

Many-body effects of dispersion interaction

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The role of many-body (MB) dispersion forces have been analyzed for strands, films, and cubic lattices in the framework of a model Hamiltonian that allows exact solution of the multiparticle Shrödinger equation. For the systems investigated the MB contribution may be as large as 7% of specific dispersion energy and 11% of solvation energy. Nonadditivity becomes particularly important for aggregation in solution, where its effect may be several times larger than the pairwise contribution. For all systems considered, the three-body Axilrod-Teller approximation was insufficient to predict the magnitude and in some cases even the sign of the full MB effect. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337283]

I. INTRODUCTION

Dispersion forces together with electrostatic and exchange ones are crucial for intermolecular interactions. It is the dispersion attraction that allows formation of crystals and liquids of noble gases and nonpolar compounds, for example, hydrocarbons. Even in the case of polar liquids such as water, dispersion makes a significant contribution relative to orientationally averaged electrostatics. Dispersion also regulates the stability of carbon nanotube complexes with each other, and with fullerenes, molecular hydrogen, and so on.

In biophysics and chemical physics it has become routine to consider systems of 10^4 – 10^5 atoms, but such systems cannot be treated *ab initio*. A practical alternative consists in a phenomenological model for intra- and intermolecular interactions—the so-called force field.^{1–5} Model parameters are often fitted to *ab initio* calculated properties of small molecules and their dimers.^{1,2} The question of transferability to large systems arises here. It is well known, for example, that simultaneous description of H₂O dimer and liquid water requires explicit treatment of nonadditive effects of electronic polarizability.⁶ Another strategy is to fit the force field directly to experimental properties of neat liquids, crystals, and solvation free energies of small molecules.^{3–5} This type of models suffers from poor transferability on the cases of highly inhomogeneous environments such as liquid-vapor interface or protein-ligand complex in aqueous solution. As a rule, both types of force field neglect nonadditive dispersion effects. So the question of the many-body (MB) dispersion contribution is directly connected to the force field transferability from the training set.

The continuum approximation becomes valid when interacting bodies (macroscopic or microscopic) are separated enough relative to interatomic scale. In this approximation it is possible to formulate the general theory of the dispersion interaction⁷ including retardation and nonadditivity. However, the phenomena investigated in the present work are directly connected to the discrete nature of liquids and crys-

tals. Unfortunately, current electron structure methods are of limited help for the MB dispersion problem. Some of them, for example, the Hartree-Fock method of self-consistent field, completely neglect electron correlations and, consequently, dispersion. Similarly, it is well known how problematic the application of density functional theory is to dispersion driven molecular complexes. Reliable results can be achieved in the framework of the Møller-Plesset method, but high CPU and, particularly, memory requirements restrict its applicability to the systems of several tens of atoms.

The perturbation approach has become the most popular method to study the dispersion interaction. The main advantage of this approach, used already by London,⁸ is the possibility to obtain simple analytical expressions. For example, the Axilrod-Teller (AT) three-body potential⁹ was obtained in the triple-dipole approximation,

$$U_{\text{AT}}(ijk) = v_{ijk} \frac{1 + 3 \cos \phi_i \cos \phi_j \cos \phi_k}{r_{ij}^3 r_{jk}^3 r_{ki}^3}, \quad (1)$$

where ϕ refers to the inner angles of a triangle formed by the particles i , j , and k . The intensity v_{ijk} depends on the types of all three interacting particles. Almost all investigations of MB dispersion effects have been restricted to the AT approximation.¹⁰ The main disadvantage of this perturbation approach consists in the slow convergence for dense multiparticle systems.¹¹ The variational method of Slater and Kirkwood¹² should be mentioned for completeness, but it suffers from complicated trial functions.

A unique possibility to exactly solve the multiparticle Shrödinger equation is provided by the coupled fluctuated dipole model (CFDM). In CFDM, particles (atoms or molecules) are treated as three-dimensional harmonic oscillators, coupled by the dipole-dipole potential.^{13,14} CFDM was applied to study the interaction between nanoclusters¹⁵ and to reveal the dependence of dispersion damping in a medium on dielectric permittivity of the medium.¹⁶ CFDM is applied in the present work to study numerically MB effects in liquids, crystals, strands, and films. Additionally, the nonadditive dispersion contribution for solvation and aggregation in solution is studied.

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II. METHODS

Every particle in CFDM is treated as a three-dimensional harmonic oscillator with mass m_i and frequency ω_i . The oscillator equilibrium coincides with the center of the particle and is treated as a fixed parameter. Also, the particle possesses an instantaneous dipole moment $e_i \xi_i$ proportional to the oscillator displacement from equilibrium ξ_i . The CFDM Hamiltonian for an N -particle system may be written as (here and below $\hbar=1$)

$$H = -\frac{1}{2} \sum_{i=1}^N \frac{\nabla_{\xi_i}^2}{m_i} + \frac{1}{2} \sum_{i=1}^N m_i \omega_i^2 \xi_i^2 + \sum_{i>j=1}^N e_i e_j \xi_i \mathcal{T}_{ij} \xi_j,$$

where $\mathcal{T}_{ij} = (\mathcal{E} - 3r_{ij}r_{ij}/r_{ij}^2)/r_{ij}^3$ is the usual dipole-dipole interaction tensor (\mathcal{E} stands for the unit matrix). After substituting $\chi_i = \sqrt{m_i} \xi_i$ and introducing the polarizability $\alpha_i = e_i^2/(m_i \omega_i^2)$, the Hamiltonian may be rewritten as

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_{\chi_i}^2 + \frac{1}{2} \sum_{i=1}^N \omega_i^2 \chi_i^2 + \sum_{i>j=1}^N \omega_i \omega_j \sqrt{\alpha_i \alpha_j} \chi_i \mathcal{T}_{ij} \chi_j.$$

This form, in particular, shows that α_i and ω_i are convenient parameters to characterize the particle. Ground state energy W and interaction energy E can be expressed as

$$W = \frac{1}{2} \sum_{k=1}^{3N} \Omega_k, \quad E = W - \frac{3}{2} \sum_{i=1}^N \omega_i, \quad (2)$$

where Ω_k^2 are eigenvalues of symmetric $3N \times 3N$ matrix \mathcal{A} , containing N^2 blocks \mathcal{A}_{ij} of size 3×3 :

$$\mathcal{A}_{ii} = \omega_i^2 \mathcal{E}; \quad \mathcal{A}_{ij} = \omega_i \omega_j \sqrt{\alpha_i \alpha_j} \mathcal{T}_{ij}, \quad i \neq j. \quad (3)$$

The familiar nonretarded pairwise dispersion interaction results from perturbation expansion of (2) in the second order,¹⁴

$$E_L = -\frac{3}{2} \sum_{i>j=1}^N \frac{\omega_i \omega_j}{\omega_i + \omega_j} \frac{\alpha_i \alpha_j}{r_{ij}^6}. \quad (4)$$

For a pair of oscillators, higher order perturbation corrections are negligible (see below) for all physically meaningful separations and polarizabilities. Thus the deviation of exact interaction (2) from pairwise energy (4) can be used as an adequate measure of nonadditivity.

The third order perturbation correction results in the AT potential (1) with intensity

$$\nu_{ijk} = \frac{3}{2} \frac{\omega_i \omega_j \omega_k (\omega_i + \omega_j + \omega_k)}{(\omega_i + \omega_j)(\omega_j + \omega_k)(\omega_k + \omega_i)} \alpha_i \alpha_j \alpha_k. \quad (5)$$

Convergence of results with growing system size is a crucial aspect of the condensed phase computational modeling. Periodic boundary conditions (PBCs) offer the usual way to accelerate this convergence. The generalized Ewald summation technique is used in this work for PBC treatment. Thus we have modified the dipole-dipole potential.¹⁷ Furthermore, interaction of the dipole with its own periodic images results in a shift of oscillator frequency. Also, PBC

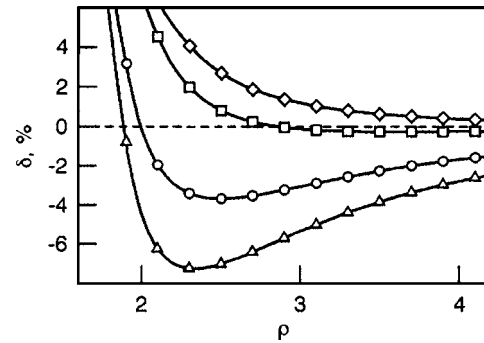


FIG. 1. MB dispersion contribution δ as a function of dimensionless nearest neighbor separation ρ for systems of identical particles: linear chain of 1000 atoms (\diamond), square lattice 30^2 (\square), simple cubic lattice 10^3 with PBC (\circ), and face centered cubic lattice 4×7^3 with PBC (\triangle).

modify the pairwise energy dependence on the interparticle separation.¹⁸

III. RESULTS

A. Systems of identical particles

Let us apply CFDM to investigate the role of MB dispersion forces in homogeneous systems of identical particles. First, a linear chain with constant step will be considered as a model for strands. The next system is the square lattice in the plane as a model for films. Finally, we will consider three cubic lattices: simple cubic (sc), volume centered cubic (vcc), and face centered cubic (fcc). As a measure of the multiparticle contribution to the interaction energy, it is convenient to introduce

$$\delta = E/E_L - 1. \quad (6)$$

Due to homogeneity and symmetry of the considered systems, δ turns out to depend only on the number of interacting particles and a dimensionless parameter

$$\rho = R/\alpha_m^{1/3}, \quad (7)$$

where R is the distance to the closest neighbor and α_m is the particle's polarizability. The typical range of ρ values can be estimated, for example, by specific molecular volume in simple liquids under atmospheric pressure divided by mean molecular polarizability. For sc lattice this procedure results in the following ρ values: methane, 2.95; ethane, 2.80; methanol, 2.79; water, 2.75; acetone, 2.70; benzene, 2.44; and phenol, 2.38. Thus the interval of primary importance is $2.3 \leq \rho \leq 3.0$.

Results of numerical calculations of systems of identical particles are presented in Fig. 1. Open boundary conditions were used for calculations of the linear equidistant chain and square lattice, while PBC were used for cubic lattices. It is seen from the figure that in the case of a linear chain, nonadditivity makes a negative contribution to the energy ($\delta > 0$) and hence strengthens dispersion attraction. The magnitude of δ monotonically decreases from 4.1% at $\rho=2.3$ to 1.2% at $\rho=3.0$. For a square lattice, MB intensification also takes place over almost the whole practically relevant range of distances, although much smaller compared to a linear chain. But near $\rho=2.9$ the nonadditive contribution changes

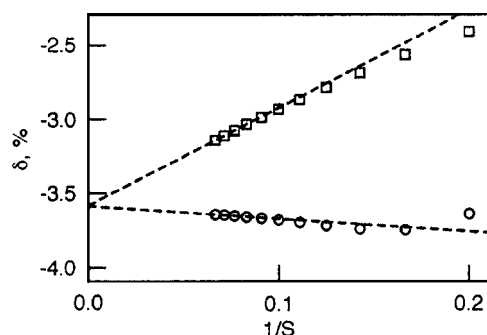


FIG. 2. MB dispersion contribution δ as a function of unit cell size of a simple cubic lattice $S \times S \times S$ at $\rho=2.5$ with open (\square) and periodic (\circ) boundary conditions. Linear extrapolations to the limit $S \rightarrow \infty$ are shown.

sign and achieves its minimum value -0.26% at $\rho=3.6$. In the case of cubic lattices, MB forces prove to be repulsive for all $\rho > 2.0$. Deviation from the pairwise result achieves the extremum $\delta(2.5)=-3.7\%$ for sc, $\delta(2.3)=-7.0\%$ for vcc, and $\delta(2.3)=-7.2\%$ for fcc lattices. Hence, there exists a correlation between nonadditivity and the number of closest neighbors in the lattice: 6 for sc, 8 for vcc, and 12 for fcc. The results for the vcc and fcc cases are close, so only the latter is presented in Fig. 1. For a pair of oscillators, δ is an order of magnitude smaller compared to the multiparticle systems: $\delta(2.3)=0.64\%$ and $\delta(3.0)=0.13\%$. So the use of δ as a measure of the MB effect is justified.

The results for linear chain and square lattice presented in Fig. 1 are practically converged at the limit of an infinite system, while the cubic systems require additional investigation due to the moderate linear size achievable. Figure 2 presents calculated values of δ at $\rho=2.5$ for a simple cubic lattice of variable size S^3 up to $S=15$ with open and periodic boundaries. First we should note the almost linear dependence of δ on S^{-1} for both types of boundaries. This allows reliable extrapolation to the limit $S \rightarrow \infty$. Moreover, independent extrapolations for both series coincide with high precision and result in $\delta=-3.58\%$. Another important result is that the use of PBC improves by an order of magnitude the accuracy of the estimation of the thermodynamic limit. This is of great value because the calculation time is proportional to the S^9 . Thus it is preferable to use PBC for investigation of the energetic properties of spatial systems. But it should be noted that for very small unit cells $S \leq 3$, when periodic images of the same particle are not well separated, artifacts may appear. For example, PBC results in $\delta=+45\%$ for $S=2$, while open boundaries give the much more reliable estimate $\delta=-1.8\%$. A very similar picture to the one presented in Fig. 2 takes place for vcc and fcc lattices, and extrapolation gives at $\rho=2.3$ (location of extremum) $\delta=-6.88\%$ and $\delta=-7.15\%$, respectively.

From a practical point of view, it is very important to answer the question about the relative contribution of three-body forces in the whole MB effect. Application of formulas (1) and (5) to the systems of identical particles considered allows reproduction of the asymptotic behavior $\delta \propto \rho^{-3}$ at low number densities $\rho \geq 5$. It is evident that the AT potential alone is incapable of providing both for existence of the minimum in dependence of $\delta(\rho)$ and for the alternating-sign

TABLE I. The lower bound ρ_c of CFDM domain of applicability, and coefficients a and b in Eq. (8) and d in Eq. (9) at $\rho=2.5$ for linear chain (L), square lattice in a plane (P), simple cubic (sc), volume centered (vcc), and face centered (fcc) cubic lattices.

	L	P	sc	vcc	fcc
ρ_c	1.69	1.72	1.75	1.76	1.80
a	0.040	0.011	-0.056	-0.103	-0.110
b	0.009	0.015	0.020	0.027	0.031
d	0.026	0.034	0.042		

character of the MB effect. Calculations with the AT potential at characteristic points give the following results: $\delta(2.3)=1.6\%$ for the linear chain, $\delta(2.3)=-2.0\%$ for the square lattice, $\delta(2.5)=-6.5\%$ for sc, $\delta(2.3)=-14\%$ for vcc, and $\delta(2.3)=-15\%$ for fcc lattice. Comparison of these values to the full nonadditive values given above leads to the conclusion that fourth order and higher corrections are always attractive (increases δ) in conformity with results of work.¹⁵ Besides, more than three-body contribution is nearly twice larger than AT energy in the cases of linear chain and square lattice, and only half as large for cubic lattices. So the perturbation series converges very slowly (see also Ref. 15 for other examples).

It should be noted that CFDM fails for ρ less than some critical value ρ_c (see Table I) when imaginary Ω_k appear in (2). This is the so-called “polarization catastrophe.” The reason for the catastrophe is evident: neither the dipole-dipole approximation nor the assumption of a linear oscillator response to an external field are valid for very dense system.

B. Solvation

Modern force fields are expected to provide high accuracy in small molecule solvation modeling. The goal of this subsection is to estimate the MB contribution to the dispersion solvation energy. Let us consider a solvent as a lattice of identical particles with polarizability α_m , and a molecule of solute as a particle with polarizability α_1 ($\omega_1=\omega_m$ for simplicity). Our goal now is to calculate the change ΔE in dispersion energy after exchanging a solvent particle for a solute one. Pairwise London approximation (4) results in the simple relation $\Delta E_L \propto (\alpha_1 - \alpha_m)$. The MB correction turns out to be small in the investigated range $0 \leq \alpha_1/\alpha_m \leq 2$, and it is quite enough not go beyond the linear approximation,

$$\Delta E = \Delta E_L (1 + a + b\alpha_1/\alpha_m). \quad (8)$$

The a and b values for various lattices at $\rho=2.5$ are given in Table I. It is seen that nonadditivity makes up a few percent and can both increase the dispersion contribution to the solvation energy (linear and square systems) and decrease it (all cubic lattices). Quantity a also corresponds to the MB contribution in the energy of vacancy creation. And finally, a nonzero value of b is evidence of strong four-body and higher contributions to the effect (AT potential gives strictly $b=0$).

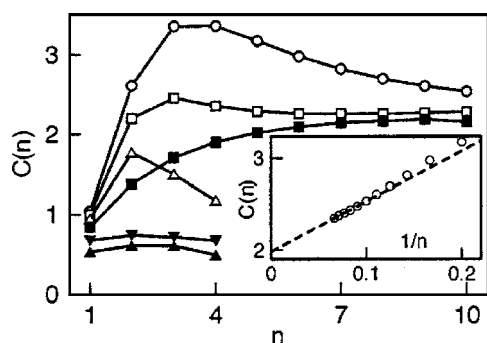


FIG. 3. MB strengthening/reduction of the dispersion interaction of an admixture of atoms in medium as a function of lattice separation n for linear chain (\circ); square lattice: directions $\{10\}$ (\square) and $\{11\}$ (\blacksquare); simple cubic lattice: directions $\{100\}$ (\triangle), $\{110\}$ (\blacktriangledown), and $\{111\}$ (\blacktriangle). For all lattices $\rho = 2.5$. Inset demonstrates asymptotic dependence for a linear chain.

C. Aggregation

The final task of this work is to estimate the nonadditive effect in the dispersion interaction of two particles immersed in medium. As done previously, medium is modeled by a lattice of identical oscillators with polarizability α_m and admixture by variation of the polarizabilities α_1 and α_2 for a pair of lattice points ($\omega_{1,2} = \omega_m$ for simplicity). Let us introduce the integer lattice distance n and the orientation $\{o_l\}$ as $\mathbf{r}_{12} = n \sum_l o_l \mathbf{u}_l$, where \mathbf{u}_l are lattice basis vectors. Dependence of the system energy V on the separation \mathbf{r}_{12} between admixture particles will be investigated. It is convenient to set the energy to zero at the configuration where impurities are as distant from each other (and their periodic images) as possible.

Pairwise London interaction results in expression

$$V_L = -\frac{3}{4} \omega_m \frac{(\alpha_1 - \alpha_m)(\alpha_2 - \alpha_m)}{r_{12}^6},$$

which is similar to Eq. (4), except that the factor $\alpha_1 \alpha_2$ is generalized by the construction $(\alpha_1 - \alpha_m)(\alpha_2 - \alpha_m)$. This result, relating polarizability and dielectric permittivity, completely agrees with results of continuum theory.⁷ Indirect dispersion interaction via medium can both assist and prevent aggregation.

Results of CFDM calculations can be presented in the following form:

$$V = V_L C(n) (1 + d\nu_1 + d\nu_2), \quad (9)$$

where $\nu_i = \alpha_i / \alpha_m$, d depends only on the lattice type and ρ , whereas C additionally depends on n and $\{o_l\}$.

In the case of the linear chain, there is only a possible orientation $\{1\}$. For the square lattice (two basis vectors) orientation $\{10\}$ and diagonal direction $\{11\}$ were considered. For simple cubic lattice (three basis vectors) orientation $\{100\}$, face diagonal $\{110\}$ and principal cube diagonal $\{111\}$ were investigated. For all listed orientations, calculations have been performed at $\rho = 2.5$ for $0 \leq \nu_i \leq 3/2$.

First, it should be mentioned that the value of d is small for all considered lattices (see Table I), and hence there is a relatively weak V dependence on ν_i . Much more pronounced is the variation of C value presented in Fig. 3.

In the absence of medium atoms between admixtures in the linear chain $C(1) = 1.04$, the MB effect is comparable to the corrections discussed above in the specific energy and solvation. But the situation changes radically when at least one medium atom separates impurities: already $C(2) = 2.61$, and at the maximum $C(4) = 3.37$. Thus, neglect of MB forces leads to an error of several times! Further increase of separation is accompanied with decrease of effect, and the relation $C(n) = 2.0 + 5.5/n$ is valid in the asymptotic region (see inset in Fig. 3).

A similar picture is observed for the $\{10\}$ direction in the square lattice, but this effect is significantly suppressed: $C(1) = 1.00$, and at the maximum $C(3) = 2.46$. In the asymptotic domain there is a saturation near $C \approx 2.2$. A different situation occurs for the $\{11\}$ direction. At contact MB forces reduce the interaction $C(1) = 0.84$ (although with increased ν_i the ratio V/V_L approaches unity). This can be explained by the existence for $\{11\}$ orientation even at $n=1$ solvent-solute pairs closer than solute-solute pair. C monotonically increases with n up to the value ≈ 2.2 (the local maximum at $n=9$ is most likely an artifact). It is interesting that at large separations the difference between the two directions disappears. It is important to note that reliable calculations of C values become possible only for PBC and for large size of the unit cell. The results presented have been obtained for a 50×50 system, but even in this case boundary effects appear as a slight nonregularity for $n \geq 8$. Elimination of PBC leads to energy dependence on the distance from admixture particle to the boundary, that is much stronger than the investigated dependence at $n \geq 4$.

In the case of the cubic lattice 15^3 with PBC, more or less reliable results were successfully obtained only for $n \leq 4$. For the $\{100\}$ direction $C(2) = 1.77$ at the maximum. We also note that $C(1) = 0.95$ and therefore the sign of the MB correction at $n=1$ essentially depends on the ν_i : nonadditivity strengthens the interaction at $\nu_1 + \nu_2 \gtrsim 3/2$. Directions $\{110\}$ and $\{111\}$ are characterized by significant MB weakening of the interaction: $C(1) = 0.68$ and $C(1) = 0.53$, respectively. By analogy with the square case, it is reasonable to suppose that orientation dependence will disappear for large n .

IV. CONCLUSION

The calculations carried out in the present work on systems of identical particles revealed an appreciable MB contribution to the specific dispersion energy. This contribution reaches 7% and can possess both repulsive and attractive character depending on the number density and geometry of the system. Nonadditivity strengthens the dispersion attraction in the case of linear chains and not too rarefied square lattices. For all cubic lattices in the physically based range of parameters, MB effects weaken the interaction. In the case of particles in medium, the nonadditive contribution to the solvation energy can be as much as 11%, and, by analogy with the specific energy correction, can change its sign depending on the lattice type modeling of the solvent. Most pronounced is the MB effect on the aggregation of particles immersed in

a solvent. In this phenomenon, nonadditivity can increase or decrease severalfold the energy dependence on the solute-solute separation.

Returning to the justification of pairwise approximation for dispersion in all modern general force fields, we can conclude that this approach is reliable in the case of neat liquids and ideal solutions. However, the simulation of aggregation in medium certainly requires accounting for the dispersion MB effects.

This paper demonstrates the insufficiency of the three-body Axilrod-Teller approximation to describe the full MB effect in real liquids and crystals. Higher contributions become comparable with AT correction. As a result, full and AT effects can actually have opposite signs.

In conclusion, it is worthwhile to outline ways to improve CFDM. First of all, it is possible to account for the diffused character of electron density in an atom and also exchange effects. The useful variant is the distributed dipole approach¹⁹ keeping the quadratic form of the Hamiltonian. Another direction is to account for the quadrupole-dipole and higher contributions to the dispersion interaction, which are, as is well known, comparable with the dipole-dipole one in the considered range of separations.²⁰ Unfortunately, the corresponding modification of the Hamiltonian prevents an exact solution of the Schrödinger equation. Finally, the possibility of a more realistic description for the polarization response of a particle in a strong external field should be mentioned, for example, in the framework of two-level model.²

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