

THE FREQUENCY OF THE TWO LOWEST ENERGIES OF INTERACTION IN DIPOLAR HARD SPHERE SYSTEMS

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Received: September 13, 2020 • Accepted: October 28, 2020

ABSTRACT

This publication was inspired by the study of chaining in dipolar systems. Two adjacent particles form a chain is usually decided by energy or distance criterion. This prompted the author to investigate the frequency of interaction energy between nearby chain-forming particles in the dipolar system. So what is the frequency of the two lowest energies. Does have *raison d'être* of the energy-based chaining criterion? Because if so, in the frequency chart qualitative change should have see at 70-75%, compared to the lowest possible energy. No such qualitative change was observed in the computer simulations. Monte Carlo simulations were performed at many densities and dipole moments in a dipolar hard sphere system. The simulation results were theoretically interpreted using the Boltzmann distribution. The theoretical relationship was generalized to a wide range of density and dipole moments by fitting three suitable parameters. The fitting was necessary due to the compressive effect of density.

Keywords: interaction energy, pair energy, dipolar hard spheres

1. INTRODUCTION

Dipolar particles are organized into chains under certain conditions. There are some types of chaining criteria. The most common is the energy criterion: e.g. if the pair energy between two adjacent particles is less than 70-75% of the minimum pair energy, they form a chain [1-4]. Another criterion combines the distance and the energy criterion [5, 6]: if the pair energy is negative and the distance is less than 1.3 (in diameter unit). So the criterion in all cases is unit jump-like. According to the author, this assumes that there must also be some kind of unit jump-like change in the energy between the particles. Therefore, in the first half of the study, Monte Carlo simulation results on the energy distribution between adjacent particles are presented. The simulations were performed in a dipolar hard sphere (DHS) system. No unit jump-like change was experienced in the pair energy distribution. A similar study was performed by Tavares et al. [4], but they treated the lowest and second lowest pair energies separately. However, they did not find a unit jump-like change either. The shape of the curves was then explained using the Boltzmann distribution. The increasing of density modifies the initial distribution, so parameters were fitted.

2. SIMULATION RESULTS

Monte Carlo simulations of DHS fluids were performed using a canonical NVT ensemble. Boltzmann sampling [7], periodic boundary conditions and the minimum-image convention were applied. In order to take into account the long-range character of the dipolar interaction, the reaction field method under boundary conditions of conduction was used. After 100,000 equilibration cycles, 500,000 production cycles were conducted involving $N = 1000$ particles. In each cycle, for each particle, the pair energy belonging to the two lowest energy neighbors was taken into account. In the DHS system, the particles must not be closer to each other than the particle diameter (d), and at a greater distance, the HS portion of the pair energy between them is zero. The dipolar pair energy is given by the following relation for point dipoles in 3 dimensions:

$$U_{ij}^{dd} = -\frac{m^2}{r_{ij}^3} \left[3(\hat{\mathbf{m}}_i \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{m}}_j \cdot \hat{\mathbf{r}}_{ij}) - (\hat{\mathbf{m}}_i \cdot \hat{\mathbf{m}}_j) \right] \quad (1)$$

where the particles have dipole moments of strength m as well as an orientation given by unit vector $\hat{\mathbf{m}}$, and the distance between the centers of the particles is denoted by r_{ij} and $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$. The dot symbolizes scalar product. Based on this, it can be easily obtained that the smallest energy value, when the dipoles are in the tail-to-nose position, is: $U_{min}^{dd} = -2m^2/d^3$. In general and hereafter, this will be the unit of energy, as this is the most favorable position in terms of energy, to which the percentage limits mentioned in the introduction. The most unfavorable position (nose to nose) is when two particles are at the minimum distance (d) but stand in opposite directions. The associated energy value is: $U_{max}^{dd} = 2m^2/d^3$. As the distance increases, these extreme energies decay cubically. Let introduce the following variable: $u = U^{dd}/U_{min}^{dd}$, and the reduced quantities as follows: $\rho^* = \rho d^3$, $m^* = m/\sqrt{d^3 k_B T}$, where ρ and d are the concentration and diameter of the particles, k_B is the Boltzmann constant, and T is the temperature. Then the minimum reduced value of the pair energy: $(U_{min}^{dd})^* = -2m^{*2}$ (while $u_{max} = 1$), and the maximum reduced value of the pair energy: $(U_{max}^{dd})^* = 2m^{*2}$ (while $u_{min} = -1$). Two osculant particles can be in a favorable energetic position even if they are in opposite directions, but then they must be located next to each other in antiparallel position. In this case: $(U^{dd})^* = -m^{*2}$, and $u = 0.5$. It has a symmetrical (parallel) position: $(U^{dd})^* = m^{*2}$, and $u = -0.5$. Fig. 1 shows all this.

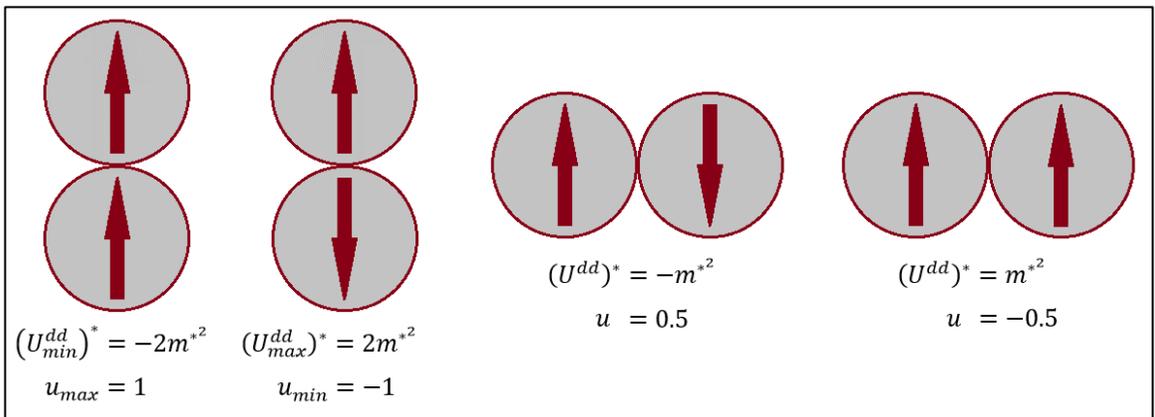


Figure 1. The privileged positions of the dipole pairs and the associated pair energies.

Fig. 2 shows the probability density functions (denoted by P) of the two lowest pair energy interactions, as simulation results for 3 dimensions. The dipole moment values from left to right: $m^* = 1$, $m^* = \sqrt{3}$, and $m^* = \sqrt{5}$. Each subfigures has 3 lines for 3 different reduced densities: $\rho^* = 0.1$ (green), $\rho^* = 0.5$ (blue), $\rho^* = 0.9$ (red). The x-axis shows the dipolar pair energy as a proportion of the minimum pair energy. Integrating P we get that:

$$\int_0^1 P(U^{dd}) du = 1 \tag{2}$$

Because it is true for all particles that the maximum values of the two lowest energy pair energies are zero. It is possible that the pair energy taken with a nearby particle is greater than zero, but even for that particle

there is a particle with zero pair energy at high distance. However, only nearby particles can be considered in the chaining, so those parts of the curves where u approaches 1 are of interest to us.

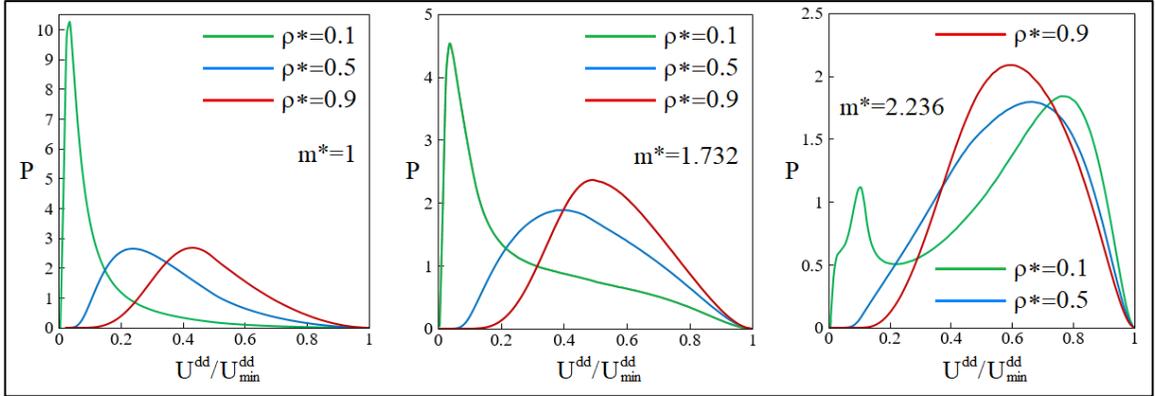


Figure 2. Simulation results of the probability density functions of the two lowest pair energy.

It can be seen that increasing both of density and dipole moment pushes the maximum of the curves to the right, towards the lower energies. The higher density forces the particles to a close location and the higher dipole moment also means lower pair energy, which increases the frequency of energetically favorable situations.

3. THEORY

The Boltzmann distribution is used to explain the curves on Fig. 2. According to the Boltzmann distribution, the probability that two particles are in a state characterized by U^{dd} pair energy in DHS conditions, is given by the following relation:

$$P(U^{dd})du = \frac{g(U^{dd}) \exp(-U^{dd}/k_B T)}{\int_0^1 g(U^{dd}) \exp(-U^{dd}/k_B T) du} du \quad (3)$$

where $g(U^{dd})$ is the number of states that realize a given dipolar energy. In DHS system for the pair energy of two dipoles with each other, the size of a part of a five-dimensional Euclidean space gives the size of $g(U^{dd})$. The direction of the two dipoles is determined by two-two angle values: the polar angle (ϑ), and the azimuthal angle (φ). The relative spatial position of the two dipoles is given by the Cartesian coordinates (x, y, z) or the two mentioned angles and a distance (ϑ, φ, r). These are seven parameters from which the direction of one of the dipoles can be fixed, so the other five parameters remain independent. The size of this five-dimensional Euclidean space is shown on a logarithmic scale as a function of pair energy on Fig. 3. The calculation can be performed with a simple computer algorithm. While keeping one of the dipoles fixed, the five parameters are scanned evenly with sufficient accuracy, and determining the dipolar energy between the two dipoles, and if the dipolar energy is in the vicinity of the selected energy level, the configuration is included in the summation. The number of aggregated configurations specifies the size of Euclidean space for that energy level. Mathematically, this is expressed by the following formula:

$$g(U^{dd}) = \int_{U^{dd}-\varepsilon < U^{dd} \leq U^{dd}+\varepsilon} p(x)dx p(y)dy p(z)dz p(\vartheta)d\vartheta p(\varphi)d\varphi \quad (4)$$

where $0 \leq \vartheta < \pi$ and $0 \leq \varphi < 2\pi$, and for Cartesian coordinates (e.g. x), $p(x)dx = dx/(x_{max} - x_{min})$, and $p(\vartheta)d\vartheta = \sin\vartheta d\vartheta/2$, and $p(\varphi)d\varphi = d\varphi/2\pi$. Fig. 3 shows that the curve $g(U^{dd})$ (blue line) approaches the linear on a logarithmic scale, at least for small u values, furthermore, for u values close to 1, it deviates from the line toward zero. Therefore, the function $g(U^{dd})$ can be approximated by the expression:

$$g(U^{dd}) \approx A \exp(B(1 - u)) \cos^C \left(\frac{\pi}{2} u \right) \quad (5)$$

where A , B , and C are constants. The value of A depends on how close u is to zero, since at zero the frequency becomes infinite. However, the values of B and C can be determined exactly by fitting. On Fig. 3, the constant B indicates the slope of the straight line, while the constant C indicates the degree of deflection. From the fitting: $B=5.034$ és $C=1.624$. On Fig. 3 the blue line indicates the size of the Euclidean space determined from the computer algorithm, and the red dotted line is the curve of the fitted formula (5) with the mentioned data.

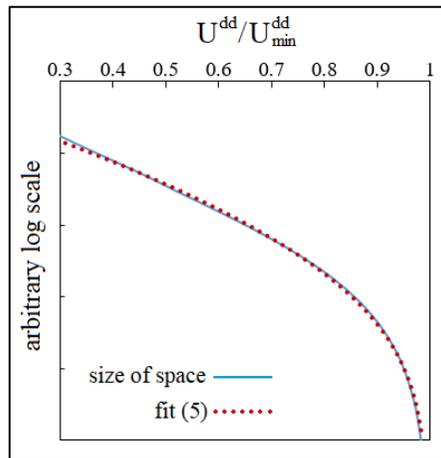


Figure 3. The number of states of the pair energy in dipolar hard sphere system

Comparing (3) and (5) for the frequency of the pair energy, we get:

$$P(U^{dd})du \approx A \exp(B(1 - u)) \cos^C \left(\frac{\pi}{2} u \right) \exp(2um^*^2) \quad (6)$$

Hereinafter, this term is used to fit the curves shown on Fig. 2, even if the increasing of dipole moment and density obviously distort the initial B and C data. Fig. 4 shows the fitting of (6) for three different dipole moments. The density does not yet appear here because (6) does not include it. For infinite dilute fluids, the distributions of pair energy are different for different dipole moments. The solid lines are the exact probability density functions, expressed as the product of the real Euclidean space size and the pair energy term:

$$P(U^{dd})du = g(U^{dd}) \exp(2um^*^2) \quad (7)$$

The dotted lines show the values of (7) fitted by (6). If $m^* = 1$, then $B=6.259$ and $C=1.072$. If $m^* = 1.732$, then $B=5.460$ and $C=1.369$. If $m^* = 2.236$, then $B=4.731$ and $C=1.584$. The vertical scale is not logarithmic.

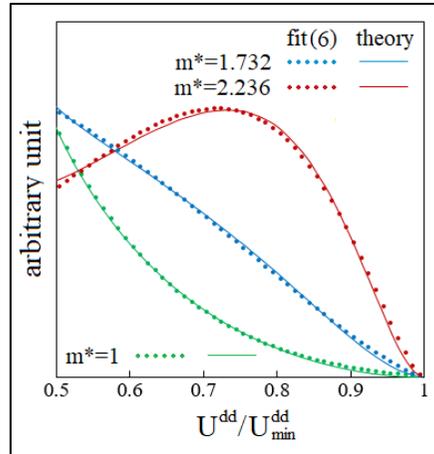


Figure 4. The probability density functions of the two lowest pair energy in infinite dilute fluids at different dipole moments.

The constants just given are, of course, distorted by the density conditions, but (6) is still suitable for describing the simulation curves shown on Fig. 2 at all densities and dipole moments. From now on, the constant A will also have a definite value, since (2) holds. Tab. 1 contains the values of the constants A, B, C at five different dipole moments and over a wide density range (per tenth), which can be substituted for (6) to obtain the pair energy distribution from at least half of the minimum pair energy to the minimum pair energy ($u = 0.5-1$).

Table 1. The constants for calculating the probability density function according (6).

	ρ^*	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$m^*=1$	A	0.00725	0.0168	0.0285	0.0445	0.0653	0.0979	0.147	0.236	0.415
	B	5.353	5.173	5.034	4.846	4.649	4.351	3.989	3.461	2.726
	C	1.322	1.351	1.365	1.401	1.432	1.493	1.564	1.670	1.818
$m^*=1.414$	A	0.00778	0.0150	0.0214	0.0274	0.0343	0.0439	0.0588	0.0845	0.131
	B	4.870	4.712	4.665	4.643	4.591	4.458	4.205	3.792	3.198
	C	1.444	1.471	1.490	1.504	1.535	1.588	1.662	1.770	1.905
$m^*=1.732$	A	0.00726	0.0101	0.0114	0.0122	0.0130	0.0144	0.0171	0.0221	0.0319
	B	4.295	4.363	4.506	4.672	4.821	4.872	4.795	4.515	4.000
	C	1.568	1.560	1.563	1.569	1.595	1.638	1.706	1.810	1.946
$m^*=2$	A	0.00482	0.00495	0.00469	0.00421	0.00400	0.00397	0.00427	0.00496	0.00628
	B	3.827	4.126	4.464	4.886	5.203	5.446	5.524	5.423	5.002
	C	1.641	1.616	1.604	1.590	1.608	1.652	1.724	1.815	1.876
$m^*=2.236$	A	0.00232	0.00194	0.00154	0.00124	0.00104	0.000939	0.000933	0.000990	0.00105
	B	3.246	3.823	4.487	5.132	5.701	6.149	6.386	6.370	6.293
	C	1.702	1.657	1.613	1.586	1.593	1.627	1.698	1.744	1.753

4. CONCLUSIONS

The two lowest energies of interaction were studied by the help of Monte Carlo simulations and Boltzmann distribution in dipolar hard sphere systems. The simulations showed that there is no unit jump-like change at 70-75% of the minimum pair energy, thus, this criterion of chaining is not theoretically substantiated. Nevertheless, the frequency of pair energy can be well explained by the Boltzmann distribution (6). For this the number of states of the pair energy (Fig. 3) calculation was required. Due to the distorting effect of density, it was necessary to fit three parameters (Tab. 1). Based on this research, it can be said that a new chaining criterion needs to be established.

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