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Kinetics of string-gel formation in a system of dipolar colloidal particles

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The formation of string-gels of dipolar colloidal particles is investigated using molecular dynamics simulations. The characteristic gelation time consistently increases as the temperature of the system increases; it also increases as the density of the system increases. This latter result suggests that the gel formation is not a simple nucleation process. In particular, the energy barriers separating the embryonic nuclei from the final phase appear to be lower for the low-density system, suggesting an important entropic contribution.

Keywords: dipolar colloids; string-gels; kinetics of gelation

1. Introduction

In recent years, there has been an increasing interest in structures formed by dipolar particles [1–4]. Particles with directional interactions form a variety of different macroscopic phases depending on the magnitude of the interparticle interaction, the concentration and the temperature. In the low-density regime, three phases can be distinguished: fluid, string-fluid and string-gels, which appear in that order as the temperature is decreased [3]. The possibility of manipulating these phases by applying external fields makes these systems attractive for the development of tunable materials. From a practical point of view, dipolar colloidal particles are being considered for many nanotechnological applications [5,6], and for the manipulation of nanoparticles in chain-like structures that may serve as quantum wires and single electron pump devices [7].

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One contribution of 17 to a Theme Issue ‘Nonlinear dynamics in meso and nano scales: fundamental aspects and applications’.

Numerical simulations of dipolar particles were pioneered by Weis & Levesque [8–10], who performed a Monte Carlo study on hard spheres with an embedded dipole. They identified the relevant energy unit,

$$u_d = \frac{\mu^2}{4\pi\epsilon_0\epsilon\sigma^3}, \quad (1.1)$$

where μ is the dipole moment of the particles, ϵ_0 is the vacuum permittivity, ϵ is the relative permittivity of the continuous medium and σ is defined as the typical centre–centre distance between particles. Using this definition, we can define a reduced temperature by

$$T^* = \frac{k_B T}{u_d}. \quad (1.2)$$

These early studies showed that the formation of chain-like structures of dipolar particles occurs at approximately $T^* < 0.25$, in agreement with recent experimental results [11].

Goyal *et al.* [3] performed an extensive molecular dynamics study of a simplified dipolar hard sphere system. Reducing the continuous dipolar interaction potential to a discretized step-like potential, and using fast discontinuous molecular dynamics, they were able to draw a complete phase diagram for dipolar particles. In the low-density regime, three different phases are clearly distinguished. For high temperatures, the system behaves like a homogeneous fluid or gas with no particle aggregation. Reducing the temperature, an intermediate phase is observed that is characterized by the aggregation of short-chain structures. For low temperatures, the system collapses into a percolated string-like cluster, resembling a polymeric gel. The determination of this phase diagram is not rigorous, since the chemical potential of the particles and the pressure of the system were not investigated. Indeed, the calculation of the thermodynamic stability of these particular systems is a challenging proposition that deserves careful examination, as the calculation of the chemical potential of the string-like structures is not simple [12].

Even though experimental systems consist of a solvent in which the colloidal particles are dispersed, all simulation attempts consider the solvent in a simplified way. The reason for this is the enormous size difference between the colloidal particles and the solvent molecules that prohibits a simultaneous atomistic description of both of them. There are several approximations for the treatment of the continuous solvent. The simplest one, used here as well as in other work [3,4], is to characterize the solvent by its relative electrical permittivity, ϵ . More realistic representations are possible, including the hydrodynamic interaction [13].

Here, we consider the kinetics of string-gel formation, starting from a dispersed dilute solution of dipolar colloidal particles. Using molecular dynamics, we monitor the time evolution of the system until the string-gel conformation is reached. We found that the time to form the gel is directly correlated to the temperature, and inversely correlated to the density of the system.

2. Model and methods

In order to isolate the dipolar interaction from any other gel-forming interaction, we model the colloidal particles by a purely repulsive spherical core plus an explicit dipole consisting of a charge pair $+q$ and $-q$ separated by a fixed distance d , which results in a dipole moment $\mu = qd$. Explicitly, the interaction between two particles separated by a distance r is

$$U(r) = U_c(r) + U_e(r) \quad (2.1)$$

with

$$U_c(r) = \left(\frac{\sigma}{r}\right)^{36} \quad (2.2)$$

and

$$U_e(r_{ij}) = \sum_{i,j} \frac{1}{4\pi\epsilon_0\epsilon} \frac{q_i q_j}{r_{ij}}, \quad (2.3)$$

where the sum runs over all the charge pairs between two particles. In all cases, we have used $\sigma = 1$ nm, $q = 0.5e$, $d = 0.5$ nm and a relative dielectric constant $\epsilon = 80$. Except for very short separations, the electrostatic interactions can be accurately described by an ideal dipole–dipole interaction,

$$U_e(r_{ij}) = \frac{\vec{\mu}_i \cdot \vec{\mu}_j - 3(\hat{n}_{ij} \cdot \vec{\mu}_i)(\hat{n}_{ij} \cdot \vec{\mu}_j)}{4\pi\epsilon_0\epsilon r_{ij}^3}, \quad (2.4)$$

where $\vec{\mu}_i$ is the dipole moment of the particle i , and $\hat{n}_{ij} = \vec{r}_{ij}/r_{ij}$.

The repulsive interaction in equation (2.2) was chosen for two reasons. First, colloidal particles are larger and harder than atoms; therefore, the sharper r^{-36} is a better representation of the system than the atom-like r^{-12} [14]. Second, a steeper repulsion is numerically convenient in order to avoid the divergency of the electrostatic interactions. The value of the relative dielectric constant was chosen to simulate typical experimental conditions, where water is often the solvent.

The total potential energy of a system with N particles is calculated summing up all the pair interactions. In figure 1, we show the potential energy between two particles in three different relative orientations. The most favourable conformation is that with the particles having their dipoles aligned head to tail. Particles with their dipoles aligned side by side attract if the dipoles are antiparallel, and repel if the dipoles are parallel. A spherical cut-off was imposed on all interactions at $r = r_c$. Therefore, we did not consider the effect of the long-range electrostatic interactions, i.e. Ewald summation. The reason for this was to have a simple and fast model for colloidal dipolar particles with continuum interactions resembling the model of Goyal *et al.* [3]. However, we evaluated the effect of the cut-off by considering two different values, $r_c = 4$ and 8 nm. These are indeed long cut-off distances, considering that the Bjerrum length is 0.7 nm. Therefore, the electrostatic energy between two elementary charges is 0.175 and $0.0875 k_B T$ for the two cut-off distances, respectively. In addition, the interaction between the particles is effectively an interaction between two dipoles (proportional to $1/r^3$; equation (2.4)); therefore, the effect of the

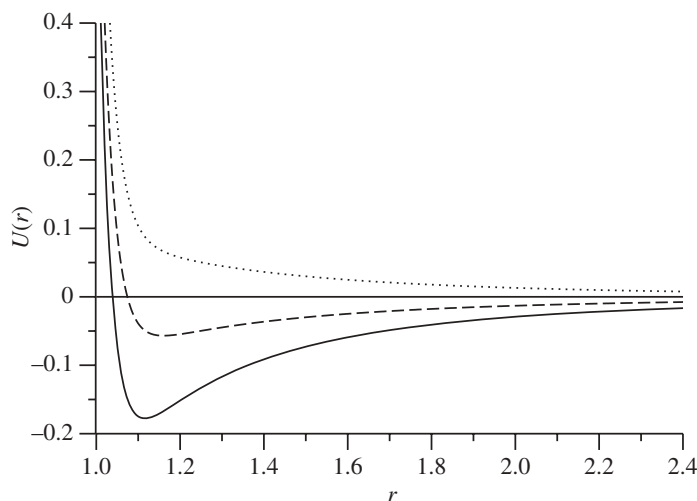


Figure 1. Potential energy between two particles in three different relative orientations: head to tail (solid line), side by side with antiparallel (dashed line) and parallel (dotted line) dipoles.

cut-off is, in principle, less important than for pure Coulombic interactions. Finally, the results obtained with the two cut-off distances showed no significant differences (see below).

Molecular dynamic (MD) simulations were performed using the GROMACS v.4.0.5 simulation package [15,16]. All simulations were performed under *NVT* conditions, with $N = 1000$, and the classical Newton's equations were integrated using the leap-frog algorithm with a time step of 0.001 ps. The temperature was maintained constant by a Nose-Hoover thermostat, with a time constant of 0.1 ps. A cubic simulation box of side L was used for all the cases. Two different volumes (densities) were studied, characterized by $L = 40$ and 45 nm, and three temperatures for each case, $T_1^* = 0.153$, $T_2^* = 0.184$ and $T_3^* = 0.215$. All simulations were performed following the same protocol. The initial random conformation was obtained from a short high-temperature simulation, and in all cases it had zero or very small potential energy. The MD simulations were started from that initial conformation with the thermostat set to the target temperature. The total simulation time varied depending on the case, since the simulations were stopped once the string-gel had formed and the potential energy of the system oscillated around a constant average value. The longest simulation spans were over 100 ns.

3. Results

In order to illustrate a typical gelation process we show in figure 2 three snapshots of representative conformations of the system. All the cases correspond to $L = 45$ nm, $T_2^* = 0.184$. First, at 5 ns of simulation, the system still shows a random gas character, very similar to the initial state. At 18 ns, which corresponds roughly to a state with one-third of the final potential energy, the system starts the

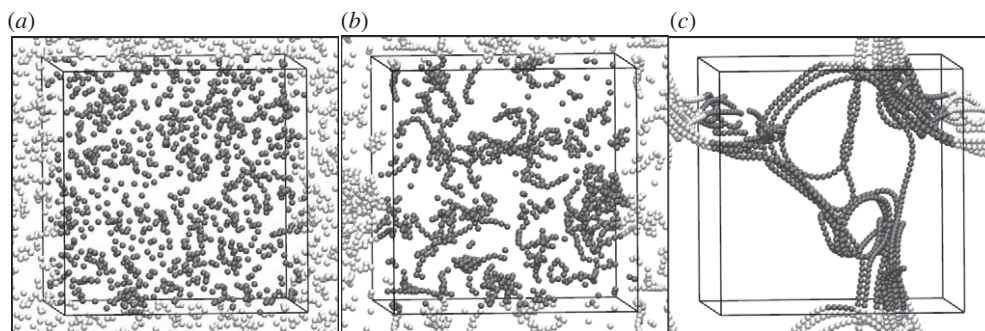


Figure 2. Typical configuration of the system at different stages during the gelling process. The darker spheres are those in the simulation box, whereas the clear ones are the periodic images added to facilitate the view of the percolated cluster. The three snapshots correspond to $L = 45$ nm, $T_2^* = 0.184$. The pictures correspond to (a) $t = 5$ ns, (b) 18 ns and (c) 50 ns, respectively.

gelation process and presents several short strings of varying length. At the end of the simulation (50 ns), the system has percolated to a single cluster. The structure of this final cluster consists of a string of colloidal particles aligned in the head to tail configuration. The flexibility of the self-associated chain allows for the formation of loops and also for the chain to fold over itself in order to decrease the energy even further owing to the favourable interaction of the antiparallel dipoles.

Whether the final state is a true thermodynamic phase or a kinetically trapped state is difficult to know. The particular packing involving several chain sections forming a bundle may suggest a tendency of the system to phase separate to a solid structure. However, in order to achieve a total phase separation the system needs to break the strings in several pieces. Owing to the low temperature of the system, the phase separation is prevented since the cost of breaking the strings is too high for the conditions within the system. These arguments suggest that the system is in a kinetically arrested state owing to the magnitude of the energy barriers [4].

There are several properties that may be used to monitor the gelation process. One of them is average cluster size. In figure 3, we show the average cluster size for the case corresponding to figure 2; namely $L = 45$ nm and $T_2^* = 0.184$. The curve shows a steady growth of the clusters as the particles aggregate to form the strings. For the time corresponding to figure 2b the average cluster size is around 10, a number consistent with the structure displayed in the snapshot. Between 20 and 30 ns, the aggregation process gains speed and the system rapidly becomes a single cluster involving all the particles in the system. Once the gel forms after 30 ns, there are fluctuations in its shape as the strings slowly move; however, no particles leave the cluster.

Another indicator of the progress of the gelation process is the variation in the potential energy of the system with time. This property is shown in figure 4 for all the simulated cases. Before any further analysis it is clear from the results that duplicating the cut-off distance does not have a significant effect on the results: the gelation time is inversely correlated to the system density. The difference in gelation time between the two cut-off distances is no larger than the normal statistical fluctuations between two different trajectories.

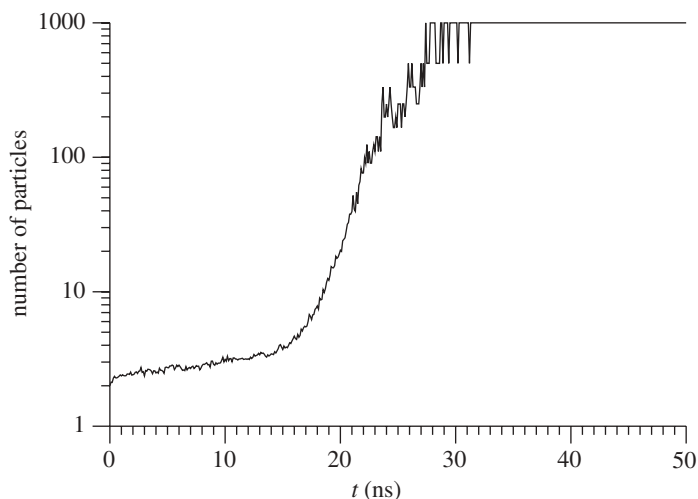


Figure 3. Time evolution of the average cluster size for the system $L = 45$ nm, $T_2^* = 0.184$. Initially there is a very slow aggregation process. Then a sudden increase in the speed of aggregation results in a complete percolation during a period of approximately 10 ns. Once the string-gel system has formed, it remains assembled throughout the rest of the simulation.

Several interesting points can be made from [figure 4](#). First, we note that all the systems reach a final equilibrium state with a potential energy that is independent of both density and temperature. This indicates that, in all cases, there are approximately the same number of particle contacts in the system. The number of head-to-tail contacts is equal to (or slightly smaller than) N , since all the particles participate in a string. The number of side-by-side antiparallel contacts is not easy to count, but judging from their energy contribution we can conclude that this is roughly the same for all the systems studied.

A second point that immediately stands out from [figure 4](#) is that the effect of temperature on the gelation time is similar for both densities. A lower temperature system reaches the final string-gel structure in a shorter time than a higher temperature system. This result is reasonable, if we consider the aggregation process as a gradual growth of randomly formed embryo clusters. At a lower temperature, the embryo clusters are more stable, facilitating their growth to a critical size and the subsequent string-gel.

The third point to note from the energy–time curves is the effect of the system’s density on the kinetics of gelation. For all three temperatures, the lower density system reached its final state in a shorter time than the higher density system. This result is somewhat surprising. If we consider that the growth of the string-gel is the result of a nucleation process, then it would be expected that the formation of the embryo nuclei is more probable in a more concentrated system. Moreover, since these are very dilute systems, the higher density system is closer to the spinodal decomposition curve than the lower density system. Therefore, according to classical nucleation theory, the kinetic barriers for nucleation should be lower in the higher density system than in the lower density one [17], which is contrary to our findings. This unusual behaviour has been observed consistently in many simulations.

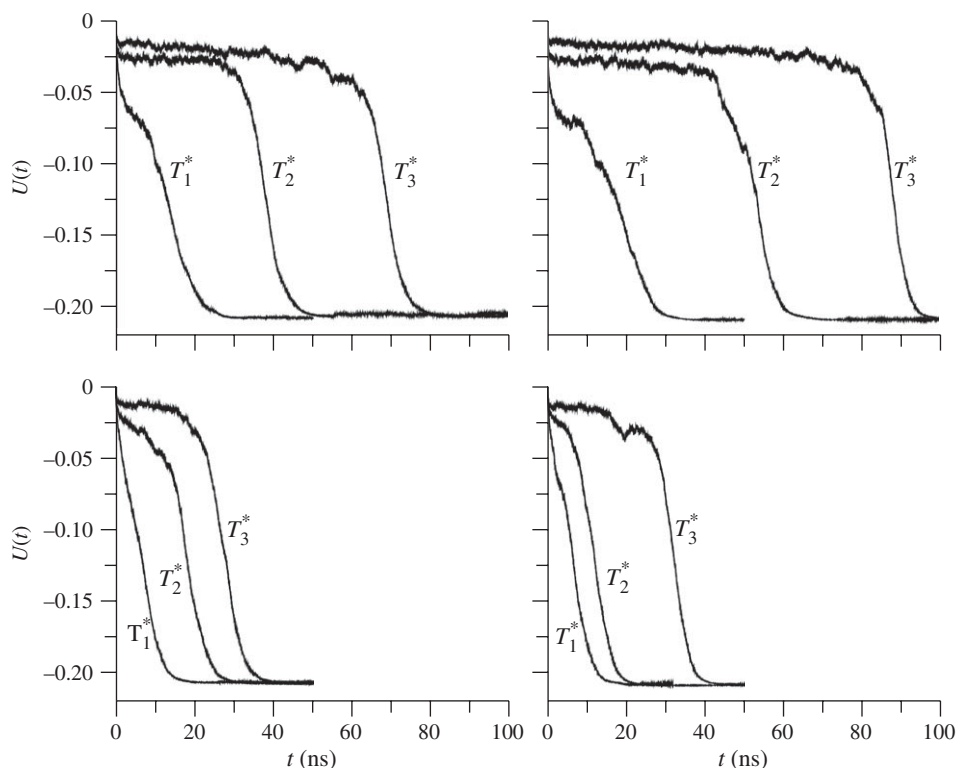


Figure 4. Potential energy of the system as a function of time. The curves correspond to $T_1^* = 0.153$, $T_2^* = 0.184$ and $T_3^* = 0.215$, as indicated on the plot. The sharp drop in the potential energy indicates the onset of gelation. Left and right panels correspond to calculations performed with $r_c = 4$ nm and $r_c = 8$ nm, respectively. Top and bottom panels correspond to $L = 40$ nm and $L = 45$ nm, respectively.

4. Discussion

The formation of string-gel of dipolar colloidal particles has been studied using molecular dynamics simulations, using a simple continuous dielectric model for the solvent component of the system. We found that the gelation time becomes shorter as the temperature is decreased, which can be understood by considering that reducing the temperature results in less thermal noise so that the seed embryonic nuclei can grow more favourably. The dependence of the gelation time on the system's density is unusual and counterintuitive. Indeed, particles interacting with short-range spherical potential have exactly the opposite behaviour. We suspect that the entropy plays a relevant role in determining the free-energy barriers separating embryo nuclei from the final gel. The final string-gel can be thought of as a polymeric network, with sections of strings connecting branching sites. The length of the connecting strings, and the holes in the resulting network, are larger for the less dense system. Therefore, it can be argued that from an entropic point of view the low-density systems have a deeper free-energy minimum than the higher

density system. Since the energetic contribution is similar in both cases, we conclude that the gelation process is dominated by the entropy of the system.

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