Transverse dipole-dipole effective interaction for sheet arrangements

Ladislav Kocbach† and Suhail Lubbad†
Department of Physics and Technology, University of Bergen, Allégaten 55, 5007 Bergen, Norway

We have succeeded to develop a model pair interaction which when added to a system of interacting particles can be tuned to arrange the interacting objects into sheets. The interaction is based on the decomposition of the dipole-dipole interaction into two components, one parallel and one perpendicular to the connecting line between the dipoles, and keeping only perpendicular part here. Various aspects of this simple interaction are discussed, in particular in connection to two recent papers on self assembly of carbon nanostructures. On the other hand, the features discussed are quite general and might be of interest in different areas of microscopic modeling.

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In many areas of physics there is often a need for simple effective interactions. Perhaps the most famous might be the Lennard-Jones potential or the spin-spin interaction of the Heisenberg ferromagnet, two models which are well known and used far outside the original applications. Our aim has been to understand the emergence of various geometrical arrangements and we have succeeded to develop a model two-body interaction which when added to a system of interacting particles would arrange them into sheets instead of the expected three-dimensional structures. This model interaction can primarily be of use in atomistic simulations, but possibly also for systems consisting of more complex particles, in principle at any scale.

We start from the usual form of the dipole-dipole interaction

\[ U(r_{12}) = \frac{A}{r_{12}^3} [\mathbf{m}_1 \cdot \mathbf{m}_2 - 3 (\mathbf{m}_1 \cdot \mathbf{e}_{12}) (\mathbf{m}_2 \cdot \mathbf{e}_{12})] \] (1)

where \( r_{12} = r_{12} \mathbf{e}_{12} \) is the vector connecting the two dipoles and \( \mathbf{e}_{12} \) its unit vector. It has probably been noticed by many, but apparently not discussed by anybody in printed form, that eq. (1) can be rewritten as

\[ U = f(r_{12}) [\mathbf{m}_1^\perp \cdot \mathbf{m}_1^\perp - 2 \mathbf{m}_1^\parallel \cdot \mathbf{m}_2^\parallel] \] (2)

The notation used follows from decomposition of both dipoles into two components

\[ \mathbf{m}_1 = \mathbf{m}_1^\parallel \mathbf{e}_{12} + \mathbf{m}_1^\perp = \mathbf{m}_1^\parallel + \mathbf{m}_1^\perp \]

The figure reminds us of the situations when each of the terms dominate. For the real dipoles the two terms are added exactly in the given radial form, but effective interactions may naturally assume any radial form and any relative strength of the two terms suitable for the physical model in question. Our model consists of only the part containing the perpendicular terms, or alignment of the intrinsic vectors in direction perpendicular to the connecting line of the two objects. We propose to call this model interaction "transverse dipole-dipole interaction", or TDDI. The effective pair potential is chosen as

\[ U(r_{ij}, \mathbf{e}_{ij}, \mathbf{m}_i, \mathbf{m}_j) = g(r_{ij}) G(1 - |\mathbf{m}_1^\perp \cdot \mathbf{m}_1^\perp|) \] (3)

where all the vectors \( \mathbf{e}_{ij}, \mathbf{m}_i, \mathbf{m}_j \) are unit vectors and the function \( g(r_{ij}) \) is an arbitrary function suitable for the model system in question. It can be of short range or long range, but preferably reaching at least two nearest neighbours to define the plane. The argument of function \( G(u) \) is zero when the two vectors point in parallel lines, in both directions. Thus \( G(u) \) must be sufficiently strongly peaked at \( u = 0 \).

Considering first just four particles with such interaction, this term will be zero only when all four particles are in the same plane, having thus a minimum. If there is also some other additional interaction leading to equilibrium distances, both the discussed four particle as well as more particle systems would prefer sheets or single layers, much like the graphene sheets, as long as the range of \( g(r_{12}) \) covers at least two neighbours. If there is an interaction arranging the objects at certain distances and perhaps also with well defined bonding angles, but without the ability to assure a planar arrangement, adding a fictive model vector - transverse dipole (TD) - to every particle, the TDDI would lead to sheet-like behavior.
even if it is only a two-body interaction. Since parallel TDs are preferred, any three neighbours would align them perpendicular to the plane in which they are lying. When all these planes become one plane, the TDDI is minimized. Thus TDDI added to a suitable two or three-body interaction would lead to self assembly of sheets.

Combining TDDI with additional terms is important because when TDDI would be the only interaction, its radial dependence \( g(r) \) would need to have a minimum to assure some equilibrium distances. This could be in conflict with the aim to establish a stable sheet structure, since it could lead to a close packing situation. All the effective internal vectors could be partially aligned but a closed packed structure will result from the existence of the minimum in the function \( g(r) \). Thus the discussed model interaction should only be used in addition to other inter-particle forces. In general, the \( g(r) \) function should be monotonically decreasing with distance, in most cases simply providing a cut-off.

The proposed TDDI is a pair interaction. The limitation to the perpendicular term for a single pair leads only to reorientation of the two internal spins with no influence on the pair of particles. The same is true for a group of three particles. All their connecting lines are in one plane, so that the internal vectors can reorient themselves without any influence on the positions of the particles. When a fourth particle is added, the torque on the internal vectors will start forcing the particles into one plane.

The present paper is to some degree inspired by the work of Rechtsman, Stillinger and Torquato [4], who show how to build structures of diamond and wurtzite type using special pair interactions. These isotropic pair interactions have minima where the radial distribution functions (RDF) of the target structures have peaks. The principle proposed here is somewhat similar.

Tewary and Yang in ref [1] construct a parametric potential for a graphene sheet. They wish to achieve similar effect as described here, but they simulate it by combining three body forces in a rather complicated way. They use a rather complex many body potential of Tersoff type [2] with an addition of three-body terms adjusting the planar geometry. Our proposed intrinsic vector model is much simpler and more flexible, and computationally appears as a two-body term. We suggest that a much simpler model than the one of ref. [1] could be based on adjusting the Stillinger and Weber model [3], which is a two plus three body interaction for tetrahedral diamond correlations, to the plane geometry with the addition of terms of the type proposed here (see also ref. [3]).

The effect of the TDDI interaction can be analyzed and explored in two dimensional case much easier than in three dimensions. In two dimensional case the role of the sheet of particles is played by a string of particles. We have implemented the TDDI into a small program which solves the molecular dynamics-like problem in two dimensions. The interactions are Morse potential, which is known to lead to the triangular-hexagonal closed packed arrangement (isotropic forces with an equilibrium distance). Then we added the TDDI interaction. Results of two runs are shown in figures 2 and 3. The variant of TDDI we used here is

\[
U (\mathbf{r}_{ij}, \mathbf{m}_i, \mathbf{m}_j) = U_0 \left[ 1 - \left( \mathbf{m}_i^\perp \cdot \mathbf{m}_j^\perp \right)^2 \right].
\] (4)

For the small number of particles the motion becomes quite disordered, therefore we have added a friction term to be able to see the "cooled" structures. Note that the starting situation is a regular, but with one particle slightly displaced. Without any tiny displacement a regular structure will simply "breathe". The difference between the calculations is clear and demonstrate the effect. The physical dipole-dipole interaction where the first term dominates would not lead to any similar effect, but it would also lead to some anisotropy.

The forces on the particles are given by the gradients of the potential energy, and it is instructive to inspect
the resulting formulae. The gradient with respect to the \( r_i \) coordinate of the transverse TDDI term \( m_i^\perp \cdot m_j^\perp \), is obtained after some rather elementary algebra to be

\[
\nabla_{r_i} \left( m_i^\perp \cdot m_j^\perp \right) = -\frac{1}{r_{ij}} \left( m_i^\parallel m_j^\perp + m_j^\parallel m_i^\perp \right) \tag{5}
\]

Clearly, this is the part important for the motion of the particles when the vectors \( m_i \), \( m_j \), are "frozen", or kept constant, the torque terms leading to their reorientation will be addressed below. The above gradient must be used in the evaluation of the forces on each of the particles. For a pair potential

\[
W(r_i, m_i, r_j, m_j) = V(r_{ij}) + G_0 \left[ 1 - (m_i^\perp \cdot m_j^\perp)^2 \right] \tag{6}
\]

the force on \( i \)-th particle from \( j \)-th particle is obtained as

\[
F_i = -\frac{r_{ij}}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} - \frac{2}{r_{ij}} \left( m_i^\perp \cdot m_j^\perp \right) \left( m_i^\parallel m_j^\perp + m_j^\parallel m_i^\perp \right) \tag{7}
\]

using the gradient formula given in eq. (5).

Now we address the question of the torque on the vectors \( m_i \) due to their mutual interaction. While the above formulae are equally valid both in two and three dimensions, we limit the discussion here to two dimensions, since a full three-dimensional discussion becomes somewhat lengthy. In two dimensions, there is only one angle specifying the orientation of each of the vectors. Denoting \( \alpha \) the orientation angle of \( i \)-th internal vector \( m_i \) and \( \theta_{ij} \) the direction of vector \( r_{ij} \),

\[
m_i^\perp \cdot m_j^\perp = \cos(\alpha_i - \alpha_j) - \cos(\alpha_i - \theta_{ij}) \cos(\alpha_j - \theta_{ij}) \tag{8}
\]

following directly (also valid in three dimensions) from

\[
m_i^\perp \cdot m_j^\perp = m_i \cdot m_j - m_i^\parallel m_j^\parallel \tag{9}
\]

To evaluate the torque on \( m_i \) we need to find the gradient (or derivative in this case)

\[
\frac{\partial}{\partial \alpha_i} \left( m_i^\perp \cdot m_j^\perp \right) = \cos(\alpha_i - \theta_{ij}) \sin(\alpha_j - \theta_{ij}) \tag{10}
\]

The torque on the \( m_i \) is zero when \( \alpha_i = \theta_{ij} + \frac{\pi}{2} \), i.e. when it already is perpendicular to the vector \( r_{ij} \), connecting the two particles. In three dimensions the internal vectors are given by two angles, as well as the connecting position vector, but the principle remains the same and the evaluation is more complicated but straightforward.

Possible applications of this model with fictive variables must solve the problem of removing the energy associated with the fictive degrees of freedom. In our application described elsewhere \cite{5} we use a model of over-damped angular motion of the internal vectors. The excitation energy resulting from the nonoptimal orientation is spurious, since the TDs are not real quantities. When the optimal orientation is reached, in normal Newtonian treatment the potential energy would be turned into some (mostly rotational) kinetic energy, leading to spurious vibrations in the angles. Thus, it should be a part of the model to dispose off this energy, through a fictive friction. We propose that this can be done by considering an over-damped motion of the model transvers dipoles, leading to first order equations, as described in detail in ref. \cite{5}.

It might be of interest to consider a further generalization of the discussed model, by including both parts of the dipole interaction, as

\[
W(r_{ij}) = t(r_{ij}) m_i^\perp \cdot m_j^\perp + p(r_{ij}) m_i^\parallel \cdot m_j^\parallel \tag{11}
\]

Here the radial functions might be such that they would lead to parallel layers, i.e. the \( p(r_{ij}) \) should have a repulsive part for small distances and a minimum at the desired distance between two layers. The part \( t(r_{ij}) \) should be similar to the \( g(r_{ij}) \) of eq. (3) or somewhat modified to model even further features.

An extensive discussion of the applications of the proposed type of model interactions is discussed in our above quoted paper \cite{3}. We would like to publish this shortened discussion of the model in this journal, since it might be useful in entirely different fields of research, or at least inspire similar applications, much in the same way as the surprising model of isotropic pair interactions leading to complex space patterns of diamond-like lattice discussed above (ref. \cite{4}) inspired our work.

\begin{center}
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