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Low-energy universality and scaling of van der Waals forces

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At long distances, interactions between neutral ground-state atoms can be described by the van der Waals potential. In the ultracold regime, atom-atom scattering is dominated by s-waves phase shifts given by an effective range expansion in terms of the scattering length α_0 and the effective range r_0. We show that while the scattering length cannot be predicted for these potentials, the effective range is given by the universal low-energy theorem $r_0 = A + B/\alpha_0 + C/\alpha_0^2$, where A, B, and C depend on the dispersion coefficients C_n and the reduced diatom mass. We confront this formula to about 100 determinations of r_0 and α_0 and show why the result is dominated by the leading dispersion coefficient C_6. Universality and scaling extend much beyond naive dimensional analysis estimates.

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van der Waals (vdw) forces account for long-range dipole fluctuations between charge neutral atomic and molecular systems [1] with implications on the production of Bose-Einstein condensates of ultracold atoms and molecules [2]. vdw forces, however, diverge when naively extrapolated to short distance scales [3,4]. Fundamental work for neutral atoms was initiated in Refs. [5–7] (see also [8]), within a quantum-defect theoretical viewpoint. In this article we systematically show that these simplified approaches work and analyze *why* they succeed. vdw forces are extremely simple in this case and are described by the potential

$$V(r) = -\sum_{n=6}^{N} \frac{C_n}{r^n}, \tag{1}$$

where C_n are the vdw coefficients which are computed *ab initio* from intensive electronic orbital atomic structure calculations (see, e.g., Ref. [9] for a compilation). Usually, only the terms with $n = 6, 8, 10$ are retained, although the series is expected to diverge asymptotically, $C_n \sim n!$ [10]. The impressive calculation in hydrogen up to C_{32} [11] exhibits the behavior $C_n \sim (1/2)^n n!$ at relatively low n values. The potential (1) holds for distances much larger than the ionization length $l_I = \hbar/\sqrt{2m_e I}$ (I is the ionization potential), which usually is a few a.u. In the Born-Oppenheimer approximation the quantum mechanical problem consists of solving the Schrödinger equation for the two atoms separated by a distance r,

$$-u_k'' + U(r)u_k + \frac{l(l+1)}{r^2}u_k = k^2 u_k, \tag{2}$$

where $U(r) = 2\mu V(r)/\hbar^2$ is the reduced potential, $\mu = m_1 m_2/(m_1 + m_2)$ the reduced di-atom mass, $k = p/\hbar = 2\pi/\lambda$ the wave number, and $u_k(r)$ the reduced wave function. For our purposes, it is convenient to write the reduced potential in vdw units,

$$U(r) = -\frac{R_6^4}{r^6}\left[1 + g_1\frac{R_6^2}{r^2} + g_2\frac{R_6^4}{r^4} + \cdots\right], \tag{3}$$

where $R_6 = (2\mu C_6/\hbar^2)^{\frac{1}{4}}$ is the vdw length scale and g_1, g_2, etc., represent the relative contributions from the terms with C_8, C_{10}, etc., at $r = R_6$, respectively. In Table I we display numerical values for several diatomic systems which are extremely small in the vdw units $g_1 \sim 10^{-2}$ and $g_2 \sim 10^{-4}$ with the exception of H and He. Thus, we may anticipate a dominance of the C_6 term in the calculations at low energies, an *implicit* assumption in Refs. [5–7] and systematically quantified in what follows.

Using the superposition principle for positive energy scattering s-waves we decompose the general solution as

$$u_k(r) = u_{k,c}(r) + k\cot\delta_0(k)\, u_{k,s}(r), \tag{4}$$

with $u_{k,c}(r) \to \cos(kr)$ and $u_{k,s}(r) \to \sin(kr)/k$ for $r \to \infty$ and $\delta_0(k)$ the scattering phase shift for the $l = 0$ angular momentum state. The potential given by Eq. (1) is both long range and singular at short distances. At short distances, the De Broglie wavelength is slowly varying and hence a WKB approximation holds [3,4], yielding for $r \to 0$

$$u_k(r) \to C\left(\frac{r}{R_N}\right)^{\frac{N}{4}} \sin\left[\frac{2}{N-2}\left(\frac{R_N}{r}\right)^{\frac{N}{2}-1} + \varphi_k\right], \tag{5}$$

where $R_N = (2\mu C_N/\hbar^2)^{1/(N-2)}$ corresponds to the highest vdw scale considered in Eq. (1). The phase φ_k is in principle arbitrary. On the other hand, at low energies one has the effective range expansion [18]

$$k\cot\delta_0(k) = -\frac{1}{\alpha_0} + \frac{1}{2}r_0 k^2 + v_2 k^4 \log(k^2) + \cdots, \tag{6}$$

where α_0 is the scattering length and r_0 is the effective range which can be calculated from

$$r_0 = 2\int_0^\infty dr\left[\left(1 - \frac{r}{\alpha_0}\right)^2 - u_0(r)^2\right]. \tag{7}$$

Here, the zero-energy solution becomes, from Eq. (4),

$$u_0(r) = u_{0,c}(r) - u_{0,s}(r)/\alpha_0, \tag{8}$$

where $u_{0,c}(r) \to 1$ and $u_{0,s}(r) \to r$ for $r \to \infty$, yielding

$$r_0 = A + \frac{B}{\alpha_0} + \frac{C}{\alpha_0^2}, \tag{9}$$

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TABLE I. van der Waals length $R_6=(2\mu C_6/\hbar^2)^{1/4}$ and the coefficients g_1 and g_2 defined by the reduced dimensionless potential $2\mu V(r)R_6^2/\hbar^2 \equiv -x^{-6}[1+g_1x^{-2}+g_2x^{-4}+\cdots]$ with $x=r/R_6$. We use results from Refs. [12–17].

Atoms	R_6 (a.u.)	g_1 (10^{-2})	g_2 (10^{-4})
Li-Li	64.9214	1.424 58	2.978 74
Na-Na	89.8620	0.923 20	1.113 69
K-K	128.9846	0.647 80	0.497 84
Rb-Rb	164.1528	0.456 47	0.233 70
Cs-Cs	201.8432	0.365 44	0.139 83
Fr-Fr	215.0006	0.273 62	0.095 26
Li-Na	73.2251	1.256 05	2.171 83
Li-K	84.2285	1.183 74	1.796 89
Li-Rb	88.0587	1.185 72	1.705 55
Li-Cs	92.8950	1.213 64	1.682 41
Na-K	106.5708	0.806 00	0.801 55
Na-Rb	115.3377	0.745 28	0.659 23
Na-Cs	123.2277	0.738 74	0.611 48
K-Rb	142.8292	0.565 43	0.371 06
K-Cs	154.2909	0.539 03	0.321 52
Rb-Cs	180.8480	0.415 20	0.186 54
Be-Be	43.3013	2.549 53	6.703 03
Mg-Mg	72.3589	1.264 14	1.603 99
Ca-Ca	111.4907	0.845 84	0.650 57
Sr-Sr	148.9023	0.551 17	0.276 32
Ba-Ba	189.4340	0.416 92	0.152 60
Cr-Cr	91.2731	1.228 21	
H-H	10.4532	17.517 60	423.454 26
He-He	10.1610	9.359 37	117.946 42

with A, B, and C given by

$$A = 2\int_0^\infty dr\left(1-u_{0,c}^2\right), \tag{10}$$

$$B = -4\int_0^\infty dr\left(r-u_{0,c}u_{0,s}\right), \tag{11}$$

$$C = 2\int_0^\infty dr\left(r^2-u_{0,s}^2\right). \tag{12}$$

Then, combining the zero- and finite-energy wave functions, we get for any $r_c>0$

$$u_k'(r)u_0(r)-u_0'(r)u_k(r)|_{r_c}^\infty = k^2\int_{r_c}^\infty u_k(r)u_0(r)dr, \tag{13}$$

where r_c plays the role of a short-distance cutoff which is innocuous provided $l_I \ll r_c \ll R_n$. Using Eqs. (4), (5), and (8), we then get for $r_c \to 0$

$$\frac{1}{R_n}\sin(\varphi_k-\varphi_0) = k^2\int_0^\infty dr\left[u_{0,c}(r)-\frac{1}{\alpha_0}u_{0,s}(r)\right] \times [u_{k,c}(r)+k\cot\delta_0(k)\,u_{k,s}(r)]. \tag{14}$$

Orthogonality between u_k and u_0 requires $\varphi_k=\varphi_0$, in which case, expanding the integrand, we get the structure

$$k\cot\delta_0(k) = \frac{\alpha_0\mathcal{A}(k)+\mathcal{B}(k)}{\alpha_0\mathcal{C}(k)+\mathcal{D}(k)}, \tag{15}$$

where

$$\mathcal{A}(k) = \int_0^\infty dr\, u_{0,c}(r)u_{k,c}(r), \tag{16}$$

$$\mathcal{B}(k) = \int_0^\infty dr\, u_{0,s}(r)u_{k,c}(r), \tag{17}$$

$$\mathcal{C}(k) = \int_0^\infty dr\, u_{0,c}(r)u_{k,c}(r), \tag{18}$$

$$\mathcal{D}(k) = \int_0^\infty dr\, u_{0,s}(r)u_{k,s}(r). \tag{19}$$

The interesting feature of Eqs. (9) and (15) is that the dependence on the scattering length α_0 and the potential is explicitly disentangled. This is a universal form of a low-energy theorem, which applies to *any* potential regular or singular at the origin which falls off faster than $1/r^5$ at large distances. We can visualize Eq. (9) as a long-distance (vdw) correlation between r_0 and α_0. If the reduced potential depends on a *single* scale R, that is, $U(r)=-F(r/R)/R^2$, one gets *universal scaling relations*

$$\frac{r_0}{R} = \bar{A}+\bar{B}\frac{R}{\alpha_0}+\bar{C}\frac{R^2}{\alpha_0^2}, \tag{20}$$

where $\bar{A}$, $\bar{B}$, and $\bar{C}$ are purely geometric numbers which depend *solely* on the functional form of the potential.

For the pure vdw case, $V=-C_6/r^6$, the effective range has been computed analytically [6,7] and in harmony with the general structure Eq. (20) reads

$$\frac{r_0}{R_6} = 1.394\,73-1.333\,33\frac{R_6}{\alpha_0}+0.637\,318\frac{R_6^2}{\alpha_0^2}, \tag{21}$$

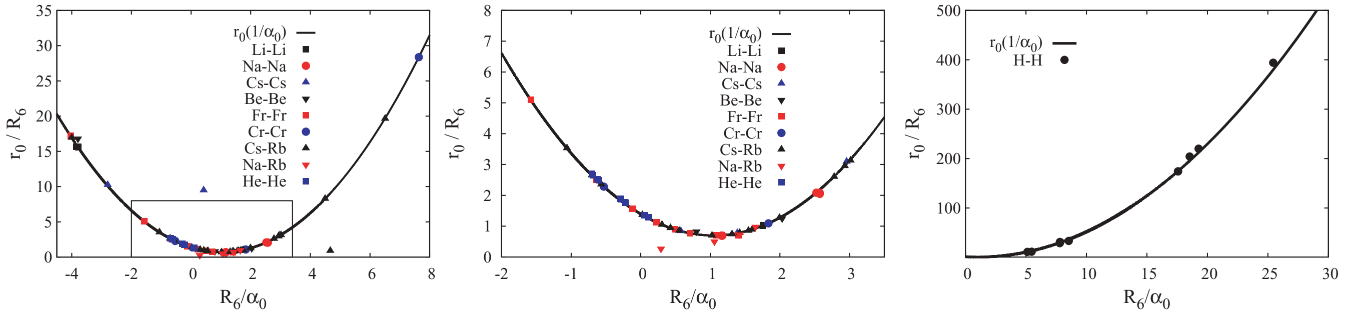

FIG. 1. (Color online) The effective range r_0 vs the inverse scattering length $1/\alpha_0$ in units of the vdw radius $R_6=(2\mu C_6/\hbar^2)^{1/4}$ for different ranges. Points are potential calculations: [19–21] (Li-Li, Na-Na), [22] (Cs-Cs), [23] (Na-Rb), [24] (Be-Be), [25] (Cs-Rb), [26] (Cr-Cr), [27] (Fr-Fr), [28–31] (H-H), [31] (He-He). The line corresponds to Eq. (21) [6,7].

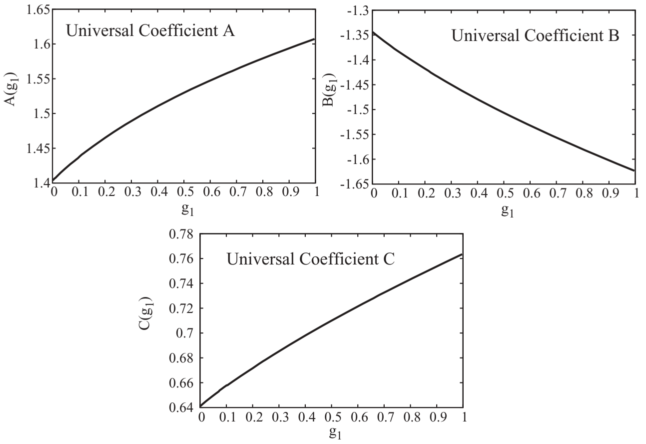

FIG. 2. The effective range coefficients A, B, and C [see Eq. (9)] as a function of the dimensionless coupling g_1 representing the $1/r^8$ correction to the vdw potential $1/r^6$.

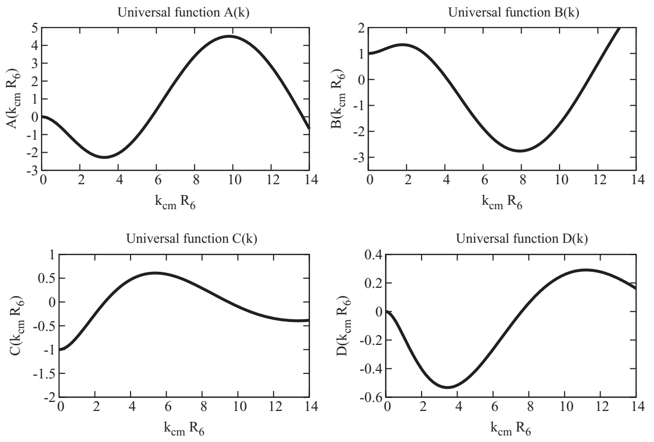

FIG. 3. The universal functions in units of R_6 defined by $2\mu V(r) = -R_6^4/r^6$, which make it possible to determine the phase shift if the scattering length is also known [see Eq. (15)].

In Fig. 1 we confront the prediction for the effective range to the result of many potential calculations in vdw units. As can be vividly seen, the agreement is rather impressive, taking into account the simplicity of Eq. (21). Alternatively, and discarding the exceptional outliers for α_0 and r_0, we perform a χ^2 fit to the form Eq. (20) for the remaining 82 points and get $A = 1.31$, $B = -1.57$, and $C = 0.66$, in good agreement with Eq. (21). As we see, Fig. 1 represents a universal correlation accurately supported by phenomenology when only the nonrelativistic $1/r^6$ potentials are considered.

We analyze the robustness of this agreement by showing in Fig. 2 the effect on the effective range coefficients, $A(g_1)$, $B(g_1)$, and $C(g_1)$ due to adding a $1/r^8$ term. From Table I we see that mostly $g_1 \sim 10^{-2}$, in which case tiny changes are expected from Fig. 2. Actually, the smallness of the deviations suggests using perturbation theory. If we expand the full solutions of the $1/r^6$ potential at small k, $u_k(r) = u_0(r) + k^2 u_2(r) + \cdots$, the change in the effective range due to inclusion of a $\Delta U(r) \sim 1/r^8$ potential keeping α_0 *fixed* reads [32,33]

$$\Delta r_0 = 4 \int_{r_c}^{\infty} \Delta U(r) u_0(r) u_2(r)\, dr, \tag{22}$$

where $r_c \sim g_1 R_6 \ll R_6$. The leading contribution is determined by the short distance behavior of $u_0(r)$ [see Eq. (5)], which acts as an inhomogeneous term for the equation satisfied by $u_2(r)$. We find $u_2(r) \sim (r/R_6)^4 u_0(r)$ yielding $\Delta r_0 \sim g_1 R_6 \log g_1 + \mathcal{O}(g_1)$. The logarithmic enhancement in g_1 can indeed be observed in Fig. 2 by the tiny curvature.

Of course, in obtaining α_0 itself, C_8 and C_{10}, as well as the short-range part of the atom-atom potential, become important in practice provided the latter is determined from low-energy data. However, *once* α_0 is given, r_0 is mainly determined by C_6 and α_0 only. For further illustration, we show in Fig. 3 the universal functions $\mathcal{A}(k)$, $\mathcal{B}(k)$, $\mathcal{C}(k)$, and $\mathcal{D}(k)$, which in conjunction with α_0 make it possible to determine the phase-shift from Eq. (15). They scale with R_6 and are uniquely determined by the power law $-1/r^6$ *once and forever*. We have found that these functions show little dependence on g_1 and g_2 at momenta as large as $kR_6 \sim 10$, a rather unexpected result, hinting that the vdw universality and scaling extend much beyond the naive dimensional analysis estimate $kR_6 \approx 1$ or the effective range expansion of Eq. (6) truncated with the first two terms. We note in passing that although such a truncation suggests a higher degree of universality, the vdw nature of the interaction prevents using (α_0, r_0) as fully independent variables in view of Eq. (21) and Fig. 1. In passing, it is interesting to notice that within a nuclear-physics context characterized by short-range Yukawa potentials stemming from meson exchange [34], the general Eq. (9) has been exploited as a means of checking SU(4) Wigner symmetry in the nucleon-nucleon interaction for the $^1S_0$ and $^3S_1$ channels with a pattern similar to Fig. 1. Actually, the renormalization limit analyzed there corresponds to take $r_c \to 0$.

We conclude by underlining that, when suitably displayed, the analytical approach to vdw forces pursued in previous works [6,7] acquires a quite universal character with indisputable phenomenological success; the leading $1/r^6$ contribution suffices to accurately describe low-energy atom-atom scattering with just two parameters in a wide energy range. We naturally expect new universality and scaling patterns to emerge from systems characterized by power law forces but less understood such as molecular interactions in the ultracold regime. From a broader perspective we stress that the lack of dependence of potential model calculations on short-distance details, unveiled from our systematic comparison, is a feature traditionally built in by the quantum-defect theory. Its natural counterpart of a smooth and controllable short-distance cutoff dependence complies with the requirement of renormalizability within a pure quantum-mechanical framework.

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