geometrical shapes. Generally speaking, to facilitate the later CG simulations, an ideal packing unit should be neither too large nor too small. In addition, an overall spherical shape is usually welcomed, and this is why spherical CG particles have been most commonly adopted in existing multiscale simulations for polymer molecules. On account of these factors, candidate \(m\) in Table I is appealingly qualified at first sight. Nevertheless, we have performed AMD simulations (see a later description) for representative candidates \(g\), \(h\), \(k\), and \(m\) to systematically evaluate their ability to capture known bulk material properties of amorphous silica.34 First, the bulk density check suggested that candidates \(h\), \(k\), and \(m\) all yield results in close agreement with the known value, i.e., 2.2 g/cm\(^3\), at the system temperature and pressure considered. A scrutiny into the predicted heat capacity, however, revealed that only candidate \(m\) was able to reasonably fulfill the requirement, i.e., 42.2 J/mol K, under the same conditions; see results shown in Fig. 1 and Table I. Note that although a certain fraction of the packing molecules might be further tied by weak chemical bonds to better mimic a real condensed state, the major results of interest in this work should be basically unaffected.

Unlike the case with bulk material density, however, heat capacity is also sensitive to the bond-angle potentials of \((\text{SiO}_2)_n\). It thus appears that only the spherelike \(\text{Si}_6\text{O}_{12}\) among all the candidates evaluated can reasonably capture the elementary chemical structures assumed by typical amorphous silica. In general, for the sole purpose of computing the interparticle potential, our conjecture is that capturing a thermal property like heat capacity that is not dominantly governed by cluster interactions might not be a critical concern at this stage. Apparently, this issue needs to be further pursued based on more extensive practical examples. In summary, considering single-component packing units, the appealing feature of spherical \(\text{Si}_6\text{O}_{12}\) as the elementary building block for bulk amorphous silica should mainly lie in its ideal size (~0.6 nm) and shape. Using an isotropic, spherical CG particle to further represent this \(\text{Si}_6\text{O}_{12}\) molecule, we show shortly that the interaction potential of CG particles can be well describe by the usual LJ 12-6 potential, with several intriguing consequences stemming from it.

In the AMD simulations described above, a commercial software package, DL_POLY_2,35 was used along with the force fields provided by Dreiding;36 see Table II for the force fields utilized. Note that, despite the availability of more sophisticated interatomic potentials for silica systems,37,38 the ability of the present AMD simulations to excellently reproduce two distinct bulk material properties of amorphous silica seems to legitimize the common strategy of multiscale simulations taking advantage of more coarse-grained force laws for capturing large-scale material properties.

Specifically, AMD simulations of 343 \(\text{Si}_6\text{O}_{12}\) molecules were performed in a Nosé–Hoover \(NPT\) ensemble at 1 atm and various system temperatures (see Fig. 1). Periodic boundary conditions were enforced along with a time step size 1 fs and a cutoff distance 15 Å. The total simulation time

![FIG. 1. (a) A front look of a \(NPT\) simulation ensemble consisting of 343 \(\text{Si}_6\text{O}_{12}\) molecules (i.e., candidate \(m\) in Table I) at 1 atm and 298.15 K. (b) The predicted bulk density and specific enthalpy (inset) as functions of the system temperature. The bulk density and heat capacity are predicted to be 2.20 ± 0.02 g/cm\(^3\) and 40.0 ± 4.0 J/mol K, respectively, compared with the known values 2.2 g/cm\(^3\) and 42.2 J/mol K (Ref. 34).](image-url)
TABLE II. The interatomic potentials and parameter values employed in the AMD simulations of amorphous silica shown in Figs. 1 and 2. The parameter values provided by the force-fields library in Ref. 36 were directly used without further modifications.

<table>
<thead>
<tr>
<th>Intramolecular potential</th>
<th>Notation</th>
</tr>
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<tbody>
<tr>
<td>Bond length</td>
<td>( U_{\text{bond}} = \frac{1}{2} k_b (r_{ij} - r_0)^2 )</td>
</tr>
<tr>
<td>Bond angle</td>
<td>( U_{\text{angle}} = \frac{1}{2} k_\theta [\cos(\theta_{ij}) - \cos(\theta_0)]^2 )</td>
</tr>
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| Intermolecular potential | \( U_{\text{vdW}} = 4 e_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \) | \( e_{ij}, \sigma_{ij} \): van der Waals parameters |

<table>
<thead>
<tr>
<th>Parameters</th>
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<tbody>
<tr>
<td>Si–O: ( k_b = 700.000 ) [kcal mol(^{-1}) Å(^{-2})] and ( r_0 = 1.587 ) [Å]</td>
</tr>
<tr>
<td>Si–O–Si: ( k_b = 106.698 ) [kcal mol(^{-1}) rad(^{-2})] and ( \theta_0 = 104.510 ) [degree]</td>
</tr>
<tr>
<td>O–Si–O: ( k_b = 112.500 ) [kcal mol(^{-1}) rad(^{-2})] and ( \theta_0 = 109.471 ) [degree]</td>
</tr>
<tr>
<td>Si–Si: ( \epsilon = 0.310 ) [kcal mol(^{-1})] and ( \sigma = 3.804 ) [Å]</td>
</tr>
<tr>
<td>O–Si: ( \epsilon = 0.096 ) [kcal mol(^{-1})] and ( \sigma = 3.033 ) [Å]</td>
</tr>
<tr>
<td>Si–O: ( \epsilon = 0.173 ) [kcal mol(^{-1})] and ( \sigma = 3.419 ) [Å]</td>
</tr>
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</table>

amounted to 1 ns, and the results were verified to be unchanged by using a greater number of Si\(_6\)O\(_{12}\) molecules. The heat capacity shown in Fig. 1 has been estimated using the relation: \( C_p = (\partial U_s / \partial T)_p = (\Delta H / \Delta T)_p = (\Delta H / \Delta T)_\text{r} + (P \Delta V / \Delta T)_p \), where \( \dot{U} \) and \( \dot{V} \) denote the specific internal energy and volume, respectively.

Later, the CGMD simulation was performed by lumping Si\(_6\)O\(_{12}\) into a single CG particle so as to find the interaction potential for the entire CG particle. The same Nosé–Hoover NPT ensemble system and DL_POLY_2 software package were utilized. The time step size can then be enlarged to 10 fs, with the same cutoff distance (15 Å) and total simulation time (1 ns) as for the AMD simulation. The CGMD simulation and major results are discussed in more detail in the next subsection.

B. Constructing the interaction potential of CG particles

By mapping Si\(_6\)O\(_{12}\) onto a single CG particle, as depicted in Fig. 2, it leaves to determine an effective pair interaction potential for the entire CG particle. This can be achieved in a reliable manner through the radial distribution function (RDF), as plotted in Fig. 2, for the same ensemble system as considered in Fig. 1(a). Because of an ideal spherical shape of the Si\(_6\)O\(_{12}\) molecule chosen, we considered the following standard LJ potential describing the CG particle interaction:

\[
U(r) = 4\epsilon_0 \left[ (\sigma_0/r)^{12} - (\sigma_0/r)^6 \right],
\]

with \( (\sigma_0, \epsilon_0) \) determined by the simplex optimization scheme described below.

For the simplex optimization, the following penalty function, \( f = \int_{r_{\text{cutoff}}}^{r_C} \text{d}r \left( \text{RDF}_{\text{AMD}}(r) - \text{RDF}_{\text{CGMD}}(r, U_{\text{CGMD}}(p_i, p_j)) \right)^2 \), was minimized with respect to the full set of parameters \( \{p_i\} \), in this case \( \{\sigma_0, \epsilon_0\} \). Using the criterion \( \|p_i - p_{i-1}\| < 10^{-3} \) (\( i \) denotes the \( i \)th iteration, as for the RDF\(_{\text{CGMD}}^i \) and \( U_{\text{CGMD}}^i \) given above) for each of the parameters belonging to \( \{p_i\} \), the total number of iterations is about ten. At the beginning of the iteration, the first guess for \( (\sigma_0, \epsilon_0) \) has been estimated from the Boltzmann inversion of the AMD simulation result: \( \text{RDF}_{\text{CGMD}}^i(r) = 4\epsilon_0 (\sigma_0/r)^{12} \) to be utilized for the next CGMD simulation. This procedure leads to a final result of \( (\sigma_0, \epsilon_0) = (6.20 \text{ Å}, 3.10 \text{ KJ/mol}) \) after ten iterations, as shown in Fig. 2. We add the remarks that postulating a form of Eq. (1) is subject also to the consideration that it has a straightforward physical meaning, some merits of which will become evident in the later discussion. Further, warranting a satisfactory RDF—whose Fourier transform offers a traditional way of experimentally determining the effective pair interaction potentials in a dense system—for the CG Si\(_6\)O\(_{12}\) particles should suffice the later purpose of computing the pair interaction potentials between two large silica nanoparticles packed by them.
It is worth noting that although the real forms of interatomic potentials could be considerably more complicated and nonadditive in general, the present CGMD simulation for amorphous silica suggests that the mean-field potential of CG particles governing representative bulk material properties could remain simple in nature and, more importantly, may be treated in a pairwise-additive manner. Notably, in this way of “renormalizing” the constituting molecules, the classical Hamaker’s theory naively summing up all the interacting pairs may be justified. In general, as the packing molecules possess no significant dipolar moments, such as the usual case with polymer latexes, spherical “cages” of varying size may be exploited to confine the constituting supramolecules undergoing self-equilibration. The equilibrated cages can then be adopted as the elementary CG particles and systematically tested against known bulk material properties. In fact, the CG particles so identified should bear a good possibility of being well described by a potential law similar to Eq. (1) so that the major simulation results presented next for silica nanoparticles would become equally applicable in properly reduced form.

III. RESULTS AND DISCUSSION

A. Bare nanoparticle interaction potentials

Using the interaction potential of the CG particle obtained in the prior section and considering hereafter nanoparticle interactions in a vacuum environment only (i.e., without the influence of a dispersing medium), the numerical construction of the pair interaction potentials for model silica nanoparticles of arbitrary sizes and shapes becomes straightforward. Below, we focus on the simplest case with spherical nanoparticles. For simplicity, the following calculations of the “bare” interaction potential (i.e., without the interference of any interfacial properties) also ignore the effect of surface imperfections, such as residue chemical bonds or defects. Moreover, considering the effective force range of the elementary CG particles, it suffices to count on the pairwise interactions of the outmost shells of the two silica nanoparticles involved, as depicted in Fig. 3. By summing up the interaction potentials of all the constituting CG particles of two like nanoparticles at various intercenter distances, the full potential curves for particle diameters ranging from 0.62 to 100 nm have been systematically established.

Before we discuss the results for spherical silica nanoparticles, it is instructive to look at a comparison between the CG model and full-atom model for a pair of thin slabs constituted by Si₉O₁₂, depicted in Fig. 4. In the full-atom model, the Si₉O₁₂ molecules are allowed to freely rotate, and thus the predicted potential curve is subject to certain fluctuations. Within such fluctuations, it can be seen that the CG model performs rather well in describing the results from atomistic simulations of the full-atom model. Thus, the agreement should help verify the CG computation results for the spherical nanoparticles discussed momentarily.

We noticed that the pair interaction potential for planar silica slabs remains describable within the fundamental LJ 12-6 potential, irrespective of the size of the slab. This essential feature might be ascribed to the fact that the interaction between two slabs is basically controlled by the packing units that are governed by the same potential function, Eq. (1), and the sole effect of geometric size is to increase the well depth $\varepsilon$ with increased slab dimension. In contrast, the potential profiles discussed next for spherical silica nanoparticles are notably affected by the geometric curvature to be increasingly deltoidal, as first noticed and utilized by Baxter in formulating an approximate potential function for spherical colloidal particles.

In search of a plausible semiempirical function describing the CG computation results for the pair interaction potential governing spherical silica nanoparticles, a special feature associated with the so-called “generalized LJ potential function” came into our notice,

$$U(r) = 4\varepsilon[(\sigma/r)^6 - (\sigma/r)^{12}],$$

where the value of $\sigma$ approximately coincides with the nanoparticle diameter and $\varepsilon$ and $\alpha$ are two fitted parameters. Figure 5 shows an illustrative case with $\sigma=10.5$ nm. It can clearly be seen that the exponent $\alpha$ can be utilized to tune the width of the potential well, while the well depth $\varepsilon$ remains essentially unchanged and corresponds to a known value from the original CG simulation data. In fact, for all the
cases examined, i.e., 0.62 nm \leq \sigma \leq 100 \text{ nm}, it seems always possible to identify an appropriate value of \( \sigma \) that can capture rather well the result from the CG computation, as illustrated in Fig. 5. As noted earlier, the potential profile becomes increasingly deltalike with increased particle diameter due to a progressively short interaction range \( \sigma_0 \) with respect to the nanoparticle diameter \( \sigma \). It remains a curious question whether the applicability of Eq. (2) is related to the fundamental potential law, Eq. (1), governing the packing units. Of course, it might be possible to consider a different form of potential function to describe the CG simulation data, yet the central implications and potential applications outlined below should be basically unaffected.

In the way described above, the parameter values of \( \varepsilon \) and \( \sigma \) as functions of the particle diameter have been tabulated into graphic forms, as sketched in Fig. 6. When cast into reduced forms as suggested in Fig. 6, the results along with Eq. (2) are expected to be applicable to a range of nanoparticle species, given the set of parameters \((\varepsilon_0, \sigma_0)\) characteristic of a specific material that may, in principle, be systematically surveyed following the notion of cage as recommended earlier. The central implication is as follows: inasmuch as the constituting molecules can be properly “renormalized” to be described within the fundamental LJ 12-6 potential, Eq. (1), the potential law prescribed by Eq. (2) for bulk spherical nanoparticles would become universal. From this perspective, the vdW potentials governing a certain range of nanoparticle species would differ from each other only in the two underlying material parameters \((\varepsilon_0, \sigma_0)\)—akin to the classical correspondence theory stating that one requires only two fundamental parameters to fully characterize the thermodynamic properties of a single-component fluid system.

Another notable feature in Fig. 6 that had rarely been noticed for nanoparticle species is the emergence of a plateau in the well depth for particle sizes exceeding \( \sigma \approx 150 \text{ nm} \) (\( \sim 90 \text{ nm} \) for silica) when the effect of geometric curvature comes into play. Thus, particle attractions cannot be further increased with increasing particle diameter beyond this limit. This essential prediction, in fact, explains one’s usual impression that larger nanoparticles seem relatively nonsticky; it also provides a way the simulation might be attested against experimental data.

As a preliminary test, Fig. 7 compares the classical theory prediction with the simulation for a silica nanoparticle with \( \sigma = 50.5 \text{ nm} \) in vacuum. Aside from the divergence of the classical theory at small interparticle separations, the overall shape of the vdW potential is in reasonable agreement. Recall, however, that the precise shape of a vdW potential at small interparticle separations is crucial for under-
standing deeply bonded systems, such as colloidal gels. Besides, the simulation yields a definite value of the potential minimum and its precise location that are not readily accessible by classical theory predictions.

B. Thermodynamic transferability

Another important merit of the reduced formulation of Eq. (2) exploiting the parameters tabulated in Fig. 6 is that thermodynamic transferability to different system temperatures and pressures may be ensured automatically. Namely, one only needs to relocate the new set of \((\sigma_0, \epsilon_0)\) at a different system temperature and pressure. To gain some feeling about how these parameter values might be affected by the system temperature, for example, similar CGMD simulations as described earlier have been performed at two additional temperatures, i.e., 250 and 350 K. Simplex optimizations yield \((\sigma_0, \epsilon_0)_{250\text{ K}}\) = \((6.19\text{ Å}, 3.72\text{ KJ/mol})\) and \((\sigma_0, \epsilon_0)_{350\text{ K}}\) = \((6.20\text{ Å}, 2.68\text{ KJ/mol})\). As might be expected, the value of \(\sigma_0\) is insensitive to changes in system temperature while there are only moderate changes in \(\epsilon_0\) as the system temperature varies by as much as 100 K. In practice, therefore, it might be sufficient to evaluate the fundamental parameters at a representative system temperature and pressure.

C. Effect of interfacial properties

One might be astounded at the first sight of a vdW potential (particularly, the well depth) as predicted by Eq. (2) in light of typical colloidal sizes, say, 10 to 100 nm, that have customarily been studied in experiments and exploited in the daily life. In these commonplace systems, in fact, the bare, strong vdW forces are usually superposed with other interaction potentials rather than interacting directly,3–6 such as the cases with charged or sterically stabilized colloids. To shed light on their influences on the interparticle attraction, we consider the colloidal particles grafted with polymer chains. In this particular example, it has been well known that the interparticle attractions can be fine-tuned by systematically varying the system temperature or, more precisely, the solvent quality of the grafted polymer. By treating the grafted chains as a purely repulsive uniform shell medium for the sake of simplicity, Eq. (2) may be modified with a known (temperature- or concentration-dependent) shell thickness, \(\Omega\),

\[
U(r) = 4\epsilon_0 \left[ \left( \frac{\sigma + \Omega}{r} \right)^{2\alpha} - \left( \frac{\sigma}{r} \right)^{\alpha} \right].
\]

Similarly, the parameter \(\Omega\) may be reduced with respect to \(\sigma_0\) in general applications.

Figure 7 also includes the predictions of Eq. (3) by systematically varying the value of \(\Omega\) from 2 to 10 Å. One notices that the presence of a tiny shell has an extraordinary screening effect on interparticle attractions. In particular, a shell thickness about 5 Å suffices to bring the well depth down to the range typically observed for attractive colloidal systems, i.e., a few \(k_B T\). A shell thickness about 1 nm further reduces the well depth to below 1 \(k_B T\) when the nanoparticles become only weakly attractive. Historically, colloidal nanoparticles have been utilized as an atomic analog to facilitate experimental studies of fundamental particle interactions and phase phenomena. In this respect, the present simulation results have lent evidence supporting such an analogy, provided that the strong vdW forces between two colloidal particles have been adequately blocked with proper interfacial modifications. It is also worth noting that the predictions of Eq. (3) could differ substantially from those of the often employed, low-powered LJ potential functions exploiting an adjustable, phenomenological well depth.

As has been noted earlier, the effective interaction range of silica nanoparticles is basically controlled by the elementary CG particle, \(\text{Si}_6\text{O}_{12}\). Thus, silica nanoparticles would behave like hard-sphere particles with a shell thickness about 2 to 3 \(\sigma_0\), or equivalently 1.2 to 1.8 nm, largely independent of the particle size or shape. In this way, the simulation may offer clear guidelines of preparing experimentally interesting hard-sphere colloidal particles made of specific materials. Indeed, we have noticed a close agreement in this implied interaction range with early experiments on the glasses formed by controllably attractive core-shell particles40–43 if the polymer latexes considered possess a similar magnitude of \(\sigma_0\) as presently found with amorphous silica. In passing, a relatively short interaction range disclosed here would imply that the “retardation effect” due to a finite propagation speed of electric waves should, in general, be unimportant for nanoparticle species in any media.3–6 As the effects of dispersing media are concerned, a straightforward modification of Eq. (2) or Eq. (3) making use of the ratio of effective Hamaker constants for the particle species and the dispersing medium, respectively, might provide a fair approximation at the present stage.3–5

Finally, we note that the results shown in Fig. 7 have also confirmed that the predicted pair interaction potentials are basically unaffected by the building particles chosen. Thus, appropriate children CG particles may, in principle, be adopted as the building units in constructing the pair interaction potentials of nanoparticles assuming arbitrary sizes and shapes, as depicted in Fig. 8. For instance, the potential functions for even larger nanoparticles (i.e., for \(\sigma > 100\text{ nm}\)) may be easily constructed using larger children CG particles as the packing units. For the cases with aspherical particles, such as those depicted in Fig. 8, the choices of...
plausible packing units—single-component or hybrid—should also be subject to the desired aspect ratios, and the resultant pair interaction potentials might be computed in a similar fashion and cast into plausible semiempirical potential functions, such as the Gay–Berne potential, which has found widespread applications for small aspherical molecules.

IV. CONCLUSION

Considering amorphous silica nanoparticles as a benchmark example, we have evaluated a potential pathway of utilizing multiscale simulation schemes to systematically construct the vdW interaction potentials over a wide range of particle diameters (i.e., 0.62–100 nm). The key step is the identification of plausible packing molecules or the so-called elementary CG particles—a task that has been challenged by the fact that amorphous materials lack definite repeating units. To overcome this prime challenge, we discussed strategies that might be utilized to systematically survey potential CG candidates for constructing the simplest model nanoparticles. The Si$_6$O$_{12}$ molecule so identified for silica nanoparticles bears an ideal size (∼0.60 nm) and shape (overall spherical) and has proven successful in producing two distinct bulk material properties known for amorphous silica in AMD simulations. On this ground, we suggested a similar procedure for future applications with other amorphous nanoparticles by exploiting a series of spherical cages comprising the supramolecules of interest to be systematically tested in AMD simulations. The success up to this stage would imply the possibility of utilizing a simple, single-component CG system for the later numerical computation of the pair interaction potentials between two large nanoparticles packed by the CG particles.

With the elementary CG particle, Si$_6$O$_{12}$, well described within the fundamental LJ 12-6 potential, the pair interaction potentials for bulk silica nanoparticles falling in the size range of 0.62–100 nm have been computed and fitted to a semiempirical, generalized LJ $2\alpha-\alpha$ potential, with $\alpha$ being a size-dependent, large integral number that helps tune the width of the potential well. In its reduced form, we further remark on how the major results obtained for silica nanoparticles might, in principle, be applied to a variety of amorphous nanoparticle species and, moreover, how thermodynamic transferability to different system temperatures and pressures may be ensured automatically. In light of future applications with colloidal suspensions, we have also briefly examined the resultant vdW potential with modified interfacial properties that grossly mimic the screening effects of electrical double layers or grafting materials atop the nanoparticle core. The general observations shed new light on strategies to attain a microscopic control over interparticle attractions.

Besides the apparent merits and specific applications discussed in the main text for a microscopic, multiscale modeling of nanoparticle interactions, the following perspectives seem worthy of further pursuing in light of the long-term applications. Firstly, experimental data on the pair interaction potentials of well-characterized nanoparticle species in a vacuum environment—or in equivalent, more convenient form—will be necessary to corroborate the results of a multiscale computation; the impact of specifically chosen single-component packing units may also be systematically evaluated then. Secondly, an appealing outlook on performing similar multiscale simulations for nanoparticles or other macroscopic objects is that it shall help bridge the current gap between the modeling of polymer chains and macroscopic objects. For instance, with the packing units of a colloidal particle or solid boundary selected to be of size in accord with the level of coarse-graining of a polymer chain, the interactions between these two can be simulated in a consistent and faithful way. Finally, modeling nanoparticles of more ordered structures is certainly worthy of pursuing in a properly extended context.

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