



Isotropic–nematic transition and dynamics of rigid charged molecules



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ABSTRACT

Using molecular dynamics, an isotropic–nematic transition was found in bulk salt-free solutions of charged rods with their counterions in the semidilute regime. This phase transition is driven primarily by electrostatics, rather than by excluded volume. The counterion condensation effect, which is controlled by the Manning parameter, leads to liquid crystalline phases of rods. For elevated values of the Manning parameter, an attraction is obtained between the rods, and the nematic phase appears. For small values of the Manning parameter the counterions de-condense, and the nematic phase disappears. Instead, in a neutral system of rods and spheres there is no appearance of nematic phase. The diffusivity of both rods and counterions is reduced with the Manning parameter.

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1. Introduction

In the 1940s, Lars Onsager explained the stability of the isotropic and nematic phases [1]. In the isotropic phase the particle orientations are disordered, but in the nematic (anisotropic) phase the particle orientations are aligned. His theory [1], based on infinitely elongated hard rigid molecules (rods), suggests that both of the phases can be predicted and the isotropic–nematic transition decreases with the aspect ratio L/σ (where L is the rod length and σ is the rod diameter). However, Onsager's theory applies only to rigid molecules in good solvents for L/σ ratios of about 100. On the contrary, the Parsons–Lee theory [2,3] yields qualitatively correct results for aspect ratios $L/\sigma = 5$ –20. Similarly in both these theories, the driving force for the formation of the nematic phase is steric repulsion, the rods can not interpenetrate each other (excluding volume effect).

Several theoretical [2–4] and simulation [5–10] and studies have examined the phase behavior of rods and liquid crystalline phases. The complete phase diagram for hard rods, as a function of the aspect ratio L/σ , has been mapped using different techniques, such as free energy calculations [5], the Gibbs–Duhem integration method [11], and isothermal-isobaric Monte Carlo (MC–NPT) simulations [6]. Moreover, isotropic, nematic, smectic phase transitions have been located by simulations [5] even at the limits $L/\sigma \rightarrow 0$ and $L/\sigma \rightarrow \infty$ (where the simulation results approach the Onsager estimations). Subsequently, the phase behavior of a suspension of rigid molecules interacting via a soft repulsive potential was investigated

[7]. In such a system, attractive dispersion interactions can influence the phase behavior [8] and can induce two liquid crystalline phases, namely a nematic and a smectic A phase. That model predicts a first-order transition from an isotropic to a nematic phase as the concentration of rods is increased.

However if the monomers are charged, rigid molecules present different behavior [12–25]. The electrostatic interaction between the molecules influence the structures and induces many different ordered phases such as the cholesteric phase (a type of liquid crystal with a helical structure [18]), a dense bundle phase [20,21], stacked rafts [15,26,27], smectic and columnar phases [25] and cubatic networks [15,22,26].

Simulation studies [9,18] of the isotropic–nematic transition predict a strong nematic ordering in the weak coupling regime, where the correlations between charged molecules are weak. For instance in a bulk salt-free solution, oppositely charged hard rods of aspect ratio $L/\sigma = 5$ exhibit an isotropic–nematic transition in the weak coupling regime, in qualitative agreement with that of the uncharged hard rods system [9]. However, in all these studies [9,17,18,24,28] the counterions have not been treated explicitly (the counterions are treated implicitly through an inverse Debye screening length κ). It is well known that counterions play a dominant role in polyelectrolyte solutions in both dilute and semidilute regimes, as well as in both the weak and strong coupling regimes, so their effect can not be neglected. Recently, the influence of charged hard spheres on the structure of charged hard rods [29] was investigated using simulations for two different systems, with charges located at the end or at the center of the rods. In particular, isotropic and nematic phases were observed for both systems [29]. At high densities the systems present a nematic–smectic-A and nematic–columnar phase transitions, respectively. Notably, this peculiar

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phenomenon of liquid crystalline phases in charged rod systems is combined by exceedingly slow dynamics [18,30]. In particular, by using a simple model where rods are positioned in a lattice (the counterions have been neglected), was shown that the unusually slow dynamics was due to the frustration in the orientational degrees of freedom [18].

In this Letter, the counterions have been treated explicitly in a bulk salt-free solution and, as it will be shown below, they mainly contribute to the formation of ordered phases (such as nematic) through their action as linkers between charged rods. A strong nematic ordering is predicted in the semidilute regime due to the Manning condensation. The diffusivity of both rods and counterions is reduced with electrostatics.

2. Simulation method

Molecular dynamics simulations were performed for a system of rigid molecules composed of linearly bonded monomers; the bond length between consecutive monomers is constrained to a fixed length b . Each of the monomers are spherically symmetric, with a diameter σ and a charge $-e$. In order to maintain the electro-neutrality of the system, spherical counterions with diameter σ and charge e are added to the system. Each monomer and counterion has size $\sigma = 0.49$, which has been used to simulate charged systems [31]. The electrostatic interaction between two ions is given by:

$$U_{\text{Coulomb}}(r) = \frac{z_i z_j e^2}{D_c r} \quad (1)$$

where r is the distance between the ions, z_i (z_j) is the valence of ion i (j), $e = 1.602 \times 10^{-19}$ C is the fundamental unit of charge, and D_c is the relative permittivity of the medium (78.356 for water at 25 °C). Excluded volume interactions between monomers and counterions are modeled using the Weeks–Chandler–Andersen (WCA) potential [32], given by:

$$U_{\text{WCA}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon & \text{for } 0 < r < 2^{1/6}\sigma \\ 0 & \text{for } 2^{1/6}\sigma \leq r \end{cases} \quad (2)$$

where ϵ is a characteristic interaction energy between particles and r is the distance between atoms. In densities $\rho \geq 0.65$ the structure (radial distribution function) of WCA fluid gives a very good agreement to that of Lennard–Jones (LJ) fluid [33]. However, it deviates from the LJ fluid structure at densities $\rho \leq 0.54$.

In addition to, the Bjerrum length λ_B is the distance where the electrostatic energy is comparable to the thermal energy, and is given by [34]:

$$\lambda_B = \frac{e^2}{D_c k_B T} \quad (3)$$

where k_B is the Boltzmann constant, and T is the temperature of the solution. Generally, in the case of rigid charged molecules, such as rigid polyelectrolytes, the Manning parameter determines the strength of the electrostatic interactions and is given by: $\gamma = \lambda_B/b$ [34], where b ($b = \sigma$), is the average distance between charges. Also, the strength of the short-ranged repulsion to the strength of the electrostatic interactions when the spheres are at a distance σ is kept constant during the simulations [21]:

$$\frac{e^2}{D_c \sigma} \frac{1}{\epsilon} = 1 \quad (4)$$

In this study two different systems have been investigated:

1. Anionic rigid rods ($L/\sigma = 8$), with fraction of charged monomers $f = 1$, and $n = 8$ monomers are used to simulate the rigid charged

molecules. Positive counterions are added to maintain the electro-neutrality of the system.

2. Non-charged (neutral) rigid rods ($L/\sigma = 8$) with $n = 8$ monomers with neutral spheres instead of counterions are used to simulate the neutral system. This corresponds to $\gamma = 0$.

The reduced temperature of the systems is $T^* = k_B T/\epsilon$, and the reduced density is $\rho^* = N\sigma^3/V$ (where N is the total number of particles, and V the volume of the system).

A harmonic bending potential is added along the molecules, in order to make them rigid, of the form: $U_{\text{bend}}(\theta) = \frac{K}{2}(\theta - \theta_0)^2$ where K is a bending constant, θ is the bond angle, and $\theta_0 = 180^\circ$ is the equilibrium bond angle. A sufficiently high value of $K = 5000$ ($k_B T$ units) was used in the simulation in order to ensure that the molecules remain rigid. NVT molecular dynamics simulations have been performed using the GROMACS package [35] at different densities and Manning parameters $\gamma = 1$ ($T^* = 1$), 4.2 ($T^* = 0.238$), 6 ($T^* = 0.167$), and 8 ($T^* = 0.125$). The equations of motion were integrated using the leap-frog-algorithm [35], the time step used was $0.0062\tau_{\text{LJ}}$ (where $\tau_{\text{LJ}} = (m\sigma^2/\epsilon)^{1/2}$ is the Lennard–Jones time, $m = 1$), and an equilibration run of 1 875 000 steps has taken place first. The length of the production runs was 3 125 000 steps. A total of 108 or 131 charged or neutral rigid molecules were inserted in a cubic simulation box for $\rho^* < 0.4$ and 144 charged or neutral rigid molecules were inserted in a cubic simulation box for $\rho^* \geq 0.4$. The length of the simulation box was always larger than twice the length of the rod molecules. The distance between charges along the rod b , is constrained through LINCS algorithm [35]. Also, the particle mesh Ewald method (PME) [36] has been used to treat the long range electrostatics with a Fourier-spacing of 0.1 nm and an order of interpolation 6. The real space cut off is 1.5 nm, and the relative accuracy of the direct/reciprocal space is 10^{-5} [36]. In addition to, the temperature of the simulations was kept constant using the Nose–Hoover algorithm [37] to a reference value with an oscillation relaxation constant $\tau_\tau = 1$ ps.

3. Results and discussion

3.1. Pressure

When the solvent is modeled as a uniform dielectric background of dielectric constant D_c and there are no explicit interaction with solvent molecules, the total pressure calculated in such a system corresponds to the osmotic pressure measured in experiment [14,16]. An important quantity to vary is the Manning parameter γ , which denotes the strength of electrostatic interactions, by varying λ_B while keeping b constant. For water at room temperature, $\lambda_B \approx 0.714$ nm. This value of λ_B in our model occurs at $\lambda_B = 1.45b$. It is well known that DNA has a charge density of $\gamma = 4.2$ and shows nematic, cholesteric and smectic ordered phases at very high concentrations [38]. Generally, there are three experimental methods to tune the charge density of the system (Manning parameter): (i) variation of charge distance b , (ii) dielectric constant of the solvent D_c , and (iii) temperature T of the solution. In this study, the charge density (Manning parameter) changes through variation of temperature T . This allows us to examine the effect of electrostatics on the counterion condensation phenomenon, and structure of rods.

In Figure 1, the variation of the system pressure with the overall density ρ^* is shown for neutral and rigid charged molecules at different values of the Manning parameter γ . We observe that as the strength of the electrostatic interactions increases, the pressure of the system, $P^* = P\sigma^3/\epsilon$, is reduced drastically. In particular, at both $\gamma = 6$, $\gamma = 8$ (for the case of rigid charged molecules), the counterion condensation takes place as can be seen from the reduction of the pressure of the system. The counterions contribute significantly

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