Theory

Modifying the chain formation model, from dipolar spheres to dipolar superballs

To begin, we shall consider only spherical particles. Once all the attributes have been made, we will introduce the superball shape parameter $q$. As noted in the manuscript, the chain formation model derived by Mendelev and Ivanov can be written in the form,

$$
\chi_0^c = \chi_0^I \left( \frac{1 + pK}{1 - pK} \right),
$$

(1)

where $\chi_0^I$ denotes the modified mean field theory of the first order, given by,

$$
\chi_0^I = \chi t \left( 1 + \frac{\chi t}{3} \right).
$$

(2)
The parameters $K$ and $p$ are quantities related to correlations and to bonding probability respectively. $K$ is the zero field coefficient, measuring the degree of correlation between the orientations of two neighboring dipolar particles in a chain. For the dipolar hard sphere fluid this can be written as

$$K = \coth\left(\frac{\lambda}{2}\right) - \frac{2}{\lambda},$$  \hspace{1cm} (3)

expressed as a function of the magnetic coupling parameter that was defined in the manuscript,

$$\lambda = \frac{\mu_0 m^2}{4\pi h^3 kT},$$  \hspace{1cm} (4)

recalling that $h$ is the height of the superball (specifically the sphere diameter in this case). The quantity $p$ is in fact a Lagrange multiplier that can be used to define the zero field chain distribution of the system. It is calculated from the following expression,

$$p = \frac{1 + 2q_0\phi - \sqrt{1 - 4q_0\phi^2}}{2q_0\phi},$$  \hspace{1cm} (5)

where the volume fraction $\phi = N\nu/V$ is for a system of $N$ particles in a volume $V$ with a single particle volume of $\nu = \pi\sigma^3/6$. The quantity $q_0$ is the zero-field two particle (dimer) partition function for spheres. It can be expressed as,

$$q_0^s = q_{\infty}\frac{1 - e^{-\lambda}}{\lambda},$$  \hspace{1cm} (6)

where $q_{\infty}$ is the analogous dimer partition function for the case of infinite field. It has the following form,

$$q_{\infty} = \frac{e^{2\lambda}}{3\lambda^2}.$$  \hspace{1cm} (7)

Combining the two previous equations gives us the dimer partition function for spheres $q_0^s(\lambda)$,

$$q_0^s(\lambda) = \frac{e^{2\lambda}(1 - e^{-\lambda})}{3\lambda^3}.$$  \hspace{1cm} (8)
Having now defined all the relevant quantities, we can explain the method with which we introduced the superball shape parameter $q$.

It is useful to address the central approximations we made to facilitate the process. The first of these was to assume the correlation coefficient $K$ is independent of $q$. At first, this appears to be a sweeping generalization, however, as evidenced by the good agreement between the simulation data and theory in the manuscript, it appears to be a valid one. Therefore, the only quantity we are seeking to modify is $p$, via a sensible modification of the dimer partition function $q_0$.

In order to find the $q$ dependence of the dimer partition function, we have used a rather implicit method to derive it. Namely, to begin, we made the following assumption - a modification to eq 6 of the following variety,

$$
q_0(q) = q_\infty(q) \frac{1 - e^{-\lambda}}{\lambda}.
$$

Whereby, we assume the influence of $q$ to act only on $q_\infty$, retaining the additional $\lambda$ dependence (due to flexible chains) for all $q$. Therefore, we have reduced our problem down to the calculation of $q_\infty(q)$. As we are dealing with superball particles in the range of $q \in [1, \infty]$, the two limiting cases are clear, $q_\infty(1)$ and $q_\infty(\infty)$. We noted $q_\infty(1)$ already in eq 7 as $q_\infty(1) = e^{2\lambda}/3\lambda^2$. Therefore as a first step we aimed to derive an expression for $q_\infty(\infty)$: the dimer partition function of perfect cubes in an infinite field.

**Dimer partition function of perfect cubes in an infinite field.**

The dimer partition function in an infinite field is defined in the following manner,

$$
q_\infty = \frac{1}{v} \int e^{-\beta U(1,2)} \, dV,
$$

where $U(1,2)$ is the pair interaction potential between two dipolar particles; $\beta = 1/kT$, the inverse of thermal energy; $dV$ is the volume element and $v$ is the appropriate normalizing
volume. The pair interaction potential is the sum of a hard-core steric repulsion and the dipolar interaction:

\[ U(1, 2) = U_s(1, 2) + U_d(1, 2). \quad (11) \]

The dipole-dipole interaction has the standard form,

\[ U_d(1, 2) = \frac{\mu_0}{4\pi} \left[ \frac{\mathbf{m}_1 \cdot \mathbf{m}_2}{|\mathbf{r}_{12}|^3} - \frac{3(\mathbf{m}_1 \cdot \mathbf{r}_{12})(\mathbf{m}_2 \cdot \mathbf{r}_{12})}{|\mathbf{r}_{12}|^5} \right], \quad (12) \]

and the steric interaction is as follows,

\[ U_s(1, 2) = \begin{cases} 
\infty, & \text{particles } i \text{ and } j \text{ overlap}, \\
0, & \text{no overlap}. 
\end{cases} \quad (13) \]

As we are in the regime of infinite field the dipoles are aligned parallel to each other in the direction of the field and have no orientation degrees of freedom. The cylindrical coordinate system used is shown in Figure S1, where particle one is centered at the origin. As such, \( \mathbf{m}_1 = \mathbf{m}_2 = m\mathbf{e}_3 \), with \( \mathbf{e}_3 \) denoting the unit vector in the positive \( z \) direction, and \( m \) the magnitude of the magnetic dipole moment. The inter-particle separation vector \( \mathbf{r}_{12} \), takes the form,

\[ \mathbf{r}_{12} = r \cos \phi \mathbf{e}_1 + r \sin \phi \mathbf{e}_2 + z \mathbf{e}_3, \quad (14) \]

were \( r \) is the distance of the second particle from the \( z \) axis. Moreover, we can conveniently express \( r \) in terms of \( z \) and \( \theta \), as \( r = z \tan \theta \). Therefore, the inter-particle separation becomes

\[ \mathbf{r}_{12} = z (\tan \theta \cos \phi \mathbf{e}_1 + \tan \theta \sin \phi \mathbf{e}_2 + \mathbf{e}_3), \quad (15) \]

the magnitude of which is given by, \( |\mathbf{r}_{12}| = z \sec \theta \). With these identifications we can reduce
Figure S1: Coordinate system used for the calculation of $q_\infty$, with all relevant quantities annotated. To the left hand side we have a view in the $x$-$z$ plane and to the right hand side we have a view from above, in the $x$-$y$ plane.

the dipole interaction from eq 12 to the following form,

$$-\beta U_d(1, 2) = \lambda \left( \frac{h}{z} \right)^3 \left[ 3 \cos^5 \theta - \cos^3 \theta \right]. \quad (16)$$

Thus in cylindrical coordinates one can express the integral from eq 10 as,

$$q_\infty = \frac{1}{v} \int_h^\infty z^2 \int_0^{2\pi} d\phi \int_0^{\tan^{-1}(\sqrt{2})} e^{-\beta U_d(1, 2)} \tan \theta \sec^2 \theta \, d\theta \, dz, \quad (17)$$

where we have inserted the volume element $dV = r \, dr \, d\phi \, dz$, which in terms of $\theta$ reads, $dV = z^2 \tan \theta \sec^2 \theta \, d\theta \, d\phi \, dz$. The steric interaction is accounted for in the limits of the integration. Inserting the form of the interaction energy and evaluating the trivial integral over $\phi$ we arrive at,

$$q_\infty = \frac{2\pi}{v} \int_h^\infty z^2 \int_0^{\tan^{-1}(\sqrt{2})} e^{\lambda \left( \frac{h}{z} \right)^3 \left[ 3 \cos^5 \theta - \cos^3 \theta \right]} \tan \theta \sec^2 \theta \, d\theta \, dz. \quad (18)$$

Now in order to solve this integral, we need to study the behavior of the integrand in question. It transpires that said integrand has a sharp maximum of $e^{2\lambda}$, occurring at $z = h$ and $\theta = 0$, which is significantly larger than one. We can account for a significant portion thereof by utilizing saddle-point integration. In this manner, we look to expand the dipole
interaction about this maxima. The corresponding criteria are: $z^3 = h^3(1 + \xi)$ with $\xi \ll 1$, and $\theta \ll 1$. Retaining angular terms up to $O(\theta^2)$ and displacement to $O(\xi)$, gives the expansion of the dipolar potential as,

$$-\beta U_d(1, 2) = \lambda(2 - 2\xi - 6\theta^2). \tag{19}$$

Adjusting the volume element, and limits of integration, for this substitution of variables leaves us with,

$$q_\infty = \frac{2\pi}{v} \frac{h^3}{3} \int_0^{\infty} \int_0^{\infty} e^{\lambda(2 - 2\xi - 6\theta^2)} \theta d\theta d\xi. \tag{20}$$

We are now in a position to evaluate the integral as,

$$q_\infty = \frac{2\pi}{v} \frac{h^3}{3} e^{2\lambda} \int_0^{\infty} e^{-2\lambda\xi} d\xi \int_0^{\infty} e^{-6\lambda\theta^2} \theta d\theta$$
$$= \frac{2\pi}{v} \frac{h^3}{3} e^{2\lambda} \frac{1}{2\lambda} \int_0^{\infty} e^{-6\lambda\theta^2} \theta d\theta$$
$$= \frac{2\pi}{v} \frac{h^3}{3} e^{2\lambda} \frac{1}{2\lambda} \int_0^{\infty} e^{-u} du; \text{ for } u = 6\lambda\theta^2$$
$$= \frac{2\pi}{v} \frac{h^3}{3} e^{2\lambda} \frac{1}{12\lambda^2}$$
$$= \frac{2\pi}{v} \frac{h^3}{3} e^{2\lambda} \frac{1}{24\lambda^2}. \tag{21}$$

All that remains to be done is to identify the normalizing volume $v$, namely,

$$v = \int_0^{h} z^2 dz \int_0^{2\pi} d\phi \int_0^{\tan^{-1}(\sqrt{2})} \tan \theta \sec^2 \theta d\theta,$$
$$v = \frac{h^3}{3} \cdot 2\pi \cdot 1 = \frac{2\pi h^3}{3}. \tag{22}$$

Thus, the final form of $q_\infty(\infty)$ arrived at is,

$$q_\infty(\infty) = \frac{e^{2\lambda}}{24\lambda^2}. \tag{23}$$
Now we have the two limiting cases we were aiming for,

\[
q_0(1.0) = q_\infty(1.0) \frac{1 - e^{-\lambda}}{\lambda} = \frac{e^{2\lambda} 1 - e^{-\lambda}}{3\lambda^2} ; \\
q_0(\infty) = q_\infty(\infty) \frac{1 - e^{-\lambda}}{\lambda} = \frac{e^{2\lambda} 1 - e^{-\lambda}}{24\lambda^2} .
\]  

(24)

**Interpolation between the two limiting cases**

The next step in the procedure was to suggest a method of connecting the region spanning \( q_0(q) \) for values of \( q \in (1, \infty) \). Our approach was to try a simple linear interpolation. Namely, we can express \( q_0(q) \) in the following way,

\[
q_0(q) = f(q) \frac{e^{2\lambda}(1 - e^{-\lambda})}{3\lambda^3}, \\
q_0(q) = f(q)q_0(\lambda),
\]

\[i.e.\] the superball dimer partition function can be expressed as the sphere dimer partition function scaled by the multiplicative \( q \) dependent factor \( f(q) \). At this point we know the following to be true \( f(1.0) = 1 \) and \( f(\infty) = 1/8 \). In order for a slightly more convenient interpretation of this function, we shall shift the argument from \( q \) to the dimensionless single superball particle volume \( \nu_{sb}(q) \), given as

\[
\nu_{sb}(q) = \frac{\Gamma\left(\frac{1}{2q}\right)^3}{12q^2\Gamma\left(\frac{3}{2q}\right)},
\]

(26)

where \( \Gamma(x) \) is the gamma function of argument \( x \). Therefore, the limiting cases of \( f(\nu_{sb}) \) are \( f(\nu_s) = 1 \) and \( f(\nu_c) = 1/8 \), where the sphere volume is \( \nu_s = \nu_{sb}(1.0) \) and the cube volume is \( \nu_c = \nu_{sb}(\infty) \). The linear interpolation required will thus have the following form,

\[
f(\nu_{sb}) - \frac{1}{8} = M (\nu_{sb} - \nu_c),
\]

(27)
where $M$ is the linear gradient, determined as follows,

$$M = \frac{1}{8} - \frac{1}{\nu_c - \nu_s} = \frac{-7}{8(\nu_c - \nu_s)}.$$  

(28)

Thus our linear interpolation in term of these parameters reduces to,

$$f(\nu_{sb}) - \frac{1}{8} = \frac{-7}{8(\nu_c - \nu_s)}(\nu_{sb} - \nu_c),$$

$$f(\nu_{sb}) = \frac{-7(\nu_{sb} - \nu_c)}{8(\nu_c - \nu_s)} + \frac{1}{8},$$

$$f(\nu_{sb}) = \frac{-7\nu_{sb} + 8\nu_c - \nu_s}{8(\nu_c - \nu_s)}.$$  

(29)

One can add the numerical values of $\nu_s = \pi/6$ and $\nu_c = 1$ if desired, yielding

$$f(\nu_{sb}) = \frac{-7\nu_{sb} + 8 - \frac{\pi}{6}}{8(1 - \frac{\pi}{6})},$$

$$f(\nu_{sb}) = \frac{-42\nu_{sb} + 48 - \pi}{8(6 - \pi)},$$

$$f(\nu_{sb}) \approx -1.8367\nu_{sb} + 1.9617.$$  

(30)

(31)

Returning to functions in terms of $q$ we can write,

$$f(q) = \frac{-42\nu_{sb}(q) + 48 - \pi}{8(6 - \pi)}.$$  

(32)

This allows us to write the full expression for the dimer partition function in terms of the superball shape parameter as,

$$q_0(q) = f(q)q_0^6(\lambda),$$

$$q_0(q, \lambda) = \left( \frac{-42\nu_{sb}(q) + 48 - \pi}{8(6 - \pi)} \right) \frac{e^{2\lambda}(1 - e^{-\lambda})}{3\lambda^3},$$  

(33)

which can be substituted back into $p(q)$ and in turn $\chi_0$, to determine how $q$ influences the ISMS. At this point our task is complete.
Cluster Analysis

As alluded to in the main manuscript we have included here the snapshot arrays for the remaining six values of reduced density investigated. The arrays appear in Figures S2-S7, in order of increasing $\rho^*$. The cluster color-coding provides the ideal way in which to ‘watch’ the system’s evolving cluster size distribution and connectivity from state-point to state-point.

Figure S2: A snapshot array of state points with a density of $\rho = 0.01$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white.
Figure S3: A snapshot array of state points with a density of $\rho = 0.025$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white.
Figure S4: A snapshot array of state points with a density of $\rho = 0.05$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white.
Figure S5: A snapshot array of state points with a density of $\rho = 0.1$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white.
Figure S6: A snapshot array of state points with a density of $\rho = 0.15$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white. The missing column on the right hand side is due to the fact that $\lambda = 4$ was not considered for this density.
Figure S7: A snapshot array of state points with a density of $\rho = 0.2$. Each row corresponds to state points with the annotated value of $q$ and each column corresponds to the annotated value of $\lambda$. The coloring of clusters is in accordance with the color bar appearing on the right-hand side of the figure, where monomers are colored white. The missing column on the right hand side is due to the fact that $\lambda = 4$ was not considered for this density.