Microscopic Calculation of the van der Waals Interaction between Small Metal Clusters

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The nonretarded van der Waals coefficients C_6 and C_8 are determined for all pairs of neutral sodium microclusters with 1, 2, 8, 20, and 40 atoms. These small systems are described self-consistently within the jellium model and their multipole dynamical polarizabilities calculated making use of the time-dependent local density approximation. It is found that quantum size effects, in particular Landau fragmentation, play a crucial role in the determination of the coefficients. Furthermore, it is found that the coefficients are very insensitive to the internal temperature of the clusters, in the range of temperatures reachable experimentally. A discussion on the accuracy of the predicted values is given.

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The ubiquitous role played by the van der Waals interaction between atoms and molecules in the characterization of different properties of matter has resulted in an increasing interest in its study over the past three decades with applications to a wide variety of physical, chemical, colloidal, and biological systems (see, e.g., Refs. [1,2] and general references therein). Furthermore, with the recent synthesis of new, gas-borne, ultrafine particles [3,4], and of new forms of bulk matter [5], the van der Waals interaction is expected to become of extreme importance in the description of cluster-cluster collisions [6,7] and associated growth of atomic and molecular clusters [8], as well as in the characterization of relative orientation of clusters in bulk matter [9,10].

Recently, much experimental and theoretical interest has been concentrated on the electric interaction between small metallic particles [11]. In this context, most of the theoretical work has been carried out using classical electrodynamics to describe their dynamic polarizabilities (cf., however, Ref. [12]). However, it is by now established that quantum size effects (QSE) play a crucial role in many properties of these small metallic particles, in particular in what concerns their dynamical polarizability [13], a feature which, being absent in the classical treatment requires, *per se*, a quantum mechanical formulation.

In this paper, we carry out, for the first time, a fully self-consistent and microscopic calculation of the leading-order coefficients C_6 and C_8 of the van der Waals interaction between pairs of neutral microclusters. For definiteness, we shall take sodium as an example, and consider the interaction between all pairs of sodium clusters with 1, 2, 8, 20, and 40 constituent atoms. The microscopic calculation is paralleled with the corresponding calculation using the classical plasmon pole approximation, in order to evidence the role played by quantum size effects in the determination of the van der Waals coefficients. Because the microscopic model we use has been extensively used and successfully compared with available experimental results [14] we expect our predictions for the nonretarded van der Waals coefficients to be correspondingly accurate. Moreover, from the knowledge of the optical properties of these small systems, we discuss some general properties pertaining to these interaction coefficients.

The nonretarded electrostatic interaction energy between two clusters A and B, at a distance R large enough so that their charge densities do not overlap, can be written in the form [2]

$$\Delta E=-C_6^{AB}/R^6-C_8^{AB}/R^8-\cdots. \qquad (1)$$

In general, the coefficients C_k^{AB} contain information on the relative orientation of the two clusters. This situation is greatly simplified when the intervening clusters are spherical, as is the case for all clusters considered in this paper. Under these conditions they can be expressed [15], making use of the dynamic multipole polarizabilities $\alpha_L(\omega)$, by

$$C_6^{AB}=C^{AB}(1,1),\quad C_8^{AB}=C^{AB}(1,2)+C^{AB}(2,1)\,, \qquad (2)$$

with

$$C^{AB}(L_1,L_2)=\frac{(2L_1+2L_2)!}{\pi^2(2L_1)!(2L_2)!}\int_0^{+\infty}d\omega_1\,\mathrm{Im}[\alpha_{L_1}^A(\omega_1)]\int_0^{+\infty}\frac{d\omega_2}{\omega_1+\omega_2}\mathrm{Im}[\alpha_{L_2}^B(\omega_2)]\,. \qquad (3)$$

In the above equation, $\mathrm{Im}[\alpha_L^K(\omega)]$ stands for the imaginary part of the dynamic polarizability α of cluster K ($K=A,B$) and multipolarity L, evaluated at the real frequency ω. It is then clear that C_6^{AB} results from the dipole-dipole interaction between clusters A and B, C_8^{AB} results from the dipole-quadrupole interaction between these two clusters, etc. Since the determination of the van der Waals coefficients requires the calculation of the dynamic multipole polarizabilities of the different clusters, which are proportional to the electronic response of the cluster to an external perturbation of multipolarity L, the properties of these coefficients will depend crucially on the detailed features of the electronic response.

We determined the dipole ($L=1$) and quadrupole ($L=2$) dynamic polarizabilities of neutral sodium clusters, with 1, 2, 8, 20, and 40 atoms. We used the spherical jellium background model with the local density approximation (LDA) [16] for the description of the ground-state properties of sodium clusters, and the time-dependent LDA (TDLDA) [17] for the determination of the screened electronic multipole response [18]. The corresponding results are shown in Fig. 1 with solid lines. The left column contains the results for the dipole response whereas the right column contains the quadrupole dynamic polarizabilities. The arrows indicate the (size-independent) peak position of the dynamical multipole polarizabilities calculated in the plasmon pole approximation. In this approximation all the strength of the multipole response is concentrated in a single peak, and we may write [12]

$$\mathrm{Im}[\alpha_L(\omega)] = \tfrac{1}{2}\pi\omega_L R_0^{2L+1}\delta(\omega-\omega_L)\,, \tag{4}$$

with

$$\omega_L = \omega_p[L/(2L+1)]^{1/2}\,, \tag{5}$$

and

$$R_0 = r_s N^{1/3}\,, \tag{6}$$

ω_p being the bulk plasma frequency ($\hbar\omega_p = 5.89$ eV for sodium), r_s the Wigner-Seitz radius in atomic units (4 for sodium), and N the number of atoms in the cluster.

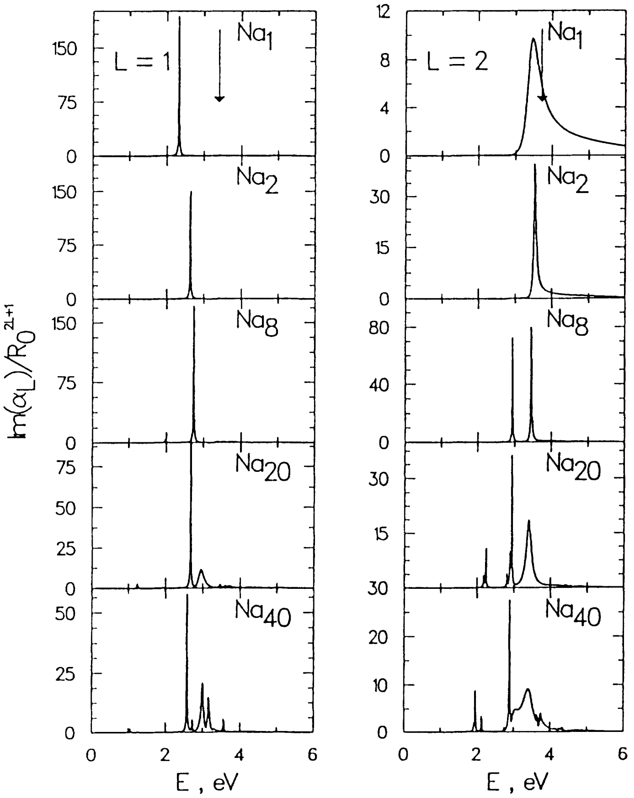

FIG. 1. Dynamical multipole polarizabilities of sodium microclusters. The dynamical dipole ($L=1$, left column) and quadrupole ($L=2$, right column) polarizabilities, divided by R_0^3 and R_0^5, respectively, are plotted as a function of $E=\hbar\omega$. The arrows indicate the (size-independent) position of the single peak corresponding to the plasmon pole approximation [cf. Eqs. (4)-(6)]. The sizable QSE present in the microscopic calculation induce large differences in the calculated values for the van der Waals coefficients.

As becomes clear from Fig. 1, there are large differences between the results of the microscopic calculation and the classical approximation, which will reflect upon the calculated values for the C_6 and C_8 coefficients. Indeed, the microscopic response evidences an overall redshift with respect to its classical counterpart, and also a sizable amount of Landau fragmentation, leading to the multipeaked structures displayed in Fig. 1. Both QSE have been detected experimentally (for $L=1$) by measuring the photoabsorption cross section of these small metallic systems [14], which clearly indicates that the plasmon pole approximation is inadequate for describing the response of these small clusters [19].

Once the dynamic polarizabilities have been determined, the van der Waals coefficients are obtained by direct integration of Eq. (3). The results are given in Table I. As expected, these results deviate strongly from the ones obtained using the classical approximation and leading to the simple following expressions for the interaction coefficients between clusters of the *same* species:

$$C_6 = (\sqrt{3}/4)\omega_p r_s^6 N_A N_B\,,$$

$$C_8 = \frac{15}{2(\sqrt{10}+\sqrt{12})}\omega_p r_s^8 N_A N_B (N_A^{2/3}+N_B^{2/3})\,.$$

Many of the present day experiments are carried out

TABLE I. Values for the van der Waals coefficients C_6 and C_8 (in eV a_0^6 and eV a_0^8, respectively) for the pair interaction between sodium clusters with 1, 2, 8, 20, and 40 constituent atoms, calculated making use of the microscopic model described in the text. For each entry, the first line gives the values for C_6 and the second line the corresponding values for C_8. The numbers follow the notation $2.49(4) = 2.49\times10^4$.

N	1	2	8	20	40
1	2.49(4) 1.88(6)	4.21(4) 3.97(6)	1.64(5) 3.33(7)	3.93(5) 1.38(8)	7.62(5) 4.17(8)
2		7.12(4) 8.08(6)	2.78(5) 6.17(7)	6.66(5) 2.47(8)	1.29(6) 7.33(8)
8			1.09(6) 3.59(8)	2.60(6) 1.25(9)	5.05(6) 3.41(9)
20				6.22(6) 3.92(9)	1.21(7) 9.98(9)
40					2.34(7) 2.40(10)

using free clusters with internal temperatures of several hundreds of kelvin. At these temperatures, the collective dipole excitations are sizably affected due to temperature-dependent processes such as those associated with fluctuations of the cluster surface and collisions with ionic phonons [20,21]. These mechanisms lead to a broadening of the associated line shapes, which can be simulated [20] by folding the electronic response (in which these damping mechanisms are clearly absent) with Gaussian functions with widths compatible with the magnitude of the relaxation mechanisms involved. A similar outcome is expected for the quadrupole response, even though the mechanisms may be different. On the other hand, and for this temperature range, the pattern of Landau fragmentation remains essentially unchanged, due to the fact that the energy gap between filled and empty shells is temperature independent [22] and much larger than the internal temperature. Therefore, and to the extent that the line broadening is smaller than the separation between the different peaks in the electronic response, we expect the van der Waals coefficients to be rather independent of the cluster temperature. Indeed, we confirmed this assumption by recalculating the C_6 coefficients for all pairs of clusters, for temperatures ranging from 100 to 500 K and including the temperature effects by folding the electronic response with Gaussian functions with widths in accord with the results of Ref. [23]. The largest variation found amounts to 0.05%.

We are unaware of any experimental data on sodium systems, except for restricted measurements on atomic sodium. The available experimental data have been combined with extensive atomic calculations in Ref. [24] to determine lower bounds of 4×10^4 eVa_0^6 and 2.9×10^6 eVa_0^8 and upper bounds of 13.6×10^4 eVa_0^6 and 5.5×10^6 eVa_0^8 for the coefficients C_6 and C_8, respectively (atomic sodium). While the results of Ref. [24] may be subject to revision (cf., e.g., Ref. [25]), in the sense that they are very sensitive to the input data which are not unambiguously established, the authors of Ref. [24] believe the true values for the C_6 and C_8 coefficients to be closer to the lower bound than to the upper bound, which is supported by our results. On the other hand, one should not forget that we described the sodium atom within the jellium plus TDLDA. This is surely an oversimplification turning out to be also one of the most unfavorable cases for the jellium model. In view of this, we expect our estimates for the interaction coefficients between larger clusters to be more reliable.

Finally, we would like to comment on the accuracy of our estimates. The comparison between the TDLDA results for the dipole polarizability and the experimentally determined photoabsorption cross sections [14] indicate that the TDLDA results are (for sodium) $\approx 7\%$ blueshifted with respect to the experimental ones. An energy shift of the TDLDA polarizabilities by $\approx 7\%$ will induce changes in the coefficients of the same order of magnitude. On the other hand, it is not clear from the available experimental data whether or not the pattern of Landau fragmentation is well reproduced at the level of TDLDA. Indirect support for our results comes, however, from recent calculations of the photoabsorption cross section of sodium microclusters making use of more realistic microscopic formulations [26] which lead to patterns of Landau fragmentation similar to the ones obtained with the TDLDA in the present paper.

To summarize, we carried out a fully microscopic, self-consistent, and parameter-free calculation of the nonretarded van der Waals interaction coefficients between pairs of sodium microclusters. QSE incorporated in the microscopic model and observed experimentally are crucial for the determination of these coefficients. Furthermore, the values of these coefficients are expected to be rather insensitive to the internal temperature of the clusters. Note, finally, that the application of this model to other metal clusters, not necessarily monovalent, which have been intensively studied recently, or to the calculation of higher-order van der Waals coefficients, poses no additional problem and requires no further ingredients. The same applies to the study of the van der Waals interaction between clusters of different atomic species.

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[13] We would like to point out that although QSE can be included in different microscopic schemes making use of, e.g., model potentials, it is essential that the dielectric properties of these small metal particles are computed in

a fully self-consistent manner. Indeed, only in this way the complex dynamical behavior of these systems is appropriately described [W. Ekardt *et al.*, Phys. Rev. B **33**, 3702 (1986)].

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