
Collective dispersion forces in the fluid state

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PACS 61.20.Ja – Computer simulation of liquid structure

PACS 34.20.Cf – Interatomic potentials and forces

PACS 05.10.-a – Computational methods in statistical physics and nonlinear dynamics

PACS 05.10.Ln – Monte Carlo methods

Abstract. - Dispersion interactions lead to effective many body interactions which go beyond the approximation of pair potentials widely used in modeling of materials, leading in the continuum limit to Lifshitz theory. We introduce quantum dispersion interaction in simulations of polarizable atoms, incorporating the fully summed, non-retarded Lifshitz theory in arbitrary fluctuating geometries. 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.

Introduction. – Quantum mechanics is the ultimate physical 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 parameterization 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].

Quantum theory shows how to express the dispersion interactions between atoms in terms of an integral over imaginary frequencies, so that the full dynamic response of atoms enters into interaction parameters. This im-

plies that in systems which contain several different atomic species the true interaction can exhibit quite complicated evolution as a function of environment due to the relative importance of different spectral features. These subtle variations in energy are undoubtedly crucial in understanding the stability and fluctuations of many biomolecules [6]. Whilst the bare pair interaction between pairs of *identical* atoms is well characterized many molecular dynamics codes mix the interaction parameters between different atoms in a rather crude manner by taking the geometric mean (Berthelot mixing) of the interaction strength of the two pure systems and the algebraic mean for the interaction radii. It is of clear interest to go beyond these crudest approximations in order to have a better understanding of the evolution of interactions with the environment.

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 [7, 8], even determining the sign of the final force. The cases where a full analytic theory are available are 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 [9–11]. 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. These methods, how-

ever, are inadapted to dynamic geometries. They assume the rigid motion of mesoscopic bodies and are not optimized for the calculation of energy differences when single atoms are displaced – as is the case in Monte Carlo simulation.

Lifshitz theory, because of its continuum formulation, tells 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. In particular one understands that systems undergoing separation or mixing should be described by effective potentials which are state dependent, evolving with the state of the system. The purpose of our paper is the exploration of the properties of a 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 often been used for the simulation of difficult quantum problems, such as the superfluid transition [12]. The result of our study is a description of materials that interpolates smoothly from microscopic atomistic interactions to lifshitz interactions at larger length scales. Note that we entirely neglect the short-ranged exchange interactions coming from overlap of electronic wavefunctions which can be expected to be dominant at small separations and strong couplings. They are best studied using density functional methods from quantum chemistry.

Model. – In this paper we describe the dispersion interactions in an atomic fluid with a model of oscillators coupled by long-ranged dipolar interactions [13,14]. If the dipole moment of atom i is \mathbf{p}_i then the Lagrangian of the system is

$$L = \frac{1}{2} \sum_i \left\{ \frac{-1}{\alpha_i \omega_i^2} \left(\frac{d\mathbf{p}_i}{dt} \right)^2 + \frac{\mathbf{p}_i^2}{\alpha_i} \right\} + \frac{1}{2} \sum_{i \neq j} \mathbf{p}_i T_{ij} \mathbf{p}_j \quad (1)$$

where α_i is the atomic polarizability of atom i and where ω_i is a characteristic frequency. The first term of eq. (1) is a kinetic energy associated with each dipole and the last term is the coupling of different atoms via the dipole tensor

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

In a first approach, we have neglected quadrupolar and higher order fluctuations, however these fluctuations can be rather easily introduced within the same formalism. We use path integral methods [12] to find the partition function associated with the Lagrangian (1). We find an effective classical action for the quantum system:

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

with $V(\tau)$ the potential energy of the Lagrangian. The positions of the classical degrees of freedom intervene

through the dipole couplings T_{ij} . If one works at zero temperature ($\beta = \infty$) and Fourier transforms eq. (3) one finds that the interaction between two identical atoms of characteristic frequency ω_0 and polarizability α_0 with $\alpha_0/r^3 \ll 1$ is

$$U = -\frac{3\alpha_0^2}{4} \frac{\hbar\omega_0}{(4\pi\epsilon_0 r^3)^2} \quad (4)$$

the London result for dispersion interactions, [15].

Our model of the dynamic properties of the coupled dipoles give a frequency dependent dielectric response at low densities dominated by a single pole.

$$\epsilon(\omega) = 1 + \chi/(1 - \omega^2/\omega_0^2) \quad (5)$$

[16,17]. It is rather remarkable that a model based on simple harmonic oscillators should give a useful account of the interaction between atoms, where interactions are far from harmonic. However, the theory of dielectrics shows that interactions between media depend only on the response function (such as eq. (5)) and not on the internal dynamics leading to the response. We are thus free to use a simplified, effective model such as eq. (1) to describe interactions mediated by long-ranged interactions. More elaborate response functions with multiple poles can be built with the use of several polarization variables for each atom. This gives rise to the representation of the response of an atom as a sum of resonances weighted with the appropriate oscillator strength [16,17].

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 eq. (4). 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]. If all atoms are identical the long-ranged part of the interaction is reduced by a factor $1/\epsilon^{3/2}$. 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 captured by the Axilrod-Teller potential only when $(\epsilon - 1)$ is small. Low-order multi-body corrections of the Axilrod-Teller form completely fail to capture these collective effects ¹.

Discretization of action. – 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 to find the natural eigenfrequencies associated with eq. (1). The contribution of each eigenfrequency is then

¹We 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. Our algorithm for the full summation of the dispersion interaction is more efficient than a direct evaluation of the Axilrod-Teller potential.

just $\hbar\omega/2$, the ground state energy of each oscillator. We programmed this method which gives the free energy of the quantum degrees of freedom in terms of the positions of the atoms; One can calculate the free energy of a single configuration in a time $O(N^3)$ leading to 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 [18]; 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 and require algorithms specifically targeted to this case. We thus use a discretized form of the action, rather than matrix diagonalization.

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 dispersion relation $e(\omega_n) = 2(1 - \cos \omega_n)$ 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 $e(\omega_n) = \omega_n^2 + O(\omega_n^p)$, $p > 4$. We compare the convergence to the continuum limit for increasing values of p for a cluster of 15 atoms. Figure 1. represents the relative error in this free energy as a function of the number of time slices, L for $p = 4, 6, 8$. It shows that this formulation indeed accelerates the convergence to the continuum limit. We use such an improved discretization with $p = 8$ in our Monte Carlo simulations with interactions out to $3\delta\tau$.

Heat bath algorithm. – We now describe a fluid of N atoms and concentrate our attention on the contribution to the action from a single particle i , located at \mathbf{r} . For notational convenience let us regroup the L vectors $\mathbf{p}_i(\tau)$ into a single $3L$ -vector \mathbf{P}_i . We replace the integral in eq. (3) by a sum and extract the terms in \mathbf{P}_i from the resulting discretized action.

$$A_i = \frac{\mathbf{P}_i M \mathbf{P}_i}{2} - \mathbf{E}_i(\mathbf{r}) \cdot \mathbf{P}_i \quad (6)$$

where the sparse derivative matrix M has dimensions $3L$. We note that the matrix M is particularly simple in struc-

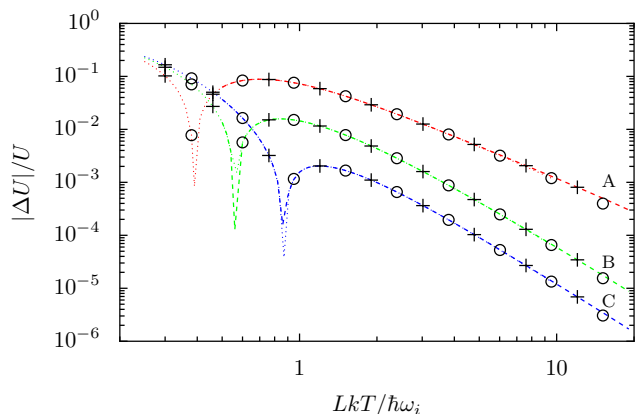


Fig. 1: Relative error in free energy for a cluster of 15 atoms for different discretizations of the time derivative. A: Second order discretization, $p = 4$, $e(\omega_n) = 2(1 - \cos \omega_n)$. B: $p = 6$, $e(\omega_n) = (15 - 16 \cos \omega_n + \cos 2\omega_n)/6$ C: $p = 8$, $e(\omega_n) = (245 - 270 \cos \omega_n + 27 \cos 2\omega_n - 2 \cos 3\omega_n)/90$. 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.

ture; it contains three banded and cyclic blocks. The local electric field is given by

$$\mathbf{e}_i(\tau, \mathbf{r}) = -\delta\tau \sum_{j \neq i} T_{ij} \mathbf{p}_j(\tau) \quad (7)$$

which can again be assembled into a single vector $\mathbf{E}_i(\mathbf{r})$ containing the value of \mathbf{e}_i for each value of τ .

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. (6); the influence of other atoms on the test particle comes through the electric field $\mathbf{e}_i(\mathbf{r}, \tau)$. 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

$$G_i(\mathbf{r}) = -\frac{\mathbf{U}_i(\mathbf{r}) \cdot \mathbf{E}_i(\mathbf{r})}{2} \quad (8)$$

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 of the atom of interest is given by $\Psi = e^{-A_i(\mathbf{E}_i)}$. In both positions we generate $(\mathbf{P} - \mathbf{U})$ with relative probability

$$r(\mathbf{P}) = e^{-(\mathbf{P} - \mathbf{U})M(\mathbf{P} - \mathbf{U})/2} \quad (9)$$

We find that the criterion for detailed balance is then

$$\Psi(o) \times \pi(o \rightarrow n) = \Psi(n) \times \pi(n \rightarrow o)$$

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

where π is the transition probability, exactly as required. The argument generalizes [19] 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 :

$$G_b = -\mathbf{P}_a T M_b^{-1} T \mathbf{P}_a / 2 \quad (10)$$

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).

Equilibration. – 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. Beyond this density Clausius-Mossotti predicts that the dielectric constant diverges and a zero eigenvalue appears in eq. (1) signalling an instability in the dipolar degrees of freedom. 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 for the dipolar degrees of freedom.

Algorithmic Complexity. – We now consider the simulation of condensed phases with the algorithm. In periodic boundary conditions we use Ewald summation to

calculate the electric field $\mathbf{e}_i(\tau)$. The Ewald 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 [20] 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 the simulation 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 of the dipole, \mathbf{r}_{in} is the new. The update requires an effort which is $O(L)$ since we must perform the calculation in each time-slice. A calculation of the new field on particle 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

$$E_f = L\rho \frac{\ell^3}{\gamma^3} + L\gamma^3 \quad (11)$$

where $\rho = N/\ell^3$ is the mean density, gives a complexity of $O(LN^{1/2})$ 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 quantum behavior leads to only a factor three slowdown 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 $L = 200$. We note that repeatedly updating the structure factor can lead to numerical drift unless one uses particular care in the order of calculation. This drift can be almost completely eliminated with a compensated summation method [21].

Binary fluid. – In order to illustrate collective, non-pairwise additive, effects we simulated a two-component hard-sphere fluid with quantum dipoles at three levels of approximation. The results are presented in 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. (I) In the Berthelot approximation, common in much numerical work, all three interactions between components 1-1, 1-2 and 2-2 are identical. The fraction of each species should be uniform $f_i = 0.5$ for all separations r . No interesting structure can develop in the fluid. (II) If we simulate a fluid

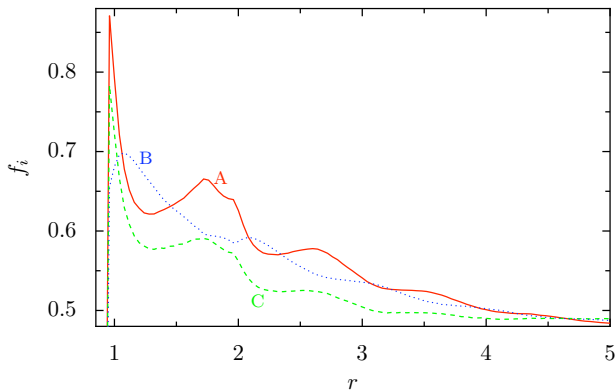


Fig. 2: *A*, *B*: fraction of species i , f_i , at distance r given that species i is also at the origin in quantum simulation. The difference between the curves is due to the differential screening properties of the fluid. The species with largest α is more concentrated at smaller separations. 4000 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.

with classical potentials using the London expression for three distinct 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. (III) 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, showing the importance of multi-body interactions in complex geometries.

Conclusion. – The first novelty of the present paper lies in the manner which we *simplify* the general formulation of quantum path integrals in order to generate dispersion interactions. Simulation of quantum systems on a classical computer is done by introducing multiple coupled replicas of the original system. The most naive Monte Carlo algorithms, when applied to these replicas display a considerable slowdown compared with the unreplicated system unless collective algorithms are used for the updates. In the case of van der Waals interactions the coupled replicas are described by a Gaussian theory. This allows the use of a heat-bath Monte Carlo algorithm which resamples quantum paths in a single Monte Carlo trial. This heat bath method is similar in spirit to orientationally biased methods described in [19,22] and is simpler to implement than the most general methods [12].

As a second technical point in this paper we introduce an optimization in the evaluation of energy changes in Ewald sums. As is well known the evaluation of the electrostatic energy of N particles with periodic boundary

conditions requires a time which scales as $N^{3/2}$ [20]; it has been assumed however that in a Monte Carlo code re-evaluation of this energy imposes a complexity of $O(N)$ for each Monte Carlo trial. In our algorithm we have developed an implementation of the Ewald method which uses dynamic updating of the structure factor in order to reduce the calculation of the change in energy to a complexity $O(N^{1/2})$ for each Monte Carlo trial. This algorithm is completely general and can be applied in both the quantum and classical context and by an appropriate optimization the slow-down in passing from a purely classical dipolar fluid to the quantum form is only a factor three. It is entirely feasible to perform high statistics simulations of quantum models with dispersion interactions.

To conclude 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 our 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, our approach generates this behaviour automatically.

The present formulation does not directly generalize to the retarded regime where interactions between atoms decay as $1/r^7$. To reproduce this result one requires a full treatment of Maxwell's equations in each time slice [23]. This would require considerable overhead in terms of memory and computational effort.

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