Gelation of a Clay Colloid Suspension

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A colloidal suspension of clay particles is modeled by a system of infinitely thin disks carrying a point quadrupole, which results from the electric double layer around the clay platelets. Monte Carlo simulations show that, at sufficiently large values of the quadrupole moment, the system undergoes a transition from a low concentration phase, where disks assemble into elongated clusters, to a space-filling gel phase at higher concentrations. The gel phase exhibits a nearly incompressible network structure similar to the "house-of-cards" structure conjectured to be typical of clay gelation.

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Clays are widely used *as thickeners* in common products of every-day life, *such as* ointments and paints, and play a key role in many industrial processes, such as oil drilling. As well as this technological aspect, the rheology of clay suspensions presents fundamental problems in statistical physics.

Clays are lamellar mineral crystals which swell when dispersed in water. They give rise to a colloidal suspension of thin, irregularly shaped platelets, which carry a surface charge linked to their cation exchange capacity. Depending on platelet and electrolyte concentration, these suspensions may exhibit gel-like rheological properties [1–3] *even* at low platelet concentration. Accounting for this solidlike behavior at low particle number density poses a basic conceptual problem. The formation of a solidlike gel in polymer solutions at low concentrations can be interpreted as a consequence of entanglement but, for compact bodies like *the clay* particles, amorphous solid phases (glasses) are normally only found at densities above that at which crystallization occurs [4] and are *not* the thermodynamic equilibrium phase. Suspensions of uncharged hard disks remain fluid at the densities of interest, but may undergo a transition to a nematic phase at much higher density [5]. It has been suggested that the gelation of clay suspensions is linked to the formation of "house-of-cards" structures [1], but direct experimental verification of this concept is lacking. Furthermore, the thermodynamic stability of this structure has not been examined—in particular, with respect to thermal motion.

The complexity of natural clay suspensions has inhibited theoretical examination of these issues. However, the recent availability of synthetic clays, made up of well-characterized, monodisperse platelets, opens up the possibility of a quantitative statistical description. In this Letter, we show, on the basis of extensive Monte Carlo (MC) simulations, that a very simple model of such a synthetic clay indeed leads to a well-defined sol-gel transition, which exhibits many of the features observed in clay suspensions and supports the role of a thermodynamically stable house-of-cards phase in accounting for this behavior.

The synthetic clay laponite, which we are considering, forms a rigid amorphous gel when suspended in water, at mass concentrations as low as a few percent [6]. Laponite is made up of microcrystalline magnesium silicate, disklike platelets of diameter $\sigma \simeq 25$ nm and thickness $h \simeq 1$ nm [6]. The platelets carry a net negative charge, due to isomorphous substitution of a fraction of the Mg^{2+} ions by Li^+ ions; the resulting few hundred elementary charges ($-e$) are uniformly distributed over the disks, while a smaller positive charge, originating from broken bonds, is concentrated along the rim. The overall negative charge of the platelets is compensated by Na^+ counterions; these, together with added salt ions, form electric double layers around the laponite disks suspended in water. In view of the cylindrical symmetry of an isolated laponite particle and its associated double layer, the simplest model of the suspension is one of infinitely thin disks, carrying a fixed point quadrupole Q at their center. Disks are not allowed to intersect; the mutual excluded volume of two disks depends on their relative orientation and shrinks to zero when they are parallel. The electrostatic interaction potential between the quadrupoles associated with disks i and j is

$$v_{QQ}(\vec{r}_{ij},\vec{n}_i,\vec{n}_j) = \frac{3Q^2}{4r_{ij}^5}\,\Phi^{224}(i,j)\,, \tag{1}$$

where the rotational invariant Φ^{224} depends on the relative orientations of the center-to-center vector $\vec{r}_{ij}$ and of the orientation vectors $\vec{n}_i$ and $\vec{n}_j$ (parallel to the normals of the disks) [7]. If $\vec{r}_{ij}$ is chosen as the polar axis for the orientation vectors $\vec{n}_i$ and $\vec{n}_j$, specified by the polar angles (θ_i, ϕ_i) and (θ_j, ϕ_j), $\Phi^{224}(i,j)$ reduces to

$$\begin{aligned}\Phi^{224}(i,j) = 1 &- 5\cos^2\theta_i - r\cos^2\theta_j \\ &- 15\cos^2\theta_i\cos^2\theta_j \\ &+ 2[\sin\theta_i\sin\theta_j\cos(\theta_i-\theta_j) - 4\cos\theta_i\cos\theta_j]^2.\end{aligned} \tag{2}$$

According to the usual convention, Q is the zz component of the quadrupole tensor in a particle-fixed frame

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with $\vec{n}$ along Oz. Electrostatic collapse, due to divergent attraction between disks in certain ranges of relative orientations, is avoided by adding an infinite repulsive barrier for center-to-center distances $r \leq \sigma/2$. This barrier does not affect the energetically favorable T-shaped (edge-to-face) pair configuration, which is expected to play an important role in a gel network formation. The relevant dimensionless state variables are the reduced concentration $n^* = N\sigma^3/V$, where N/V is the number of platelets per unit volume, and the dimensionless quadrupolar coupling constant

$$\beta^* = \frac{Q^2}{\epsilon k_B T \sigma^5}, \tag{3}$$

where T is the temperature, k_B Boltzmann's constant, and ϵ the dielectric constant of water. Previous MC simulations have shown that, in the absence of a quadrupole moment (i.e., for $\beta^* = 0$), disks undergo a transition from an isotropic to a nematic phase, where the normals to the disks order parallel to each other, when $n^* \simeq 4$ [5]. Such stacking is energetically unfavorable when $Q \neq 0$ ($\beta^* > 0$); the quadrupolar interactions tend to orient neighboring platelets at a finite angle, the T-shaped configuration being that of lowest energy.

The competition between these tendencies has been examined in MC simulations, in which the quadrupole interaction parameter β^* has been progressively increased. The equation of state of the model, equivalent to the osmotic pressure Π versus concentration n^* for a clay suspension, is readily obtained by subjecting the simulated sample to a gravitational potential $\phi(z) = mgz$ in the z direction, while the system satisfies periodic boundary conditions in the x and y directions. The equilibrium sedimentation profile $\rho(z)$ is measured, and the equation of state derived by integrating the osmotic equilibrium condition [8–10]

$$\frac{d\Pi(z)}{dz} = -mg\rho(z). \tag{4}$$

The resulting equations of state for several values of β^* are shown in Fig. 1; they remain very close to that of bare disks ($\beta^* = 0$) [5] up to $\beta^* = 0.01$. However, the $\Pi(n^*)$ curve changes dramatically for $\beta^* = 0.1$. The measured osmotic pressure drops considerably for concentrations up to $n^* \simeq 2.8$, but thereafter it rises steeply, showing that the suspension has become nearly incompressible, which is the signature of a very rigid structure. In order to analyze the structure of the system at low and high densities, conventional MC simulations were carried out in the canonical (constant temperature and density) ensemble on samples of $N = 250$ disks, with periodic boundary conditions. The pressure, as calculated from the virial theorem, agrees with the data obtained by inverting the sedimentation profile (see Fig. 1).

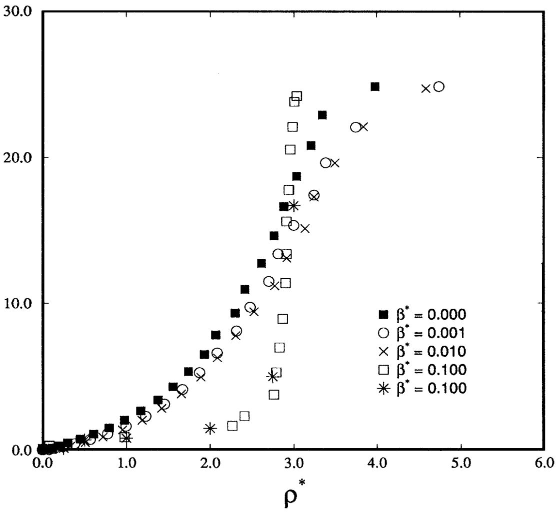

FIG. 1. Reduced osmotic pressure $\Pi^* = \Pi\sigma^3/k_BT$ versus reduced density n^*. Full squares, circles, crosses, and open squares are the results obtained from simulations of the sedimentation equilibrium, for increasing values of the quadrupolar coupling constant β^*. The stars represent the data from constant temperature–constant density MC simulations at $\beta^* = 0.1$. The bending over of the equation of state data at high densities, for $\beta^* \leq 0.01$, may be attributed to the onset of nematic ordering.

Careful examination of typical equilibrium configurations generated in the constant density Monte Carlo runs leads to the following observations. At low coupling ($\beta^* \leq 0.01$), the platelets are homogeneously distributed over the accessible volume. When β^* increases, the platelets tend to form wormlike clusters. A typical low density configuration is shown in Fig. 2. This clustering leads to the strong reduction in osmotic pressure at low concentrations. The clusters fluctuate considerably in size, shape, and composition, thus ensuring that configuration space is adequately sampled in the simulations (ergodicity). As the concentration increases, the clusters must pack into the shrinking available volume, and a space-filling network emerges, as illustrated in Fig. 3. Since electrostatics oppose the more efficient parallel stacking, the resulting house-of-cards network is very rigid, leading to the dramatic increase in osmotic pressure shown in Fig. 1.

These observations suggest an analogy between the origin of gelation in clay suspensions and in multicomponent amphiphilic mixtures [11]. The wormlike clusters are analogous to the micelles which form in such mixtures at low concentration. When the concentration of micelles reaches the point at which they must overlap, a transition to three-dimensional connected structures with greatly increased rigidity occurs.

Examination of typical gel configurations, and of the orientational pair correlation functions, establish the importance of certain local arrangements of disks, such as those highlighted in Fig. 2. The three- and four-membered rings may be regarded as the basic building

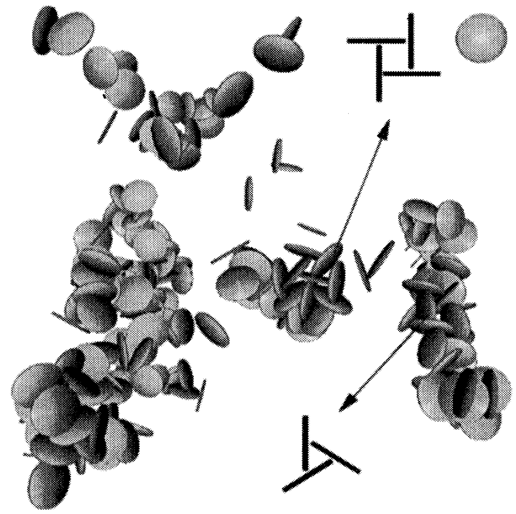

FIG. 2. A typical configuration of quadrupolar disks, from a constant temperature–constant density simulation, at $\beta^* = 0.1$ and low concentration ($n^* = 0.25$). Typical three- and four-platelet rings are schematically shown as insets; arrows point to such rings occurring within the clusters.

blocks of a disordered and frustrated house-of-cards structure. These idealized ring structures, in which the disks just touch, have energies of $-54Q^2/\sigma^5$ and $-99.4Q^2/\sigma^5$ per particle, respectively. If the full gel structure were associated with a random assembly of such rings, a rough lower bound of the gelation density would be obtained by dividing the number of platelets (3 or 4) in the ring by the volume of the circumscribed sphere in units of σ^3. The resulting estimates are $n^* = 1.99$ and $n^* = 1.93$, roughly consistent with the density $n^* \simeq 2.8$ at which a rapid increase in the equation of state occurs.

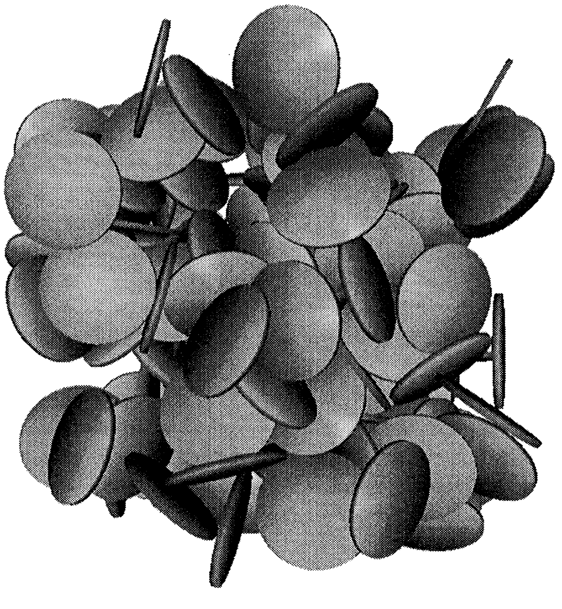

FIG. 3. A typical configuration of quadrupolar disks, as in Fig. 2, but at a much higher concentration ($n^* = 3.00$). The clusters observed at lower density have now collapsed into a single "house-of-cards" network.

This general picture is confirmed by the orientational pair correlation function $g_{\mathrm{or}}(r)$, an example of which is shown in Fig. 4. If $\theta(r)$ denotes the angle between the orientation vectors of two disks with center-to-center distance r, $g_{\mathrm{or}}(r)$ is defined as the statistical average of the second Legendre polynomial:

$$\begin{aligned} g_{\mathrm{or}}(r) &= \langle P_2[\cos\theta(r)]\rangle \\ &= \langle[\tfrac{3}{2}\cos^2\theta(r) - \tfrac{1}{2}]\rangle, \quad r \geq \sigma/2. \end{aligned} \tag{5}$$

Figure 4 shows that for the shortest allowed distances ($r \simeq 0.5$), $g_{\mathrm{or}}(r)$ is negative, i.e., angles $\theta \geq \pi/3$ are favored, while the disks are mainly parallel to each other for distances $r \simeq \sqrt{2}/2$ and $r \simeq 1$, as expected from a four-particle ring, and from an H-like configuration, where two parallel disks are separated by a third disk in contact with and orthogonal to the former. Despite the different topological nature of the particles involved, the observed open gel structure, resulting from electrostatic frustration, is reminiscent of the cross-linked network structure typical of polymer gels.

Close examination of the equation of state for $\beta^* = 0.1$, shown in Fig. 1, points to the existence of a nearly horizontal portion in the $\Pi(n^*)$ curve similar to that observed in recent measurements on laponite [3] in the same concentration range. The shape is suggestive of coexistence between a low density "cluster phase" and a relatively high density "gel phase." To explore this possibility further, we carried out Gibbs ensemble Monte Carlo simulations [12]. In these simulations separate low and high density samples of the system are allowed to exchange volume and particles at a given fixed temperature, until the volumes and numbers of particles in the

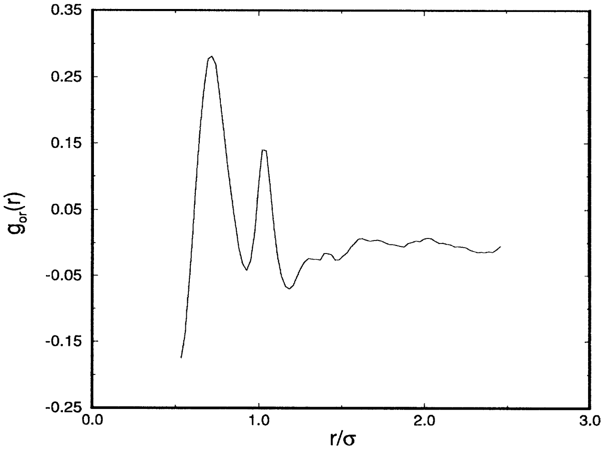

FIG. 4. Orientational correlation function $g_{\mathrm{or}}(r)$ versus center-to-center distance r in units of the disk diameter σ.

two systems reach stationary values, within fluctuations. The resulting densities in the two samples are those of two phases coexisting at some given pressure and chemical potential. In the present quadrupolar disk model, we found that the reduced concentrations of the coexisting phases are $n_1^* = 0.48$ and $n_2^* = 2.16$ at $\beta^* = 0.1$. Under the weaker coupling conditions $\beta^* = 0.08$, the two densities are $n_1^* = 0.64$ and $n_2^* = 1.19$; i.e., the densities of the coexisting phases are closer, as one would expect for liquid-vapor coexistence. These results suggest that there is a two-phase coexistence region below some critical reduced temperature $T_c^* = (\beta_c^*)^{-1}$ (roughly in the range $0.05 < \beta^* < 0.08$). If quenched into that region (e.g., by changing the salt concentration and hence the effective quadrupole moment Q), an initially homogeneous suspension of quadrupolar disks will separate into a low-concentration cluster phase and a gel phase at higher concentrations. Our association of this phase with a gel is based upon its near incompressibility. A complete characterization of the phase we have found would involve the examination of its properties under shear, which will be the subject of future work. It is worth stressing that the house-of-cards gel structure occurs at reduced densities n^* well below that of the nematic (stacked) phase observed for bare disks ($\beta^* = 0$) [5].

The present model tacitly assumes that the quadrupole moment associated with the electric double layer around each clay platelet is independent of concentration. This is certainly an oversimplification, since at sufficiently high concentrations the double layers of neighboring platelets will overlap and the point quadrupole picture must break down. The instantaneous double layer around each platelet is expected to be configuration dependent, a situation which has been successfully treated by a density functional approach in the simpler case of spherical colloidal particles [13]. We are presently extending this method to a model of uniformly charged platelets and microscopic co-ions and counterions, whose density profiles evolve adiabatically, such as to ensure the lowest free energy for each platelet configuration.

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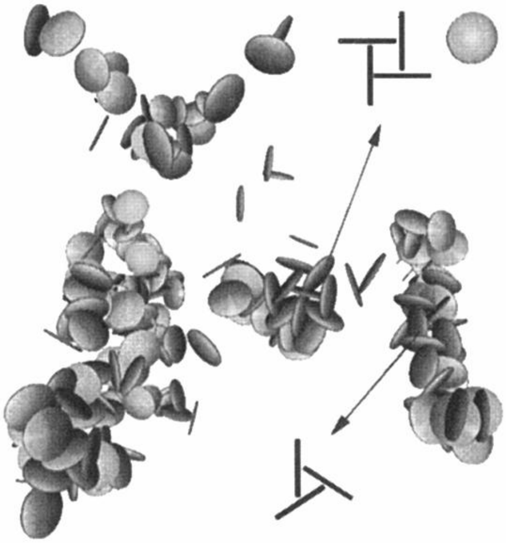

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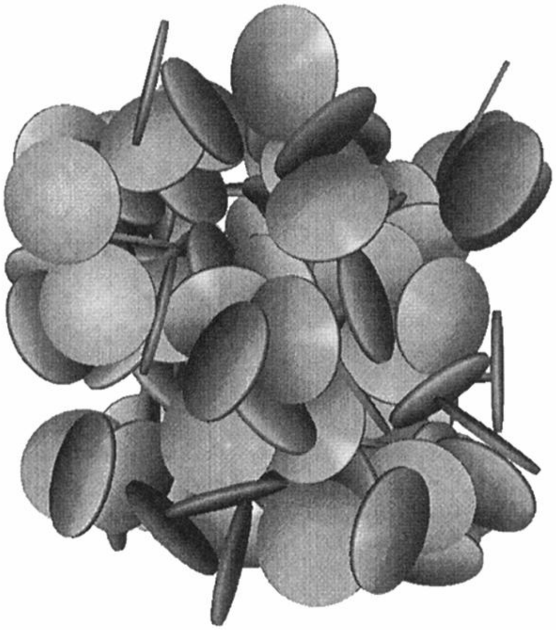

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