

Collective dispersion forces in the fluid state

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Dispersion interactions lead to effective many body interactions which go beyond the approximation of pair potentials often used in modeling of materials. We introduce the full, quantum dispersion interaction in simulations of polarizable atoms, thus incorporating all multi-center van der Waals potentials. We sample the quantum degrees of freedom using a heat-bath algorithm adapted to the polarization fluctuations of individual atoms. We demonstrate asymmetric screening of interactions in a binary fluid.

Quantum mechanics is the ultimate explanation of many material properties; this is particularly clear at low temperatures for phenomena such as superfluidity. However even at room temperature the most important cohesive mechanism in molecular and soft condensed-matter has a direct quantum origin; this is the dispersion interaction, commonly called van der Waals forces [1]. This interaction has as its origin the coupled fluctuations of the electronic degrees of freedom [2] and gives rise to an effective potential which guides the nearly classical degrees of freedom of the centers of mass of atoms. In much numerical work these subtle quantum effects are modeled by a pairwise interaction in $1/r^6$.

This parametrization misses many important qualitative effects which occur in real materials. Multi-body screening implies that potentials derived in the gas phase are rarely transferable to condensed-matter [3]. Attempts to go beyond the pair approximation by including the three-body Axilrod-Teller interaction only partially capture these multi-body effects [4]. Modifications in the effective potential are also important in systems of low symmetry such as surfaces and interfaces (the Axilrod-Teller form is non-central) and also in cases of strong heterogeneity such as critical points where they lead to anomalies in the form of the coexistence curves [5].

In systems which contain several different atomic species the true interaction which arises from an integral over frequencies can exhibit quite complicated evolution as a function of environment due to the relative importance of different spectral features in materials. These subtle variations in potentials are undoubtedly crucial in understand the stability and fluctuations of many biomolecules [6]. Many phenomenological force fields mix the interaction parameters between different atoms in a rather crude manner by taking the the geometric mean (Berthelot mixing) of the interaction strength of the two pure systems.

If one moves slightly up in length scales the dispersion interaction between continuous media is calculated using Lifshitz theory [1]. Again experience has shown that collective, multi-body effects are crucial, even determining the sign of the final force. The cases where a full analytic theory is available is however limited to the simplest geometries such as parallel plates, spheres or cylinders.

Recent numerical work has shown how to apply Lifshitz theory to more complicated geometries [7–9]. These studies are based on factorization of interaction matrices, or calculation of the Maxwell stress tensor; they give accurate accounts of the interaction between bodies in a macroscopic continuum limit. In a number of geometries paradoxical effects have been found such non-monotonic variation of forces as a function of separation [10, 11] which go beyond those which might be expected from pair potentials. These methods however tell us very little about behavior at the atomic scale where structure and density are changing in a self-consistent manner in reaction to state-dependent potentials.

The purpose of our paper is the exploration of the properties of an atomic system with full summation of state-dependent dispersion energies in the non-retarded regime; we use a standard mapping onto a replicated classical system. These mappings have been used for the simulation of difficult quantum problems, such as the superfluid transition [12]. The novelty of the present paper lies in the manner which we simplify the general formulation in order to generate dispersion interactions. The fully-summed van der Waals interactions are generated by a Gaussian theory which can be sampled with efficient algorithms; non-linearities as a function of atomic position parametrize the strength of the couplings between the polarization degrees of freedom. We introduce a heat-bath Monte Carlo algorithm which resamples quantum paths in a single Monte Carlo trial.

Van der Waals interactions are best understood as due to the decrease in zero-point energy of coupled atomic degrees of freedom. In our simulations we generate dispersion interactions with a model of oscillators coupled by long-ranged dipolar interactions [13]. If the dipole moment of atom i is \mathbf{p}_i then the total potential energy is

$$V = \sum_i \frac{\mathbf{p}_i^2}{2\alpha_i} + \frac{1}{2} \sum_{i \neq j} \mathbf{p}_i T_{ij} \mathbf{p}_j \quad (1)$$

where α_i is the atomic polarizability of atom i . The dipole tensor is

$$T_{ij} = \frac{1 - 3|r_{ij}\rangle\langle r_{ij}|}{4\pi\epsilon_0 r_{ij}^3} \quad (2)$$

We then associate a kinetic energy with each dipole, $\dot{\mathbf{p}}_i^2/(2\alpha_i\omega_i^2)$ where ω_i is a characteristic frequency, and use path integral methods [12] to find the partition function. We find an effective classical action for the quantum system:

$$A = \int_0^\beta \left\{ \sum_i \frac{1}{2\alpha_i\hbar^2\omega_i^2} \left(\frac{\partial \mathbf{p}_i}{\partial \tau} \right)^2 + V(\tau) \right\} d\tau \quad (3)$$

The positions of the classical degrees of freedom intervene through the dipole couplings $T_{ij}(\mathbf{r}_{ij})$. If one works at zero temperature ($\beta = \infty$) and Fourier transforms eq. (3) one finds that the interaction between two identical atoms with $\alpha_i/r^3 \ll 1$ is

$$U = -\frac{3\alpha_i^2}{4} \frac{\hbar\omega_i}{(4\pi\epsilon_0 r^3)^2} \quad (4)$$

the London result for dispersion interactions.

This model of the dynamic properties of the coupled dipoles give a frequency dependent dielectric response dominated by a single pole. More sophisticated models can be built either using several coupled polarization variables for each atom but also including higher multipole fluctuations. Already, single pole models give rise to rich behavior in the presence of heterogeneous values of characteristic frequency ω_i ; behavior that is neglected in most parameterizations of molecular potentials. A pair of particles with characteristic frequency ω_1 in a background of particles ω_2 such that $\omega_1 \gg \omega_2$ interacts with the unscreened London form. If $\omega_1 \ll \omega_2$ the interaction is reduced by a factor $1/\epsilon_2^2$ where ϵ_2 is the static dielectric constant of medium 2 [4]. Even quite modest values of the dielectric constant, imply that the long-ranged component of the effective potential is substantially reduced compared with its vacuum value, or that assumed in simulations of molecular systems. This screening is only captured by the Axilrod-Teller potential when $(\epsilon - 1)$ is small. We also note that a direct evaluation of the Axilrod-Teller potential requires an effort $O(N^3)$ for N atoms and is rather cumbersome to work with in simulations.

In order to perform Monte Carlo simulation of a model including interactions of the form eq. (1) one could proceed by diagonalizing the interaction matrix using methods from linear algebra. The method would give the free energy of the quantum degrees of freedom in terms of the positions of the atoms; this gives the free energy of a single configuration in a time $O(N^3)$ with a complexity of N^4 per sweep for a Monte Carlo algorithm. Simple trials quickly lead to the conclusion that this method becomes unwieldy beyond 50 atoms, enough to study the thermodynamics of nano-clusters but not dense condensed-matter phases. If one is interested in the interactions of frozen clusters the method can be pushed much further, recent reports consider the interaction of static clusters of

several thousand atoms and confirm the difficulty of using a single energy description on multiple scales ranging from atomic to mesoscopic [14]; in this case only a few diagonalizations are needed to extract useful information. In our simulations of fluids we require 10^8 Monte Carlo steps (thus diagonalizations) to generate high statistics data on equilibrated fluids.

We discretize the action integral, eq. (3), with L time slices and define $\delta\tau = \beta/L$. We require $L > \hbar\omega_i/kT$ in order to sample correctly the quantum fluctuations. Standard derivations of path integral quantization replace the derivative with respect to τ in eq. (3) by a finite difference, which can then be transformed to Fourier space.

$$\left(\frac{\partial \mathbf{p}}{\partial \tau} \right)^2 \rightarrow \frac{(\mathbf{p}(\tau) - \mathbf{p}(\tau + \delta\tau))^2}{\delta\tau^2} \rightarrow \frac{2(1 - \cos \omega_n)}{\delta\tau^2} \tilde{\mathbf{p}}^2$$

where $\omega_n = 2\pi n/L$. This discretization has the advantage of simplicity, but expansion of the cosine function in powers of ω_n shows that there are corrections to the continuum limit at order ω_n^4 . An alternative is a discretization using interactions extending to several neighbors in the τ direction with coefficients chosen so that the expansion in frequency space is $\omega_n^2 + O(\omega_n^p)$, $p > 4$. Tests, Fig. 1, show that this indeed accelerates convergence to the continuum limit. We use such an improved discretization in our work with interactions out to $3\delta\tau$. For notational convenience let us regroup the L vectors $\mathbf{p}_i(\tau)$ into a single $3L$ -vector \mathbf{P}_i .

We now concentrate our attention on the contribution to the action from a single particle i , located at \mathbf{r} . We replace the integral in eq. (3) by a sum and extract the terms in \mathbf{P}_i from the resulting discretized action.

$$A_i = \frac{\mathbf{P}_i M \mathbf{P}_i}{2} - \mathbf{E}_i(\mathbf{r}) \cdot \mathbf{P}_i \quad (5)$$

where the sparse derivative matrix M has dimensions $3L$. We note that the matrix M is particularly simple in structure; it contains three banded and cyclic blocks. The local electric field is given by

$$\mathbf{e}_i(\tau, \mathbf{r}) = -\delta\tau \sum_{j \neq i} T_{ij} \mathbf{p}_j(\tau) \quad (6)$$

which can again be assembled into a single vector $\mathbf{E}_i(\mathbf{r})$.

Our Monte Carlo algorithm consists of a displacement of an atom together with a coupled heat-bath update of its polarization degrees of freedom. All of the polarization degrees of freedom of the test atom are described by eq. (5); the influence of other atoms on the test particle comes through the electric field $\mathbf{e}_i(\mathbf{r}, \tau)$. We thus avoid the diagonalization of the large interaction matrix discussed above. We find the equilibrium configuration of the polarization, $\mathbf{U}_i(\mathbf{r})$, in the external field from the equation $\mathbf{U}_i(\mathbf{r}) = M^{-1} \mathbf{E}_i(\mathbf{r})$. We then define a partial free energy

$$G_i(\mathbf{r}) = -\frac{\mathbf{U}_i(\mathbf{r}) \cdot \mathbf{E}_i(\mathbf{r})}{2} \quad (7)$$

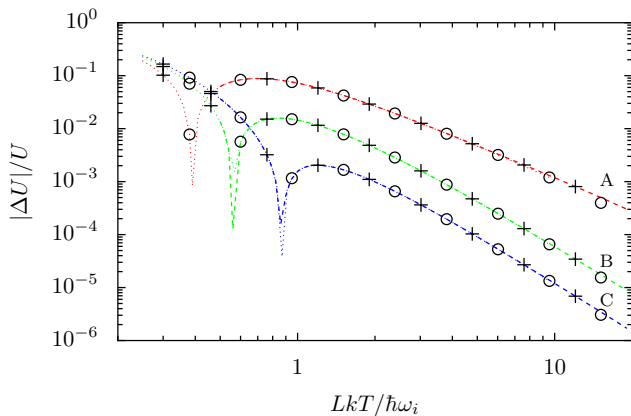


FIG. 1: Relative error in free energy for a cluster of 15 atoms for different discretizations of the time derivative. A: Second order discretization, $2(1 - \cos \omega_n)$. B: Fourth order discretization, $(15 - 16 \cos \omega_n + \cos 2\omega_n)/6$. C: Sixth order discretization, $(245 - 270 \cos \omega_n + 27 \cos 2\omega_n - 2 \cos 3\omega_n)/90$. In our simulations we use the form C with interaction to third neighbor in the τ direction. Data for $\hbar\omega_i/KT = \{100 +, 200 \circ\}$ superpose.

Consider now an “old” position of the atom, o , and a “new” position n and calculate the two free energies G_o and G_n for the atom i . We use these two partial free energies in a Metropolis criterion for the position of the atom in real-space, $p_m(o, n) = \min(1, e^{-(G_n - G_o)})$, where p_m is the probability of accepting the move from o to n . After the Metropolis choice we resample the polarization of the atom with $\mathbf{P}_i \rightarrow \mathbf{U}_i + R^{-1}\xi$ where R obeys $R^T R = M$ and ξ is a vector of $3L$ normal random numbers.

We now show that this choice respects detailed balance: At each position the statistical weight is given by $P = e^{-A_i(\mathbf{E}_i)}$. In both positions we generate $(\mathbf{P} - \mathbf{U})$ with relative probability $r(\mathbf{P}) = e^{-(\mathbf{P} - \mathbf{U})^T M (\mathbf{P} - \mathbf{U})/2}$. We find that the criterion for detailed balance is then

$$P(o) \times \pi(o \rightarrow n) = P(n) \times \pi(n \rightarrow o) \\ e^{-A_i(o)} \times p_m(o, n) r(\mathbf{P}_n) = e^{-A_i(n)} \times p_m(n, o) r(\mathbf{P}_o)$$

where π is the transition probability, exactly as required. The argument generalizes [15] so that we can add additional classical potentials to G_i . In particular our code includes a repulsive potential in $1/r^{12}$, or alternatively a hard-core repulsion.

It is interesting to calculate G_i for two widely separated particles, $\{a, b\}$ in a vacuum. The free energy for moving b in the presence of a configuration \mathbf{P}_a :

$$G_b = -\mathbf{P}_a T M_b^{-1} T \mathbf{P}_a / 2 \quad (8)$$

For large separations we average over an undisturbed ensemble for \mathbf{P}_a and find $\langle G_b \rangle = -\text{Tr}(T M_a^{-1} T M_b^{-1})/2$. This is exactly the London form eq. (4). In the low temperature limit, $\hbar\omega_i/kT \gg 1$, fluctuations in G_b turn out to be small.

As a first test of the algorithm we verified that we reproduce simulations using the London potential. We simulated two hard-core particles with either the Metropolis algorithm with the explicit London potential or our quantum algorithm with corresponding physical parameters. The radial distribution function of the two systems showed that our algorithm indeed generates the correct effective interaction.

We also studied the dynamics of equilibration of the polarization fluctuations to check that we do efficiently sample polarization fluctuations. We froze the position of N atoms in a face-centered cubic lattice and applied the algorithm to update the polarization degrees of freedom. We simulate at densities such that $\alpha\rho < 3$, with ρ the number density, where Clausius-Mossotti predicts that the dielectric constant diverges [17]. We recorded the $\omega = 0$ component of the total polarization, $\mathbf{p}_0 = \sum_{i\tau} \mathbf{p}_i(\tau)$ as a function of simulation time; fluctuations in this quantity are directly linked to the static dielectric constant. We found that the autocorrelation time of polarization fluctuations remains close to a single sweep independently of the number of particles; it is only very close to the point $\rho\alpha = 3$ that we observed a modest increase in autocorrelation times. We conclude that the addition of the large number of polarization degrees of freedom does not introduce any new, slow modes in the dynamics. It is here that we see the importance of the heat-bath algorithm; the Metropolis method leads to an autocorrelation time diverging as L^2 sweeps.

We now consider the simulation of fluid phases with the algorithm. In periodic boundary conditions we use Ewald summation to calculate the electric field $\mathbf{e}_i(\tau)$. The method separates the slowly converging dipolar sum in a periodic box of size ℓ into two parts. The first sum falls off rapidly in real space beyond a distance ℓ/γ , where ℓ/γ is an arbitrary splitting scale. The second sum is a Fourier sum over discrete wavevectors $\mathbf{q} = 2\mathbf{m}\pi/\ell$ which falls off rapidly beyond $\mathbf{m}^2 = \gamma^2$. The Fourier sum depends on the structure factor of the dipoles, $\mathbf{s}(\tau, \mathbf{q}) = \sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j} \mathbf{p}_j(\tau)$. As shown in [16] the full Ewald sum for the energy of N charges requires an effort of only $N^{3/2}$ to evaluate. We now consider the complexity of updating the calculation when a single dipole is displaced. It has been widely assumed that this update requires a complexity that is linear in N .

We start by initializing the structure factors $\mathbf{s}(\tau)$ and stocking them in a table. When a particle moves we update as follows: $\mathbf{s} \rightarrow \mathbf{s} - \mathbf{p}_{io} e^{i\mathbf{q}\cdot\mathbf{r}_{io}} + \mathbf{p}_{in} e^{i\mathbf{q}\cdot\mathbf{r}_{in}}$ where \mathbf{r}_{io} is the old position \mathbf{r}_{in} is the new. The update requires an effort which is $O(L)$. A calculation of the new field on i requires calculating interactions in real-space over a volume ℓ^3/γ^3 ; in Fourier space $L\gamma^3$ modes contribute to the energy. Minimizing the total effort gives a complexity of $O(N^{1/2})$ with the choice $\gamma \sim N^{1/6}$. Thus, the complexity for a single sweep of the algorithm is $O(LN^{3/2})$. In practice the most time-consuming part of the Ewald

sum, such as the calculation of transcendental functions, is identical for each τ . Because of this we find that simulating the full quantum behavior leads to only a factor three slowdown in the full quantum simulation compared to the simulation of a classical dipolar system with the Ewald method, even when we use rather fine discretizations in the τ direction of $L = 200$.

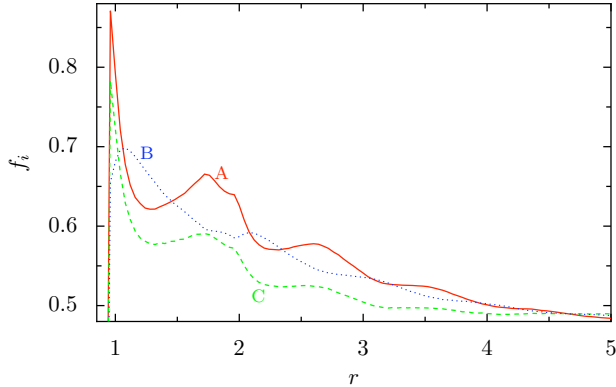


FIG. 2: A, B: fraction of species i , f_i , at distance r given that species i is also at the origin in quantum simulation. The difference between the curves is due to the differential screening properties of the fluid. The species with largest α is more concentrated at smaller separations. 4000 atoms, $L = 200$, $\alpha^2 \hbar \omega_i / (4\pi\epsilon_0)^2 kT = 0.73$. C: The same curves for the London pair approximation; curves for the two species overlap to within statistical errors.

In order to study collective, non-pairwise additive, effects we simulated a two-component hard-sphere fluid with quantum dipoles. Fig. 2. To emphasize the effects of differential screening of interactions we chose two components for which the amplitude in the London potential, $\alpha_i^2 \omega_i$, is identical, but for which the values of α_i and ω_i are different. In the Berthelot approximation, common in much numerical work, all three interactions between components 1-1, 1-2 and 2-2 are identical, $f_i = 0.5$ for all separations r . No interesting structure develops in the fluid. If we simulate a fluid with classical potentials using the London expression for the interactions we find that 1-2 interactions are weaker than the 1-1 and 2-2 interactions. This leads to the segregation of particles visible in the curve C of Fig. 2. Each kind of particle prefers to be in contact with the same species. Nevertheless, there is still full symmetry in the fluid between 1-1 and 2-2 structure factors when using London potentials. When we perform a simulation using the quantum algorithm we find an asymmetry between 1-1, (curve A) and 2-2 structure factors (curve B); even though the interactions 1-1 and 2-2 are identical in vacuum. We interpret this as due to partial screening of interactions in the fluid.

We have studied the properties of a fluid with state-dependent van der Waals interactions and shown that

methods based on pair potentials can lead to subtle errors in effective potentials. We argue that the use of unscreened van der Waals interactions leads to strong overestimates to the long-ranged potential tail in condensed matter simulations. If applied to heterogeneous phase separated components the method gives the correct, non-retarded Lifshitz interaction between bodies without any need to adjust empirically the effective amplitudes of van der Waals parameters; standard results from Lifshitz theory show that the Hamaker constant between two bodies of dielectric constant $\epsilon = 10$ can be incorrect by 30% if pairwise summation is assumed.

In our simulations we entirely neglect the short-ranged exchange interactions, which are best studied using density functional methods from quantum chemistry; most density functionals are unable to reproduce the collective van der Waals interactions of the sort modeled in this paper.

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