Universal Nonsingular van der Waals Potentials

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Universal spherical nonsingular van der Waals interactions are developed through considering the effects of finite molecular size. The frequency integration upper limit of this interaction has been determined for the first time to be on the order of 10^{18} rad s^{-1} regardless of the intermolecular separation. This potential has been tested successfully for the following representative systems: H_2 ($^3\Sigma$), He_2, NaK ($^3\Sigma$), and LiHg.

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The van der Waals interaction plays an important role in a host of phenomena such as adhesion, physical adsorption, and wetting. The dispersion component of this interaction is usually the dominant contribution and is the only contribution for neutral nonpolar systems. Because of its smallness, the direct *ab initio* calculation of the dispersion energy requires very complex time-consuming configuration interaction calculations, which have only been successfully carried out for a few systems such as H(1S)-H(1S) and He-He. The semiempirical approach is more favorable since such constructed potentials are theoretically correct at long range and at short range, and are possibly able to describe the "intermediate region" interaction correctly.

The widely used semiempirical van der Waals potential is $V(R) = Ae^{-\mu R} - C_6/R^6 - C_8/R^8 - C_{10}/R^{10}$. The short-range exponential repulsive term is largely due to exchange as well as electrostatic forces and can be determined fairly accurately, for example, by SCF (self-consistent-field) calculations. However, the long-range attractive terms, obtained from the asymptotically ($R \rightarrow \infty$) correct *ab initio* dispersion series, are usually problematic around the van der Waals minimum, the region of interest. For example, even though the above model with SCF values for A and μ and theoretical values for C_6, C_8, and C_{10} was able to predict the experimentally available rare gas dimer well parameters to within a few percent [1], it gives purely attractive interaction with no potential minimum for the alkali-atom–rare-gas systems. This indicates the inappropriate use of the asymptotically correct attractive interactions in the region around the van der Waals minimum.

The divergence problem inherent in the dispersion point-multipole expansion and the short-distance singular behavior for each term in the expansion series have long been noticed by Brooks [2], Roe [3], and Dalgarno and Lewis [4]. Various efforts have been made to solve this short-distance singular behavior from both first principles and semiempirically [5–9]. Partial success has been reached and considerations are limited to the nonretarded region. The purpose of this Letter is to derive a nonsingular attractive interaction which includes retardation effects and is correct at least around the van der Waals minimum, and for larger intermolecular separation. Therefore this new attractive potential can replace the above, only asymptotically correct, attractive terms so that the resulting potential can be used universally.

Mahanty and Ninham were probably the first to use the semiclassical field approach of Casimir and Polder [10,11] to consider the finite molecular size effect [12,13]. They took a Gaussian form of the polarizability density simply for mathematical convenience. As a result, their retarded potential is very complicated and it is very hard to go beyond the dipole-dipole interaction. This is probably the reason that Richardson [14] later generalized only nonretarded interactions for higher multipoles. The semiclassical field approach follows the physically intuitive description of dispersion forces. Consider the interaction between two molecules as an example. The variable electric field produced by the instantaneous dipole in one molecule acts on the other, therefore, polarizing it. Using the linear (quantum) response theory [15], the Fourier component of the polarizability density tensor with the consideration of the effects of finite molecular size can be expressed [13] as

$$\boldsymbol{\alpha}_n(\vec{k}, \omega) = -\frac{e^2}{\hbar} \times \sum_q \left(\frac{\langle n|\vec{r}\,|\,q\rangle\langle q|e^{i\vec{k}\cdot\vec{r}}\,|\,n\rangle}{\omega_{nq} + \omega} + \frac{\langle q|\vec{r}\,|\,n\rangle\langle n|e^{i\vec{k}\cdot\vec{r}}\,|\,q\rangle}{\omega_{nq} - \omega} \right) \frac{i\vec{k}}{k^2}, \quad (1)$$

where $\omega_{nq} = (E_n - E_q)/\hbar$, $|n\rangle$ usually stands for the unperturbed molecular ground state, and $|q\rangle$ the possible unperturbed molecular states. If more than one electron is involved, the position vector $\vec{r}$ and $e^{i\vec{k}\cdot\vec{r}}$ in Eq. (1) should be understood as $\sum \vec{r}_i$ and $\sum e^{i\vec{k}\cdot\vec{r}_i}$, respectively. From electrodynamics, we know that once a time-varying polarization is present, there is a current associated with it. Therefore the electromagnetic field surrounding one molecule must be changed relative to that when the molecule is isolated. In other words, the electromagnetic wave spectrum must be shifted in some fashion. This shift can be determined by solving the corresponding Maxwell equations with this current as the source and by choosing the Lorentz gauge. As in the Drude model, the sum of the

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frequency shifts multiplied by the Planck constant for the entire spectrum of the two-molecular system must give the dispersion interaction energy of the system. As a preliminary investigation, we focus here only on the dipole-dipole dispersion interaction. This interaction including retardation can be written [13], in general, as

$$V(R) = -4\pi\hbar \int_{-\infty}^{\infty} d\xi \, \mathrm{Tr}\{\mathbf{G}_2(\vec{R}_1, \vec{R}_2; i\xi) \cdot \mathbf{G}_1(\vec{R}_2, \vec{R}_1; i\xi)\}, \tag{2}$$

where R is the center-to-center distance of the two molecules, $\vec{R}_1$ and $\vec{R}_2$ are the center position vectors of the two molecules, respectively, and

$$\mathbf{G}(\vec{r}_1, \vec{r}_2; i\xi) = \frac{1}{(2\pi)^3} \int d^3k \frac{(\xi^2/c^2)\,\mathbf{I} + \vec{k} \cdot \vec{k}}{\xi^2/c^2 + k^2} e^{i\vec{k}\cdot(\vec{r}_1 - \vec{r}_2)} \times \int d^3u \, \boldsymbol{\alpha}(\vec{u}, i\xi) \, e^{-i\vec{k}\cdot\vec{u}}, \tag{3}$$

where c is the speed of light and $\mathbf{I}$ is the unit tensor. Note that the polarizability density tensor (PDT), $\boldsymbol{\alpha}(\vec{r}, i\xi)$, depends on both position vector and frequency. It is clear from Eqs. (2) and (3) that once the PDT is known, the potential can be obtained simply by performing a few integrations. Our job is to find a general spherical-symmetric PDT for atoms and small molecules. The detailed derivation is given in [16]; here we simply state the necessary steps to lead to the general PDT. Applying Eq. (1) to the hydrogen atom, the only one whose Schrödinger equation can be solved exactly and analytically, we end with

$$\boldsymbol{\alpha}(\vec{r}, \omega) = -\frac{e^2}{\hbar} \mathbf{I} e^{-r/a_0} \sum_{q \geq 2} \frac{f_{1q} G_{q-1}(r/a_0)}{\omega_{1q}^2 - \omega^2} e^{-r/qa_0}, \tag{4}$$

where a_0 is the Bohr radius, $G_{q-1}(r/a_0)$ is a $(q-1)$th-order polynomial of variable r/a_0, and f_{1q} is a constant. In reaching Eq. (4), the specific properties used are purely from the angular part of entire wave functions and some residue theorems are frequently used. The distance damping effect is dominantly controlled by the exponential factor $\exp(-r/a_0)$ in front of the sum in Eq. (4), which is the one in the ground state wave function. For example, as $r \gg a_0$, that $\boldsymbol{\alpha}(\vec{r}, \omega)$ goes to zero is dominantly controlled by this exponential. As $r \sim a_0$, the polynomial $G_{q-1}(r/a_0)$ is almost a constant compared to various exponential factors in Eq. (4), and the exponential factors within the sum in Eq. (4), except for the first few q's, can essentially be taken as 1. For simplicity and universal purpose, a good approximation of Eq. (4) can be taken as

$$\boldsymbol{\alpha}(\vec{r}, \omega) = \mathbf{I} \frac{e^{-\beta r/a_0}}{8\pi(a_0/\beta)^3} \alpha(\omega). \tag{5}$$

The parameter $\beta = 1.2$ is introduced to account for the atomic size effect by taking the $(q = 5)$ exponential $\exp(-0.2r/a_0)$ out of the sum and combining it with the dominant $\exp(-r/a_0)$, and all r-dependent terms remaining within the sum are set to constants. Also,

$$\alpha(\omega) = -\frac{e^2}{\hbar} \sum_{q \geq 2} \frac{f_{1q} g_{q1}}{\omega_{1q}^2 - \omega^2}, \tag{6}$$

where g_{q1} is the collection of those constants and a possible normalization factor. From the above, we conclude that the distance damping effect to the PDT is determined by the exponential $\exp(-r/a_0)$ in the ground state wave function of the atom with a replacement of a_0, the Bohr radius, by a_0/β, the atomic size parameter. For other atoms, exact or even accurately correlated wave functions are, in practice, seldom available; only the fairly accurate Hartree SCF wave functions are easily accessible. The SCF wave functions, which are essentially the extension of the radial part of the hydrogen atom wave function to all the other atoms, satisfy just our needs. Since the radial part of the SCF wave function for any atom always has an exponential function similar to $\exp(-r/a_0)$ and the angular part is the same as that of the hydrogen atom, Eqs. (5) and (6) should also hold with a proper interpretation of the quantities in these equations for the corresponding atom. Similar arguments using molecular wave functions from molecular orbital theory lead to the same conclusion for small molecules too. For large molecules, due to the appearance of many centers of polarization and many-body effects, we postpone the study of this case to elsewhere. Following our recipe, one sees that Mahanty and Ninham's Gaussian form of the PDT corresponds actually to choosing a molecular ground state as a harmonic oscillator wave function. We emphasize that, unlike the situation in the point-multipole expansion, the correct electronic wave function must be used to correctly account for the finite molecular size effect, as indicated in [17].

So far we have proved that, to a good approximation, the following expression for the PDT is physically correct in general for atoms and small molecules:

$$\boldsymbol{\alpha}(\vec{r}, \omega) = \frac{1}{8\pi a^3} e^{-r/a} \mathbf{I} \alpha(\omega), \tag{7}$$

where a is the atomic or molecular size parameter and the frequency expression for $\alpha(\omega)$ looks similar to Eq. (6). The explicit potential follows from Eqs. (2) and (3) as

$$V(R) = -\frac{3\hbar}{2\pi R^6} \int_0^{\infty} d\xi \, \mathcal{V}(R, a_1, a_2; \xi), \tag{8}$$

where

$$\mathcal{V}(R, a_1, a_2; \xi) = \alpha_1(i\xi)\,\alpha_2(i\xi)\,e^{-2R\xi/c}\,[F(R, a_1; \xi)\,F(R, a_2; \xi) - F(R, a_1; \xi)\,G(R, a_2; \xi) - G(R, a_1; \xi)\,F(R, a_2; \xi) + 3G(R, a_1; \xi)\,G(R, a_2; \xi)], \tag{9}$$

with a_1 and a_2, the two atomic or molecular size parameters, respectively; and

$$
\begin{aligned}
F(R,a;\xi) &= \frac{1}{[1-(a\xi/c)^2]^2}\Bigg[\Bigg[1+\frac{R\xi}{c}-\left(\frac{R\xi}{c}\right)^2\Bigg]+\Bigg(\left(\frac{R\xi}{c}\right)^2\Bigg\{1+\frac{R}{2a}\Bigg[1-\left(\frac{a\xi}{c}\right)^2\Bigg]\Bigg\} \\
&\qquad -\Bigg\{1+\frac{R}{a}+\frac{R^2}{2a^2}\Bigg[1-\left(\frac{a\xi}{c}\right)^2\Bigg]\Bigg\}\Bigg)e^{-(R/a)(1-a\xi/c)}\Bigg], \qquad (10)\\
G(R,a;\xi) &= \frac{1}{[1-(a\xi/c)^2]^2}\Bigg(\Bigg[1+\frac{R\xi}{c}+\frac{1}{3}\left(\frac{R\xi}{c}\right)^2\Bigg] \\
&\qquad -\Bigg\{1+\frac{R}{a}+\frac{R^2}{6a^2}\Bigg[3-\left(\frac{a\xi}{c}\right)^2\Bigg]+\frac{R^3}{6a^3}\Bigg[1-\left(\frac{a\xi}{c}\right)^2\Bigg]\Bigg\}e^{-(R/a)(1-a\xi/c)}\Bigg).
\end{aligned}
$$

Looking at Eq. (9) as well as Eq. (10), one sees a common frequency factor $1/[1-(a_1\xi/c)^2]^2[1-(a_2\xi/c)^2]^2$, which is almost unity if both $a_1\xi/c$ and $a_2\xi/c$ are much less than 1. Equation (9) seems to go to infinity if both $a_1\xi/c$ and $a_2\xi/c$ approach 1. However, this is not the case if one looks at Eq. (10) carefully. The above discussion implies that this factor does not play a role in (9) unless $a_1\xi/c$ and $a_2\xi/c$ are much greater than 1. For example, if $a_1\xi/c$ and $a_2\xi/c$

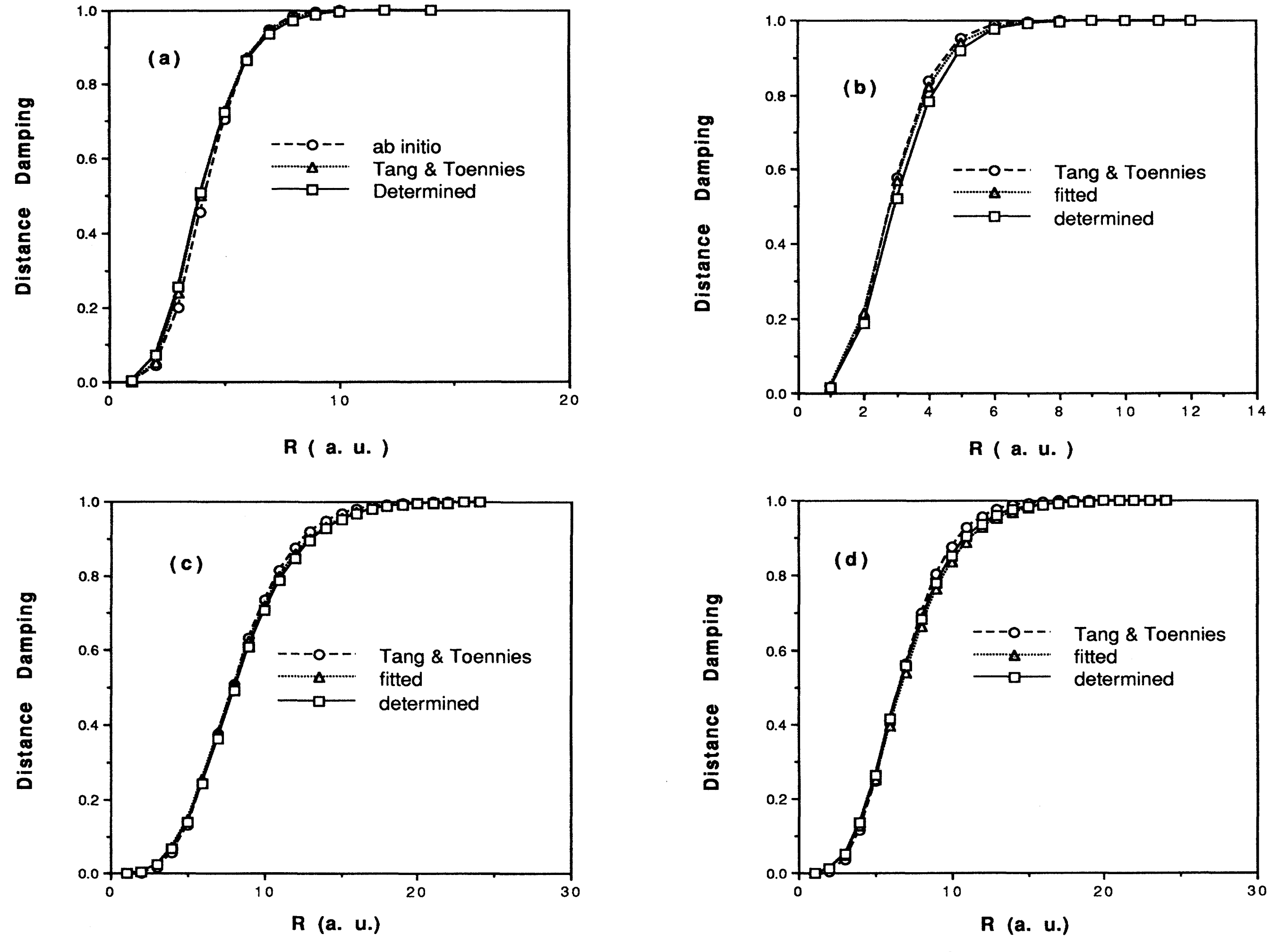

FIG. 1. Distance damping of $f_6(R)$ as a function of intermolecular separation R. (a) For H_2 ($^3\Sigma$), *ab initio* (Koide *et al.* [18]), Tang and Toennies [7] ($b = 1.67$ a.u.), determined (this paper with $1/a_H = 1.2$ a.u.). (b) For He_2, Tang and Toennies [7] ($b = 2.388$ a.u.), fitted (this paper with $1/a_{He} = 1.695$ a.u.), determined [this paper with $1/a_{He} = 1.2(I_{He}/I_H)^{1/2} = 1.614$ a.u.]. (c) For NaK ($^3\Sigma$), Tang and Toennies [7] ($b = 0.8414$ a.u.), fitted (this paper with $1/a_{Na} = 0.6454$ a.u. and $1/a_K = 0.56$ a.u.), determined [this paper with $1/a_{Na} = (I_{Na}/I_H)^{1/2} = 0.6147$ a.u. and $1/a_K = (I_K/I_H)^{1/2} = 0.565$ a.u.]. (d) For LiHg, Tang and Toennies [7] ($b = 1.012$ a.u.), fitted (this paper with $1/a_{Li} = 0.61$ a.u. and $1/a_{Hg} = 0.8758$ a.u.), determined [this paper with $1/a_{Li} = (I_{Li}/I_H)^{1/2} = 0.6297$ a.u. and $1/a_{Hg} = (I_{Hg}/I_H)^{1/2} = 0.8758$ a.u.].

take the value 10, the factor would be 10^{-8}, negligibly small. Therefore it is legitimate to set the frequency-integration upper limit in (8) as $\xi_0 = \max\{c/a_1, c/a_2\}$, which is on the order of 10^{18} rad s^{-1} by noticing that $c = 3 \times 10^{10}$ cm/s and $a \sim 10^{-8}$ cm. This is entirely consistent with the physically intuitive consideration that the energy involved in atomic and molecular phenomena is at most on the order of keV, i.e., x-ray energy, giving frequency 10^{18} rad s^{-1}. Further numerical study shows that Eq. (9) is negligibly small if the frequency ξ is greater than $0.5c/a$ regardless of the intermolecular separation R. To our knowledge, this is the first time that such a fact has been taken into account explicitly in the intermolecular potential. We stress that no such conclusion can be reached if either the nonretarded limit is taken ($c \rightarrow \infty$) or the molecular size parameters a_1 and a_2 are set to zero. The nonsingular nonretarded potential can be obtained from Eq. (8) by setting $c \rightarrow \infty$ in Eqs. (9) and (10) as

$$V(R) = -\frac{C_6 f_6(R)}{R^6}, \tag{11}$$

where $C_6 = (3\hbar/\pi) \int_0^{\xi_0} d\xi\, \alpha_1(i\xi)\, \alpha_2(i\xi)$, and the distance damping function $f_6(R)$ is

$$f_6(R) = \frac{1}{3} \prod_{j=1}^{2} \left\{ 1 - \left[1 + \frac{R}{a_j} + \frac{1}{2}\left(\frac{R}{a_j}\right)^2 \right] e^{-R/a_j} \right\} + \frac{2}{3} \prod_{j=1}^{2} \left\{ 1 - \left[1 + \frac{R}{a_j} + \frac{1}{2}\left(\frac{R}{a_j}\right)^2 + \frac{1}{4}\left(\frac{R}{a_j}\right)^3 \right] e^{-R/a_j} \right\}. \tag{12}$$

As expected, if both a_1 and a_2 are set to zero, Eq. (8) goes to the usual point dipole-dipole retarded potential while Eq. (11) goes to the famous London potential.

Noticing that the maximum peak frequency in $\alpha(\omega)$ is, in general, much less than the ξ_0 given before, the $R \rightarrow 0$ limit in both retarded and nonretarded potentials gives $V(R \rightarrow 0) = -C_6/72(a_1 a_2)^3$, finite as expected. As is well known, true dispersion energies are small in nature and are completely negligible at short intermolecular separation in comparison with the tremendously large repulsive energies. The above $R \rightarrow 0$ limit is merely used to show that the short-distance singular behavior inherent in the London potential is removed, and the potentials developed here are analytical and finite at all separation.

The comparison of our potential to those previously obtained is equivalent to that of the corresponding damping functions. This has been done for the following representative systems: H_2 ($^3\Sigma$), He_2, NaK ($^3\Sigma$), and LiHg, for which either nearly exact *ab initio* potentials [18] or the very successful semiempirical potential [7] are available. The parameter a in our damping function has been determined accordingly by the formulas given in [19] (atomic units are used). Except for the H_2 ($^3\Sigma$) system, a fitted curve is also given for each of the remaining systems. The fitted parameter a is within 5% of the corresponding above determined value. As shown in Figs. 1(a)–1(d), the very good agreement indicates the universality of the current potential, since the representative systems include four chemically different types of van der Waals interactions, giving interactions from very weak to very strong, and potential wells from very narrow to very wide.

In summary, a universal PDT with spherical symmetry, to a good approximation, has been determined, which is used to calculate nonsingular potentials for both retarded and nonretarded cases through a semiclassical field approach. The finite molecular size effect incorporated in the PDT is crucial to remove the short-distance singular behavior from the widely used potentials which are obtained from the point-molecular approximation. Very importantly, we are able to show, for the first time, that the frequency-integration upper limit of the van der Waals interaction is $0.5c/a$, instead of infinity.

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