PHYSICAL REVIEW E VOLUME 54, NUMBER 3 SEPTEMBER 1996

Structure of strongly dipolar fluids at low densities

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(Received 16 April 1996)

We propose a simple statistical mechanical theory for a strongly dipolar fluid at low densities, based on the analogy between a polymer chain and a chain formed by strongly polar particles. The general methods developed in the theory of semiflexible polymers enable one to obtain simple expressions for the energy and conformational entropy of a long dipole chain. We then consider the equilibrium between chains of different lengths and derive a general expression for the free energy as a functional of the chain length distribution. Both steric and dipolar interactions between long chains are shown to be weak and as a result the rarefied fluid of strongly dipolar spheres resembles the ideal gas of noninteracting polydisperse chains. It is shown that the chain length distributions found in simulations are compatible with the assumption of very weak interchain interactions if strong finite-size effects are taken into account. We also investigate whether sufficiently strong attractive van der Waals forces between particles can cause dissociation of the chains. Finally, we discuss the case of a dipolar fluid in an applied field and argue that the coexistence between two aligned phases of chains, as observed by computer simulation, is unlikely to occur in an infinite system. [S1063-651X(96)10109-4]

PACS number(s): 61.20.Gy, 75.50.Mm, 64.70.−p

I. INTRODUCTION

Dipolar fluids are a widely studied model in statistical mechanics [1]. Not only are dipolar interactions omnipresent in nature, they also occur, and play a prominent role, in many artificial systems, such as ferrofluids and electrorheological fluids. Ferrofluids are stable colloidal dispersions of ferromagnetic particles coated with surfactants and dispersed in a host liquid, such as water or paraffin [2]; these are interesting by virtue of their high magnetic susceptibility. Electrorheological fluids, on the other hand, are colloidal dispersions of highly polarizable particles in solvents with low dielectric constant, whose rheological and mechanical properties change dramatically when an electric field is applied [3].

Quite apart from their potential applicability, dipolar fluids also raise a number of intriguing fundamental questions, relating to (i) the intrinsically *long-range* character of the dipole-dipole interaction, which leads to a dependence of some physical properties on the shape of the system [4–9], and (ii) its *anisotropy* and especially the strong coupling between the orientations of a pair of interacting dipoles and that of the interdipole vector (two parallel dipoles will repel each other if placed side by side, but attract each other if in a head-to-tail configuration). In particular, the role of dipolar forces in the stabilization of different fluid phases is only poorly understood. Indeed, contrary to the predictions of a number of theories [10–19] and to early simulations [20], more recent numerical work on the dipolar hard-sphere (DHS) [21], dipolar soft-sphere (DSS) [22–24], and Stockmayer [22,25] fluids suggests that a minimum amount of isotropic attractive energy may be necessary to stabilize the liquid-vapor coexistence in a zero applied field. Moreover, simulations further indicate that, at low densities, dipoles tend to associate into chains akin to living polymers [22,24,26,27].

The limited success achieved in the theoretical description of strongly dipolar fluids can be traced back to the nature of the approximations employed, namely, angular averages of the dipole-dipole potential [10,15], or various types of perturbation expansion in the dipole moment (with [12] or without [6,7,12,14,17,19,28,29] Padé resummation). Whereas the former average out all orientational correlations, the latter are restricted to small values of the dipole moment. Both strategies neglect the very strong short-range correlations favoring head-to-tail alignment of dipoles, which are effective even at very low density and lead to the formation of chains. As discussed by Wertheim in [30], highly directional forces tend, if attractive, to promote association into aggregates whose shape depends on the geometry of the repulsion and the directional attraction. Higher-order terms in the usual expansion in the one-particle density ρ then contain an increasing number of ''strong bonds,'' which correspond to strong interactions between neighboring molecules. As a result, the

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1063-651X/96/54(3)/2597(13)/$10.00

free energy of such a system can only be calculated after infinite resummations of these terms, a mathematically very complicated procedure. Consider as a simple example a fluid of hard spheres with one dimerizing site, in an attractive mean field. For sufficiently strong site-site interactions, the fraction of monomers will be very low even in the vapor phase [31] and the thermodynamics will be dominated by dimers. Strongly dipolar fluids present the additional complication that the dipole-dipole interaction is long ranged and thus does not saturate when chains are formed. In this case it is therefore essential to separate short-range effects, leading to chaining, from long-range ones responsible for interchain interactions.

We can estimate the range of validity of the usual low-density expansions in the following simple way. Consider a fluid of spherical molecules of diameter σ and dipole moment μ. The second term in the Mayer expansion of the equation of state is

$$b_2=\rho B_2=-\frac{1}{2V}\rho\int\frac{d1}{4\pi}\frac{d2}{4\pi}\{\exp[-\beta\phi(12)]-1\}, \quad (1)$$

where B_2 is the second virial coefficient, V is the volume of the system, 1 and 2 denote the complete set of position and orientation coordinates of particles 1 and 2, ρ is the density, $\beta=(k_BT)^{-1}$, and $\phi(12)$ is the sum of the dipole-dipole interaction

$$\phi_{dd}(12)=-\frac{\mu^2}{r_{12}^3}[3(\hat{\boldsymbol{\mu}}_1\cdot\hat{\mathbf{r}}_{12})(\hat{\boldsymbol{\mu}}_2\cdot\hat{\mathbf{r}}_{12})-\hat{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{\mu}}_2], \quad r_{12}>\sigma \quad (2)$$

and some short-range repulsive potential. In Eq. (2), $\hat{\boldsymbol{\mu}}_1$ and $\hat{\boldsymbol{\mu}}_2$ are unit vectors along the dipole moments of particles 1 and 2, respectively, and $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/r_{12}$ is a unit vector along the intermolecular axis. For strongly DHSs, the integral can be evaluated asymptotically to give [10]

$$b_2\approx-\frac{\pi\rho^*}{18\lambda^3}e^{2\lambda}, \quad (3)$$

where $\rho^*=\rho\sigma^3$ is the reduced density and $\lambda=\mu^2/k_BT\sigma^3$ is the reduced dipole moment, respectively [32]. While in the case of hard or soft spheres the Mayer-expansion parameter is the packing fraction $\xi\approx(1/2)\rho^*$, for DHSs it is $\pi\rho^*\exp(2\lambda)/18\lambda^3$: the dipolar interaction contributes an additional factor of order $\Delta=\pi\exp(2\lambda)/18\lambda^3$, which can be very large if $\lambda\gg1$. The density at which the Mayer expansion breaks down due to chaining can now be estimated from $\rho^*\Delta\sim1$; for $\lambda=9$, this yields as low a density as $\rho^*\sim10^{-4}$.

The first theory of dipolar fluids to include chains was that of Jordan [33,34], who, following Dolezalek [35], described clustering as an equilibrium chemical reaction. Jordan studied in detail the properties and length distribution of noninteracting dipole chains, the main advantage of his theory being that it is not restricted to small dipole moments. On the other hand, the equations for the N-mer densities are very complex in the limit of large N. Here the onset of chain formation is given by

$$\frac{4\pi\rho^*}{81a^*\lambda^3}e^{2\lambda\zeta(3)}\sim1, \quad (4)$$

where $a^*\sim1$ and $\zeta(x)$ is the Riemann zeta function [36]. Using this criterion, Stevens and Grest [24] found $\rho^*\sim10^{-4}$ for $\lambda=6.25$, in qualitative agreement with their computer simulation results. Note that, at such low densities, the only aggregates present are (a small number of) dimers; long chains only appear when $\rho^*\Delta\gg1$.

As already noted by Jordan, there is not, in general, a phase transition between a simple fluid and a phase of chains: rather, the length of the chains grows continuously, as seen in recent simulations of living polymers [37]. At a given density (chemical potential), the onset of chain formation is signaled by a maximum in the specific heat at the polymerization temperature, but the thermodynamic functions are analytic over the whole range of temperatures. In line with current usage, we call the temperature that separates the high-temperature ordinary fluid from the low-temperature isotropic *structured* fluid, a Lifshitz temperature. A phase transition from a high-temperature disordered phase into a low-temperature structured phase of *infinitely* long chains [38–41] may also occur in these systems at a *particular* value of the chemical potential. Although a detailed description of the polymerization transition is beyond the scope of this paper, in Sec. II we shall discuss the conditions under which it might obtain.

We are now faced with the paradox of a low-density regime where the usual low-density approximations are inapplicable. However, this is only a paradox if we insist on describing the system in terms of the one-particle density ρ: for sufficiently strong dipoles, the chains are fairly stable and can be treated as ''molecules'' themselves. All strong short-range correlations are thus absorbed into the intrachain structure. The formation of stable chains preempts an isotropic-to-ferroelectric transition at low density; this will be discussed in detail elsewhere [42]. In addition, as argued in Sec. II B below, the chains are essentially noninteracting and consequently do not order ferroelectrically themselves. This is consistent with the absence of orientational order found in simulations of semiflexible, noninteracting (except for the excluded volume) lattice polymers [43].

In this paper we adopt an approach that is rigorous in the case of very long chains of strong dipoles at low densities (i.e., if $\rho^*\Delta\gg1$ but $\rho^*\ll1$). In this regime, chains are locally rigid and can be treated by the standard methods of polymer theory, which yield simple expressions for the free energy. Obviously our treatment will be quantitatively less accurate if the chains are shorter, but it results in a major simplification and enables one to derive the free-energy functional for the phase of chains in terms of the length and orientation distribution functions. More importantly, interchain interactions can readily be included at the lowest level of approximation in a mean-field fashion. We shall use this functional to investigate the structure and phase behavior of equilibrium dipole chains, including possible polymerization, orientational (ferroelectric) transitions, and phase separation in an applied field.

This paper is organized as follows. In Sec. II we develop the statistical mechanical theory of the fluid of long noninteracting dipole chains. We start by deriving an expression for the free energy of a single (orientationally disordered) chain using the theory of semiflexible polymers; in the Appendix we generalize this to allow for possible orientational order and for an applied field. We argue that interchain interactions are weak in the low-density regime and obtain the chain length distribution for the fluid of noninteracting chains. This is shown to be compatible with Stevens and Grest's data [23] if one takes into account the fact that the number of particles in the simulation is rather small. We compare our predictions for the mean chain lengths with Weis and Levesque's simulation results and thereby illustrate the importance of finite-size effects at large dipole moments. In Sec. III we extend our formalism to consider the steric, dipole-dipole, and van der Waals interactions between chains and discuss the dissociation of long chains as a function of the strength of the isotropic attraction between dipolar particles. Finally, in Sec. IV we tackle the general issue of phase equilibria and orientational order in low-density strongly dipolar fluids and contrast our theory with various other theoretical approaches to this problem.

II. STATISTICAL MECHANICS OF LONG NONINTERACTING CHAINS OF DIPOLAR SPHERES

A. Free energy of a single long chain

The statistical mechanical theory of semiflexible polymers with orientational degrees of freedom was originally introduced by Khokhlov and Semenov [44,45]. This formalism and some of its subsequent developments have been reviewed by Dijkstra (see [46], Appendix to Chap. 2). We note that the original theory was developed for a simple model interaction potential between monomers that are rigidly bound in a chain. Still the general methods employed enable one to use any interaction potential provided the same is strongly peaked for the relative position and orientation of two neighboring particles that correspond to them being part of a chain. Here we shall consider this in more detail and present the derivation of an expression for the free energy of a single chain in the case where the only interaction between constituent particles (besides excluded volume) is of the dipolar type.

In a first approximation, we neglect all interactions beyond nearest neighbors [10] and write the partition function of an N-particle chain ($N \gg 1$) as

$$\mathcal{Z}_{\mathrm{ch}}=\int_{\{|\mathbf{r}_k-\mathbf{r}_{k+1}|\geqslant\sigma\}} d1\,d2\cdots dN\ \exp[-\beta\phi_{dd}(1,2)-\beta\phi_{dd}(2,3)-\cdots-\beta\phi_{dd}(N-1,N)], \tag{5}$$

where $1,\ldots,N$ denote the complete set of position and orientation coordinates of particles 1 to N and $\phi_{dd}(k,k+1)$ is the dipolar interaction between two consecutive particles. $\mathcal{Z}_{\mathrm{ch}}$ can also be written in the form

$$\mathcal{Z}_{\mathrm{ch}}=\int d\mathbf{a}_k\int_{\{|\mathbf{r}_k-\mathbf{r}_{k+1}|\geqslant\sigma\}} d\mathbf{r}_k\,\mathcal{Z}_k(\mathbf{a}_k,\mathbf{r}_k)\,\mathcal{Z}_{N-k+1}(\mathbf{a}_k,\mathbf{r}_k), \tag{6}$$

where $\mathcal{Z}_k(\mathbf{a}_k,\mathbf{r}_k)$ is the partition function of the first k segments, such that $\mathbf{a}_k$ and $\mathbf{r}_k$ are, respectively, the orientation and position of the kth segment ($|\mathbf{a}_k|=1$). In the spirit of the statistical theory of long polymer chains, we write the recursion relation for the partition function $\mathcal{Z}_k(\mathbf{a}_k,\mathbf{r}_k)$,

$$\mathcal{Z}_k(\mathbf{a},\mathbf{r})=\hat{\Psi}\mathcal{Z}_{k-1}(\mathbf{a},\mathbf{r}), \tag{7}$$

where $\hat{\Psi}$ is the integral operator

$$\hat{\Psi}\mathcal{Z}(\mathbf{a},\mathbf{r})=\int d\mathbf{a}'\int_{|\mathbf{r}-\mathbf{r}'|\geqslant\sigma} d\mathbf{r}'\times\exp[-\beta\phi_{dd}(\mathbf{r}-\mathbf{r}';\mathbf{a},\mathbf{a}')]\mathcal{Z}(\mathbf{a}',\mathbf{r}'). \tag{8}$$

It is convenient to normalise the operator $\hat{\Psi}$ and introduce new functions $\mathcal{Z}_k=||\hat{\Psi}||^{k-1}\tilde{\mathcal{Z}}_k$. Equation (7) becomes

$$\tilde{\mathcal{Z}}_k=\hat{\Psi}_0\tilde{\mathcal{Z}}_{k-1}, \tag{9}$$

where $\hat{\Psi}_0=\hat{\Psi}/||\hat{\Psi}||$ and the norm of $\hat{\Psi}$ is defined as

$$\begin{aligned}||\hat{\Psi}||&=\frac{1}{V}\int d\mathbf{a}\int d\mathbf{r}\hat{\Psi}(\mathbf{a},\mathbf{r})\\&=\frac{1}{V}\int d\mathbf{a}d\mathbf{a}'\int_{|\mathbf{r}-\mathbf{r}'|\geqslant\sigma} d\mathbf{r}d\mathbf{r}'\exp[-\beta\phi_{dd}(\mathbf{r}-\mathbf{r}';\mathbf{a},\mathbf{a}')]\\&=\int d\mathbf{a}d\mathbf{a}'\int_{|\mathbf{r}-\mathbf{r}'|\geqslant\sigma} d(\mathbf{r}-\mathbf{r}')\\&\quad\times\exp[-\beta\phi_{dd}(\mathbf{r}-\mathbf{r}';\mathbf{a},\mathbf{a}')].\end{aligned} \tag{10}$$

If the reduced dipole moment $\lambda \gg 1$, the kernel $\exp[-\beta\phi_{dd}(12)]$ is strongly peaked and we can transform the integral equation (9) into a differential equation by performing a gradient expansion of $\tilde{\mathcal{Z}}_k$:

$$\begin{aligned}\tilde{\mathcal{Z}}_k(\mathbf{a}',\mathbf{r}')=&\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})+(\mathbf{a}'-\mathbf{a})\cdot\nabla_{\mathbf{a}}\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})\\&+(\mathbf{r}'-\mathbf{r})\cdot\nabla_{\mathbf{r}}\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})\\&+\frac{1}{2}[(\mathbf{a}'-\mathbf{a})\cdot\nabla_{\mathbf{a}}]^2\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})\\&+\frac{1}{2}[(\mathbf{r}'-\mathbf{r})\cdot\nabla_{\mathbf{r}}]^2\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})\\&+[(\mathbf{a}'-\mathbf{a})\cdot\nabla_{\mathbf{a}}][(\mathbf{r}'-\mathbf{r})\cdot\nabla_{\mathbf{r}}]\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r})+\cdots,\end{aligned} \tag{11}$$

where $\nabla_{\mathbf{a}}$ is the gradient on the surface of the unit sphere of orientations $\mathbf{a}$. Insertion of Eq. (11) into Eq. (9) and integration by parts yield

$$\tilde{\mathcal{Z}}_k-\tilde{\mathcal{Z}}_{k-1}=\Omega\nabla_{\mathbf{a}}^2\tilde{\mathcal{Z}}_{k-1}+\sigma^2\Omega\nabla_{\mathbf{r}}^2\tilde{\mathcal{Z}}_{k-1}+\cdots, \tag{12}$$

where $\nabla_{\mathbf{a}}^2$ is the angular part of the Laplacian and $\Omega=(2\lambda)^{-1}$. Taking the segment index k to be a continuous variable, we make the approximation $\tilde{\mathcal{Z}}_k-\tilde{\mathcal{Z}}_{k-1}\approx\partial\tilde{\mathcal{Z}}_k/\partial k$ and obtain a partial differential equation for $\tilde{\mathcal{Z}}_k$:

$$\frac{\partial \tilde{\mathcal{Z}}_k}{\partial k} = \Omega(\nabla^2_{\mathbf{a}} + \sigma^2 \nabla^2_{\mathbf{r}})\tilde{\mathcal{Z}}_k. \tag{13}$$

When the azimuthal variation is irrelevant, the solution of Eq. (13) is

$$\tilde{\mathcal{Z}}_k(\mathbf{a},\mathbf{r}) = \sum_{l,m} \tilde{\mathcal{Z}}^{(l)}(\mathbf{a})\tilde{\mathcal{Z}}^{(m)}(\mathbf{r}) e^{\lambda_{lm}k}, \tag{14}$$

where $\tilde{\mathcal{Z}}^{(l)}(\mathbf{a})$ and $\tilde{\mathcal{Z}}^{(m)}(\mathbf{r})$ satisfy the eigenvalue equations

$$\lambda_l^{\mathbf{a}} \tilde{\mathcal{Z}}^{(l)}(\mathbf{a}) = \Omega \nabla^2_{\mathbf{a}} \tilde{\mathcal{Z}}^{(l)}(\mathbf{a}), \tag{15}$$

$$\lambda_m^{\mathbf{r}} \tilde{\mathcal{Z}}^{(m)}(\mathbf{r}) = \sigma^2 \Omega \nabla^2_{\mathbf{r}} \tilde{\mathcal{Z}}^{(m)}(\mathbf{r}). \tag{16}$$

Explicitly,

$$\tilde{\mathcal{Z}}^{(l)}(\mathbf{a}) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta), \tag{17}$$

$$\tilde{\mathcal{Z}}^{(m)}(\mathbf{r}) = \sqrt{\frac{2}{V}} \cos\left(\frac{z}{\sigma} m\right). \tag{18}$$

The ground-state eigenvalue is $\lambda_{11} = \lambda_1^{\mathbf{a}} + \lambda_1^{\mathbf{r}} = -3\Omega = -3/2\lambda$. At large chain lengths N only the ground state of $\hat{\Psi}_0$ contributes significantly and we can retain only the first term in Eq. (14) (higher-order terms give finite-chain corrections, which are exponentially smaller). Substituting

$$\mathcal{Z}_k(\mathbf{a},\mathbf{r}) \approx ||\hat{\Psi}||^{k-1} \tilde{\mathcal{Z}}^{(1)}(\mathbf{a}) \tilde{\mathcal{Z}}^{(1)}(\mathbf{r}) e^{-\lambda_{11}k} \tag{19}$$

and the equivalent expression for $\mathcal{Z}_{N-k+1}(\mathbf{a},\mathbf{r})$ into Eq. (6) and recalling that the eigenfunctions of $\hat{\Psi}_0$ are normalized, we obtain, for the free energy of the long dipole chain,

$$\begin{aligned} F_{\text{ch}} &= -k_B T \ln \mathcal{Z}_{\text{ch}} \approx -(N-1)k_B T\left(\ln||\hat{\Psi}|| + \frac{N}{N-1}\lambda_{11}\right) \\ &\approx -(N-1)k_B T\left[\ln\left(\frac{\pi\sigma^3}{18\lambda^3} e^{2\lambda}\right) - \frac{3}{2\lambda}\right], \end{aligned} \tag{20}$$

where we have used the asymptotic expression of $||\hat{\Psi}||$ for large λ, which coincides with the asymptotic expression for the second virial coefficient of the DHS fluid [10]. We see that the second term in square brackets in Eq. (20), the conformational entropy of the long chain, is a small correction at large λ, in which case the free energy is simply the sum of average bond energies $S_0 = \ln[\pi\sigma^3 \exp(2\lambda)/18\lambda^3]$ at finite temperature.

B. Distribution of chain lengths

At low densities, interchain interactions are expected to be weak and can be neglected. Here we shall summarize a few semiquantitative results in support of this statement and refer the reader to Sec. III for details of the theory.

(i) The interaction energy between two dipoles belonging to different chains at average separation is of the order of $\rho\mu^2$. Taking $\lambda = 9$, $\rho\mu^2/k_B T = \rho^*\lambda \ll 1$ if $\rho^* \ll \lambda^{-1} \sim 10^{-1}$.

(ii) Because of symmetry, the dipole-dipole interaction between different chains averages to zero in the isotropic phase [47]. Thus only higher-order correlations contribute to the free energy, which in a first approximation are proportional to $(\rho^*\lambda)^2 \ll 1$ and therefore very weak.

(iii) The interaction between two parallel, infinitely long chains of dipoles vanishes identically.

(iv) At very low densities, excluded volume effects are negligible and the dominant contribution to the free energy is that of the single chain (see Sec. III for details).

In what follows we shall derive the distribution of chain lengths in a fluid of noninteracting chains. For sufficiently large dipole moments as have been used in the simulations, the chains that form at low densities are fairly stable; the free-energy density can then be written as [cf. Eq. (A8)]

$$\beta f = \beta\frac{F}{V} = \sum_{N=1} \rho(N)[\ln\rho(N) - 1] - \sum_{N=1} \rho(N)\ln\mathcal{Z}_N, \tag{21}$$

where $\rho(N)$ is the density of chains of length N and $\mathcal{Z}_N$ is the partition function of the N-sphere chain. Here we have adhered to the convention of Cates and Candau (see [48], Eq. 2.1). The distribution function $\rho(N)$ can be found by minimizing the free energy Eq. (21) subject to the constraint

$$\sum_{N=1} N\rho(N) = \rho, \tag{22}$$

where we recall that ρ is the density of *molecules* (spheres). $N\rho(N)$ is the density of molecules in chains of length N, whence the mean chain length is

$$\overline{N} = \frac{\sum_{N=1} N\rho(N)}{\sum_{N=1} \rho(N)} = \frac{\rho}{\beta P}, \tag{23}$$

P being the pressure. For $\lambda \gg 1$ we approximate the free energy of a chain by

$$\ln\mathcal{Z}_N \approx (N-1)\ln\left(\frac{\pi\sigma^3}{18\lambda^3} e^{2\lambda}\right) = (N-1)S_0. \tag{24}$$

Note that Eq. (24) gives the right limit when $N \to 1$: indeed, one expects $\mathcal{Z}_1 = 1$ for a single sphere (i.e., a monomer) in a zero external field. It is also correct at zero temperature, where $\ln\mathcal{Z}_N$ is just the sum of $N-1$ bond energies. Minimization then yields

$$\rho(N) = e^{N(S_0+\nu)} e^{-S_0}, \tag{25}$$

where ν is a Lagrange multiplier (it is essentially the chemical potential for monomers divided by $k_B T$ [49]). From Eq. (25) we readily recover van Roij's result [see [50], Eqs. (3) and (4)]

$$\frac{\rho(N)}{[\rho(1)]^N} = \frac{\mathcal{Z}_N}{\mathcal{Z}_1^N} = e^{(N-1)S_0}, \tag{26}$$

leading to the identification $\exp[(N-1)S_0] = \mathcal{V}_1^N/\mathcal{V}_N$, where $\mathcal{V}_N$ is the thermal volume of an N-mer [51]. Note that this

TABLE I. Mean chain lengths from Weis and Levesque's simulation ($\overline{N}_{\rm sim}$) [26] and from the present theory ($\overline{N}_{\rm calc}$).

ρ^*	λ	$\overline{N}_{\rm sim}$	$\overline{N}_{\rm calc}$
0.3	4.0	2.7	2.1
0.3	6.25	5.2	8.1
0.3	9.0	16.5	69.2
0.3	12.25	27.0	1115.8
0.2	12.25	24.6	911.2
0.1	4.0	2.6	1.5
0.1	6.25	6.7	4.9
0.1	9.0	24.5	40.1
0.1	12.25	24.2	644.4
0.05	12.25	30.4	455.8
0.02	4.0	2.3	1.1
0.02	12.25	8.4	288.5

differs from Jordan's result, who has, however, used a slightly different definition of the partition function.

Inserting $\rho(N)$ from Eq. (25) into the constraint Eq. (22), we obtain

$$\rho=\frac{\rho(1)}{[1-e^{S_0}\rho(1)]^2}=\frac{e^{\nu}}{(1-e^{S_0+\nu})^2}, \tag{27}$$

whence we must have $\alpha=S_0+\nu<0$. This is an implicit equation for the density of monomers, of the same form as van Roij's [50], which also yields the chemical potential ν. For large $|\alpha|$, we have

$$\alpha\approx-(\rho e^{S_0})^{-1/2}\approx-\left(\frac{18\lambda^3}{\pi\rho*}\right)^{1/2}e^{-\lambda}. \tag{28}$$

$N\rho(N)/\rho$, the fraction of particles in chains of length N, has a maximum for $N=|\alpha|^{-1}$. This result is very close to that of Jordan, who obtained upper and lower bounds for the mean chain length $\overline{N}$ ($\overline{N}\approx N_0$, the most probable chain length, when the distribution is strongly peaked). These are of order $|\alpha|^{-1}$ in the limit of large λ (see [34], Appendix). Note that $N_0\approx|\alpha|^{-1}$ is very large already at very low densities: if we take $\lambda=9$, $N_0\sim130(\rho^*)^{1/2}$ and $N_0\approx13$ for $\rho^*=0.01$. More accurate estimates for chain lengths can be obtained by solving Eq. (27) numerically for ν and then inserting $\rho(N)$ from Eq. (25) into Eq. (23). This gives

$$\overline{N}=\frac{1}{1-e^{\alpha}}. \tag{29}$$

The resulting mean chain lengths are compared with Weis and Levesque's [26] in Table I.

In Fig. 1 we plot $N\rho(N)/\rho$ for different densities and dipole moments. Increasing the dipole moment at constant density [Fig. 1(a)] causes chains to grow dramatically and the distribution to flatten and broaden. At constant λ [Fig. 1(b)], the most probable chain length decreases with decreasing density, while the distribution becomes more sharply peaked.

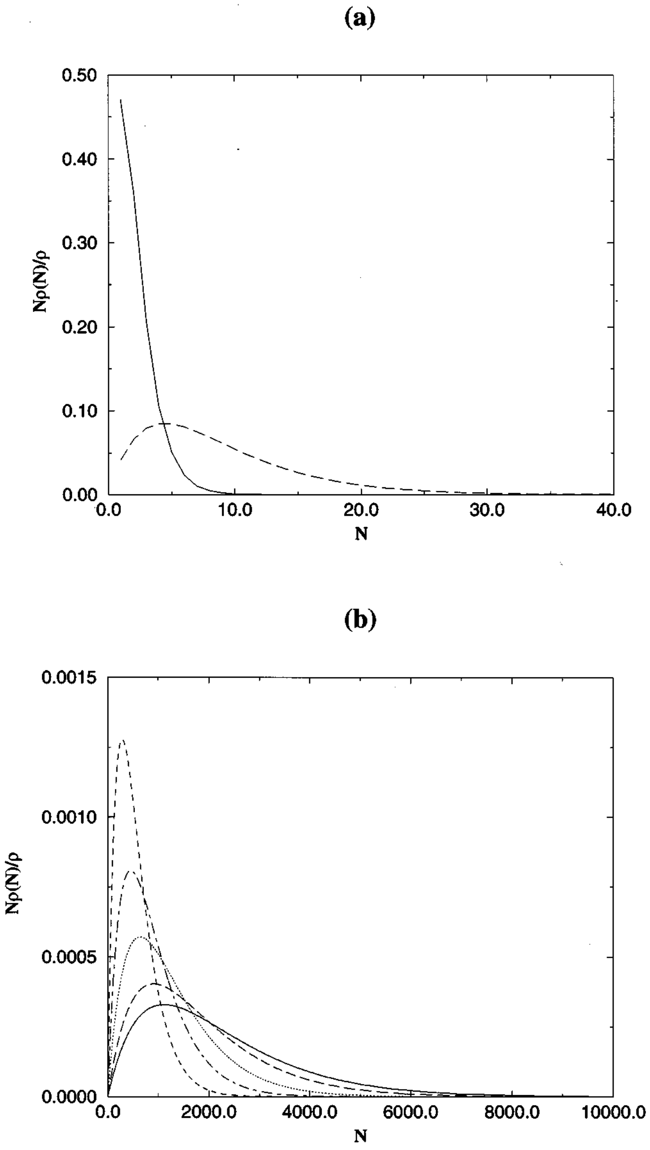

FIG. 1. Fraction of particles in (noninteracting) chains of length N. (a) $\rho^*=0.1$. Solid line, $\lambda=4.0$; dashed line, $\lambda=6.25$. (b) $\lambda=12.25$. Solid line, $\rho^*=0.3$; dashed line, $\rho^*=0.2$; dotted line, $\rho^*=0.1$; dot-dashed line, $\rho^*=0.05$; short-dashed line, $\rho^*=0.02$.

Stevens and Grest have calculated chain length distributions from their computer simulation data for $\lambda=9$ in the broad range of densities $0.001\leqslant\rho^*\leqslant0.7$ [24]. The shape of their distributions is similar to $N\exp(-|\alpha|N)$, but the most probable chain length is very small (5–10 spheres). This is in contradiction with the theoretical result that the most probable chain length should be greater than or equal to 13 already at $\rho^*=0.01$ and grow as $(\rho^*)^{1/2}$. In the absence of interactions, we would thus expect an eightfold increase when ρ^* goes from 0.01 to 0.7. The discrepancy at low densities is not related to the approximate character of the present simple theory: the same qualitative results can be obtained using the expression for the lower bound of the mean chain length $\overline{N}$ given by Jordan. This suggests that the chain length distributions extracted from simulation data are affected by strong finite-size effects, which are very difficult to estimate accurately. Already at very low densities the most probable chain length is of the order of the size of the simulation box and at higher densities chain lengths are se-

TABLE II. Pressures and chemical potentials from simulation and theory for $\lambda=4.5$. The simulation data are from Table I in [21].

βP_0	ρ^*_{sim}	$\Delta(\beta\nu_{\mathrm{sim}})$	βP_{calc}	$\Delta(\beta\nu_{\mathrm{calc}})$
0.15	0.3585	0.53	0.1231	0.4085
0.13	0.351	0.475	0.1216	0.4041
0.11	0.317	0.385	0.1143	0.3822
0.09	0.2965	0.34	0.1097	0.3673
0.08	0.295	0.315	0.1094	0.3661
0.07	0.2765	0.255	0.1051	0.3511
0.06	0.251	0.205	0.0990	0.3279
0.05	0.2335	0.175	0.0946	0.3099
0.04	0.216	0.125	0.0901	0.2897
0.03	0.1835	0.085	0.0812	0.2451
0.0275	0.1365	0.035	0.0669	0.1551
0.025	0.1255	0.025	0.0633	0.1273
0.0225	0.1225	0.015	0.0623	0.1191
0.02	0.0885	0.00	0.0499	0.0000

verely constrained (see Sec. IV).

The pressure of the fluid of noninteracting chains is given by

$$\beta P=\sum_{N=1}^{\infty}\rho(N)=\frac{e^{\nu}}{1-e^{\nu+S_0}}, \tag{30}$$

where we have used Eq. (25). Our pressures and chemical potentials are compared with Caillol's simulations [21] in Tables II and III: wherever $N_\phi>1$ (more than one class of states per state point), the simulation result quoted is the arithmetic mean of the corresponding entries in Caillol's tables. To avoid any ambiguity related to different choices of the zero of ν (see also [49]), we present $\Delta(\beta\nu)=\beta(\nu-\nu_0)$, where ν_0 is the chemical potential at the lowest density in each table. The present theory predicts too weak a density dependence for the pressure and the chemical potential. (But note the considerable uncertainty in the simulation data, especially for the pressure.) We believe the disagreement to be due, in part, to the fact that we are dealing with relatively small dipole moments, whereof the implications are twofold. First, any chains will be short (although no chain lengths are reported in Caillol's paper), thus rendering our long-chain theory less applicable. Second, the asymptotic expression for $||\hat{\Psi}||$ we used [see Eq. (20)] will be less accurate (see also the discussion in Sec. IV).

TABLE III. Pressures and chemical potentials from simulation and theory for $\lambda=5.555\ldots$. The simulation data are from Table IV in [21].

βP_0	ρ^*_{sim}	$\Delta(\beta\nu_{\mathrm{sim}})$	βP_{calc}	$\Delta(\beta\nu_{\mathrm{calc}})$
0.11	0.413	0.46	0.0709	0.18059
0.09	0.3715	0.525	0.0669	0.17039
0.07	0.354	0.3	0.0651	0.16556
0.05	0.2725	0.265	0.0563	0.13726
0.03	0.303	0.26	0.0598	0.14918
0.02	0.3015	0.18	0.0596	0.14863
0.01	0.2545	0.22	0.0542	0.12925
0.005	0.221	0.21	0.0501	0.11182
0.003	0.218	0.1	0.0497	0.11007
0.001	0.1935	0.11	0.0465	0.09427
5×10^{-4}	0.181	0.065	0.0447	0.085
3×10^{-4}	0.119	0.125	0.0351	0.01939
2×10^{-4}	0.1067	0.00	0.0329	0.00000

We end this section by briefly discussing the possibility of a continuous polymerization transition in the strongly dipolar fluid. In a system of living or equilibrium polymers, a continuous phase transition occurs when the initiation equilibrium constant vanishes [38–41]. In this case the thermodynamic functions exhibit singularities characterized by nontrivial critical exponents that belong to a universality class determined by some of the details of the system. The derivation of the present theory neglects interactions and fluctuations (cf. the ground-state approximation for the partition function) and thus it would be equivalent, in the event of such a transition in a dipolar fluid, to a mean-field approximation. We can, however, identify the small parameter (or field) in this problem as α, which is the difference between the free energy per particle $-S_0$ and the chemical potential of the monomers ν. A continuous phase transition is thus expected to occur as $\alpha\to0^-$, at which value of the chemical potential the system undergoes a transition from a high-temperature ordinary fluid phase to a low-temperature isotropic structured fluid one characterized by *infinite* mean chain length [cf. Eq. (29)]. The condition is then $-\nu=S_0$. By recalling that S_0 is minus the free energy per particle, we conclude that the phase transition may only occur at zero density (pressure) for all dipolar systems.

III. INTERACTION BETWEEN CHAINS AND CHAIN DISSOCIATION

In the preceding section we considered the distribution of chain lengths for a system of noninteracting chains. As discussed above, this approximation is correct at low densities. However, at liquid densities excluded-volume and long-range effects must obviously be important and this can result in chain dissociation (indeed, the chains are not observed in simulations at densities higher than 0.2 [27]). Furthermore, it is reasonable to expect that dissociation of chains can also be caused by additional attractive interactions between dipolar particles. According to the simulations by van Leeuwen and Smit [22], a sufficiently strong attraction between DSSs induces a gas-liquid phase separation, which is absent if the additional attractive interaction is too weak. Thus it is necessary also to discuss the influence of attractive interactions between dipolar particles on the chain length distribution. This will be done in Sec. III B. Next we shall examine the steric and dipole-dipole interactions between long chains and estimate the corresponding contributions to the free energy.

A. Dipolar and excluded-volume interactions between long chains

It follows from the semiquantitative arguments presented at the beginning of Sec. II B that interactions between chains are expected to be weak and therefore it is reasonable to treat them at the level of the mean-field approximation. For simplicity we consider first the case of monodisperse chains; the chain length distribution will be introduced in Sec. III B. The contribution from interchain interactions to the free energy density is then

$$\begin{aligned} f_{\rm int}=&\frac{1}{2}\rho_{\rm ch}^2 k_B T\int\{\exp[-\beta\Phi_{\rm ster}(\Gamma_1,\Gamma_2)]-1\}\\ &\times\hat{f}(\Gamma_1)\hat{f}(\Gamma_2)d\Gamma_1 d\Gamma_2\\ &+\frac{1}{2}\rho_{\rm ch}^2\int\exp[-\beta\Phi_{\rm ster}(\Gamma_1,\Gamma_2)]\Phi_{dd}(\Gamma_1,\Gamma_2)\\ &\times\hat{f}(\Gamma_1)\hat{f}(\Gamma_2)d\Gamma_1 d\Gamma_2. \end{aligned} \tag{31}$$

Here $\rho_{\rm ch}$ is the number density of chains; Γ_i denotes the position of a chain in phase space, i.e., the positions and orientations of all spheres in chain i; $\hat{f}(\Gamma_i)$ is the one-chain orientational distribution function (ODF); $\Phi_{\rm ster}(\Gamma_1,\Gamma_2)$ is the short-range repulsive part of the interaction potential between chains, which is determined by the repulsion between hard or soft spheres; and $\Phi_{dd}(\Gamma_1,\Gamma_2)$ is the sum of all dipole-dipole interactions between spheres in different chains.

As discussed in detail in [42,52], we now need to separate the second term on the right-hand side (rhs) of Eq. (31) into short- and long-range parts. This is because the long-range part of the dipole-dipole interaction yields a contribution to the free energy that is dependent of system size, shape, and boundary conditions if the overall polarization is nonzero. It is, however, given exactly by Maxwell's equations and equals the electrostatic energy of the average electric field in the volume of the fluid. In the present case this separation is straightforward: it suffices to add to and subtract from Eq. (31) the integral over the dipole-dipole interaction without the steric cutoff. The second term on the rhs of Eq. (31) becomes

$$\begin{aligned} &\frac{1}{2}\rho_{\rm ch}^2\int\{\exp[-\beta\Phi_{\rm ster}(\Gamma_1,\Gamma_2)]-1\}\\ &\quad\times\phi_{dd}(\Gamma_1,\Gamma_2)\hat{f}(\Gamma_1)\hat{f}(\Gamma_2)d\Gamma_1 d\Gamma_2\\ &\quad+\frac{1}{2}\rho_{\rm ch}^2\int\Phi_{dd}(\Gamma_1,\Gamma_2)\hat{f}(\Gamma_1)\hat{f}(\Gamma_2)d\Gamma_1 d\Gamma_2. \end{aligned} \tag{32}$$

The second term in the foregoing expression can be transformed into $-\int\mathbf{E}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r}$, the energy of the electrostatic field in the volume of a fluid of polarization $\mathbf{P}$. This vanishes when the average field $\mathbf{E}$ is zero (i.e., when the sample is surrounded by a conducting medium). The first term is the integral of the dipole-dipole potential within the excluded volume of two chains; this is the same excluded volume as in the first term on the rhs of Eq. (31).

For large dipole moments the local intersection of two chains is the same as that of two rods since the chains are locally rigid. Then, as is known from the theory of nematic polymers, the excluded volume of two long chains can be expressed in terms of the excluded volume of two rods. Let us introduce the relatively rigid chain segment of length ℓ. If N is the total number of spheres in a chain, then each chain contains $N\sigma/\ell$ such rigid segments. Now the first term in Eq. (31) can be rewritten as [45]

$$\frac{1}{2}\rho_{\rm ch}^2 k_B T\left(\frac{N}{\ell}\right)^2\sigma^2\int\hat{f}(\mathbf{a}_1)B(\mathbf{a}_1,\mathbf{a}_2)\hat{f}(\mathbf{a}_2)d\mathbf{a}_1 d\mathbf{a}_2, \tag{33}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors along the two rods and $B(\mathbf{a}_1,\mathbf{a}_2)$ is their excluded volume

$$B(\mathbf{a}_1,\mathbf{a}_2)\approx 2\ell^2\sigma|\sin\gamma_{12}|, \tag{34}$$

with $\gamma_{12}=\cos^{-1}(\mathbf{a}_1\cdot\mathbf{a}_2)$ the angle between the two rods (end corrections have been neglected). Insertion of (34) into (33) gives

$$\rho_{\rm ch}^2 k_B T N^2\sigma^3\int\hat{f}(\mathbf{a}_1)|\sin\gamma_{12}|\hat{f}(\mathbf{a}_2)d\mathbf{a}_1 d\mathbf{a}_2, \tag{35}$$

which does not depend on ℓ, the length of the rigid segments. In the isotropic phase $\hat{f}(\mathbf{a}_i)=1/4\pi$, and this reduces to

$$\frac{\pi}{4}\rho_{\rm ch}^2 k_B T N^2\sigma^3=\frac{3}{2}\rho_{\rm ch}N k_B T\xi_{\rm ch}, \tag{36}$$

where $\xi_{\rm ch}=(\pi\sigma^3/6)N\rho_{\rm ch}$ is the volume fraction of chains. The total number of particles in chains per unit volume is, of course, $N\rho_{\rm ch}$. This is a purely repulsive contribution to the free energy.

Now let us consider the contribution from the dipole-dipole interaction between chains. In a uniform system, the first term in expression (32) reduces to

$$\frac{1}{2}\rho_{\rm ch}^2 N^2\mathcal{D}p^2\sigma^3, \tag{37}$$

where $\mathbf{p}=\int d\mathbf{a}\boldsymbol{\mu}\hat{f}(\mathbf{a})$ is the orientational average of the dipole moment vector of a rod and

$$\mathcal{D}=\sigma^{-3}\int_{V_{\rm exc}}d\mathbf{r}_{12}\frac{1-3\cos^2\theta}{r_{12}^3} \tag{38}$$

is the integral of the dipole-dipole interaction over the excluded volume of two chains. Since, as mentioned above, the chains are locally similar to rigid rods, this excluded volume is locally platelike. In general, it will have some ribbonlike shape. The elementary ''fragment'' of the excluded volume of two chains, however, is that of two rigid rods of length ℓ: it has length and width of order ℓ and thickness of order σ. Thus the integral in Eq. (38) is approximately equal to that over some flat thin layer. In this case, $\mathcal{D}$ is exactly the depolarization factor of such a layer (or of a thin disk). The depolarization factor of an infinitely thin disk is known to be zero when the polarization is in the plane of the disk, whence $\mathcal{D}$ is also expected to be very small for sufficiently long chains (where the dipole moments are directed along the rigid segments). $\mathcal{D}$ for spheroids has been calculated numerically by Terentjev and Petschek [53] and found to be proportional to the inverse aspect ratio d/l, for $l/d\gg 1$. In the case of chains we expect $\mathcal{D}$ to be even smaller.

The above arguments enable us to conclude that the dipolar contribution to the free energy of a system of interacting chains is negligibly small at sufficiently low densities because it is proportional to two small parameters: the square of the chain volume fraction $\xi_{\rm ch}\ll 1$ and the depolarization factor $\mathcal{D}\sim\sigma/\ell$. Furthermore, it should be noted that this contribution is nonvanishing only in the presence of an external electric field or of spontaneous polarization, since $p=0$ in the isotropic phase [cf. Eq. (37)].

The contribution from the excluded-volume interaction between long chains is also proportional to the square of the chain volume fraction $\xi_{\rm ch}$. The relative significance of interchain interactions in the isotropic phase is determined by the balance between the total bond energy of all chains [the second term on the rhs of Eq. (A8)] and the average interchain interaction [given by the last term in Eq. (A8)]. The ratio of these two terms is of order $S_0(\rho^*)^{-1}\gg 1$ when $\rho^*\ll 1$. Thus in a first approximation the excluded-volume interaction is important only at liquid densities $\rho^*\sim 1$.

B. Dissociation of chains caused by interparticle attraction

We now come back to the general case of a mixture of chains of different lengths in ''chemical'' equilibrium. In the Appendix we generalize the expressions obtained in the preceding section and write down the free-energy functional for a polydisperse fluid of long dipole chains in an external field [Eq. (A8)]. This can readily be extended to include an additional attraction $\phi_{\rm attr}(12)$ by supplementing it with the term

$$\frac{1}{2}\sum_{N,N'=1} N\rho(N)N'\rho(N')\int d\mathbf{r}_{12}d\mathbf{a}_1 d\mathbf{a}_2 \times H(r_{12}-\Xi_{12})\hat{f}(\mathbf{a}_1)\phi_{\rm attr}(12)\hat{f}(\mathbf{a}_2), \qquad (39)$$

where $H(r_{12}-\Xi_{12})$ is the step function [$H(x)=1$ if $x<0$ and zero otherwise], which determines the steric cutoff for two interacting spheres belonging to different chains, and we neglect intrachain interactions. The function $H(r_{12}-\Xi_{12})$ is zero if the two chains with spheres at fixed positions and orientations 1 and 2 penetrate each other, i.e., within the excluded volume of two chains. If the chains are locally rigid, then $\Xi_{12}=\Xi(\mathbf{r}_{12},\mathbf{a}_1,\mathbf{a}_2)$ is highly anisotropic: it is the distance of minimum approach between spheres 1 and 2 that belong to different chains. In the most general case it depends on the orientation of the two dipolar spheres and on the configuration of the two chains. We note, however, that the attractive potential in Eq. (39) is short ranged and therefore only small interparticle separations contribute. Consequently, Ξ_{12} is approximately equal to the corresponding function for two rigid rods of length l ($\gg\sigma$) and diameter σ and takes values between σ and l.

With these simplifications, Eq. (39) can be rewritten in the form

$$\frac{1}{2}\sum_{N,N'=1} N\rho(N)N'\rho(N')U_0=\frac{1}{2}\rho^2 U_0, \qquad (40)$$

where the constant U_0 characterizes the strength of the attractive interaction

$$U_0=\int d\hat{\mathbf{r}}_{12}d\mathbf{a}_1 d\mathbf{a}_2\int_{\Xi_{12}}^{\infty} dr_{12}r_{12}^2\hat{f}(\mathbf{a}_1)\phi_{\rm attr}(r_{12})\hat{f}(\mathbf{a}_2) \qquad (41)$$

and, as before, $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/r_{12}$. U_0 can be estimated in the following way. Taking the attraction potential to be of the simple van der Waals form $\phi_{\rm attr}(12)=-\epsilon_0(\sigma/r_{12})^6$, one obtains

$$\int_{\Xi_{12}}^{\infty} dr_{12}r_{12}^2\phi_{\rm attr}(r_{12})=-\frac{\epsilon_0\sigma^6}{3}\Xi_{12}^{-3}. \qquad (42)$$

Following van der Meer (see [54], p. 43), we write down the simplest interpolation expression for Ξ_{12}^{-3},

$$\Xi_{12}^{-3}=\sigma^{-3}+\frac{1}{2}(l^{-3}-\sigma^{-3})[(\mathbf{a}_1\cdot\hat{\mathbf{r}}_{12})^2+(\mathbf{a}_2\cdot\hat{\mathbf{r}}_{12})^2], \qquad (43)$$

which is exact for $\mathbf{a}_1\|\mathbf{a}_2\perp\hat{\mathbf{r}}_{12}$ and for $\mathbf{a}_1\|\mathbf{a}_2\|\hat{\mathbf{r}}_{12}$. Finally, this yields

$$U_0\approx-\frac{8\pi\epsilon_0\sigma^3}{9}, \qquad (44)$$

where we have taken into account that $l^3\gg\sigma^3$.

The free-energy density of the fluid of interacting chains is now

$$f=k_BT\sum_{N=1}\rho(N)[\ln\rho(N)-1]-k_BT\sum_{N=1}\rho(N)(N-1)S_0 +\frac{\pi}{4}\sum_{N,N'=1}N\rho(N)N'\rho(N')k_BT\sigma^3 +\frac{1}{2}\sum_{N,N'=1}N\rho(N)N'\rho(N')U_0, \qquad (45)$$

where we have neglected the dipole-dipole contribution, which is small at low densities as discussed above. The last two terms, the steric and attractive contributions, can be combined by defining an effective interaction strength $U_0^{\rm eff}=(\pi/2)k_BT\sigma^3+U_0$, whereupon they become $\frac{1}{2}\rho^2U_0^{\rm eff}$. As we shall see below, the inclusion of repulsions has no qualitative effect on the dissociation of chains; we retain them for consistency and with a view to a future treatment of condensation and θ points, where they will play a crucial role.

We note that the last two terms in Eq. (45), coming from the interchain interactions, are strongly oversimplified. The attractive term describes correctly only the interaction between very long chains (which correspond to $Nl/\sigma\gg 1$). By contrast, the repulsive term is the simplest contribution arising from the excluded volume of two hard rods, which we took as chain subunits [see above the derivation of Eq. (36)]. The absolute value of the interchain interactions is, however, largely irrelevant in what follows. As long as the parameter $U_0^{\rm eff}$ is independent of N, the form of the chain length distribution is unchanged from the noninteracting case [48]. One needs, however, to refine these estimates if a description of phase transitions is also required.

For shorter chains one has to take into account in U_0, end effects, and other corrections that are of order $(\sigma/l)^3$ or σ/L, where L is the length of the (short) chain. These corrections are not expected to be very large even for dimers and, in principle, one can neglect them at this stage. However, the interaction between *monomers* needs to be considered separately. For this purpose it is useful to single out the term with $N=N'=1$ in the interaction part. We thus rewrite the free-energy density as

$$f\approx k_BT\sum_{N=1}\rho(N)[\ln\rho(N)-1]-k_BT\sum_{N=1}\rho(N)(N-1)S_0+\frac{1}{2}\sum_{N,N'=1}N\rho(N)N'\rho(N')U_0^{\rm eff}+\frac{1}{2}\rho(1)^2(U_1^{\rm eff}-U_0^{\rm eff}), \tag{46}$$

where $\rho(1)$ is the density of monomers and $U_1^{\rm eff}=(4\pi/3)k_BT\sigma^3+U_1$. $U_1=-(4\pi/3)\epsilon_0\sigma^3$ is the integrated attractive potential between two spheres and we have treated the repulsive contribution on the level of the second-virial approximation. Now $|U_0^{\rm eff}|<|U_1^{\rm eff}|$ if the attraction is sufficiently strong, in which case chains are expected to dissociate.

Minimization of the free energy Eq. (46) again yields Eq. (25) for the density of chains of length $N>1$ and

$$\rho(1)=\exp[-S_0+\alpha-\beta\rho(1)(U_1^{\rm eff}-U_0^{\rm eff})], \tag{47}$$

for the density of monomers. $\alpha=S_0+\nu$, with ν the chemical potential, is determined from the normalization condition

$$\rho=\sum_{N=1}N\rho(N)=\sum_{N=2}N\rho(N)+\rho(1), \tag{48}$$

whence

$$\rho e^{S_0+|\alpha|}=\frac{1}{(1-e^{-|\alpha|})^2}-1+e^{\beta\rho(1)(U_0^{\rm eff}-U_1^{\rm eff})}, \tag{49}$$

where we have taken into account that α must be negative. Equations (47) and (49) can be solved simultaneously for ν and $\rho(1)$ and $\rho(N)$ is obtained from Eq. (25).

We now compare Eq. (49) with the corresponding equation (27) for noninteracting chains. In the context of the present simple model, the interaction between chains manifests itself only in the second term of Eq. (49). If the interaction constants $\rho(1)U_0$ and $\rho(1)U_1$ are small, we basically recover Eq. (27) and Eq. (49) has practically the same solution as in the case of non-interacting chains (i.e., α is very small, $\alpha^2\sim\rho^{-1}e^{-S_0}$). On the other hand, if the interaction constant $\rho(1)U_0^{\rm eff}$ is large (we recall that $|U_1^{\rm eff}|>|U_0^{\rm eff}|$), the last term in Eq. (49) can be of the same order as ρe^{S_0}. This relation can be expressed more quantitatively as

$$\rho e^{S_0}\sim e^{\beta\rho(1)(U_0^{\rm eff}-U_1^{\rm eff})}. \tag{50}$$

In this case, which corresponds to a strong van der Waals attraction between particles, Eq. (49) has a solution α of order unity. This means that the chain length distribution function $\rho(N)\propto\exp(-|\alpha|N)$ decays rapidly with increasing N. As a result, all long dipole chains are dissociated due to a sufficiently strong isotropic attraction between particles. The effect of the interaction constant $\rho(1)(U_0^{\rm eff}-U_1^{\rm eff})$ on the chain length distribution is illustrated in Fig. 2: the fraction of particles in chains of length N decays marginally faster at large N, while the system is enriched with monomers. In addition, for large $\beta\epsilon_0/S_0$ the set of equations (47) and (49) can have one other physical solution corresponding to the system being composed almost exclusively of monomers, i.e., to complete dissociation of chains. This is precisely what van Roij found [50], which is not surprising given the close similarity of the two theories. The question of the global stability of the phase of chains, as well as of the nature of the transitions between chain- and monomer-dominated phases, is currently under investigation and will be discussed elsewhere.

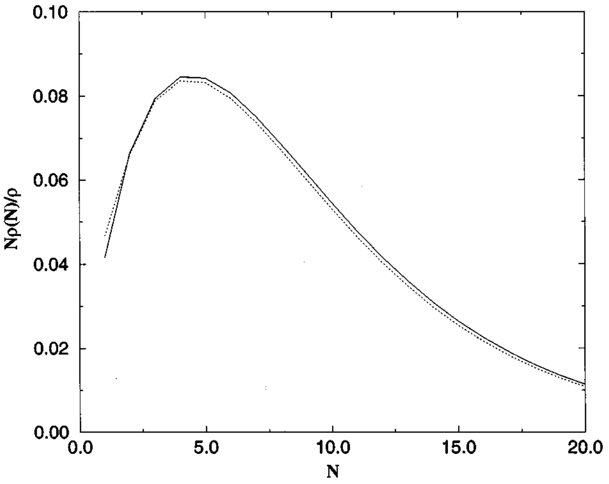

FIG. 2. Effect of isotropic attraction on the fraction of particles in chains of length N, for $\rho^*=0.1$ and $\lambda=6.25$. Solid line, noninteracting chains; dotted line, $\beta\epsilon_0=20$.

IV. DISCUSSION AND CONCLUSIONS

We have developed a theory for fluids of dipolar soft or hard spheres, with and without additional isotropic interactions, in the limit of low densities and large dipole moments. The very strong and highly directional short-range correlations between particles have been taken into account by assuming that they associate into chains, which are then treated within the formalism of polymer theory. Furthermore, we have argued that interchain interactions are negligibly weak and derived the chain length distribution for a system of noninteracting chains by assuming that the kinetics of chain growth is dominated by an equilibrium scission-recombination mechanism. Although in simulations rings have been observed [26,27], they are relatively rare; hence in the structured phase it suffices to take into account long linear chains. Our approach yields an exponential form for the chain length distribution Eq. (25). For long chains $|\alpha|^{-1}$ is the mean chain length, given in terms of model parameters by Eq. (28), where $\lambda=\mu^2/k_BT\sigma^3=2E/k_BT$, with $E=2\mu^2/\sigma^3$ equal to (minus) the bond energy at $T=0$. This result is identical to the mean-field chain length distribution of living polymers, where E is the scission-recombination energy, i.e., the energy required to break a bond.

As discussed in Sec. II, the chain length distributions given by Eqs. (25) and (28) do not agree quantitatively with the computer simulation results of Weis and Levesque [26]. This may cast doubts on the validity of our approach to describe the static equilibrium properties of a system of living polymers, as the low-density phase of strongly dipolar fluids appears to be. We note, however, that recent Monte Carlo simulations by Rouault and Milchev [37] on a (lattice) model of living polymers (of completely flexible chains, with zero nonbonding interactions) have revealed that the distribution of chain lengths is indeed exponential, in agreement with the mean-field prediction and with Eq. (25). Moreover, simulations indicate that the mean chain length increases with density as a power law, with an exponent that is close to 0.5, except for chains in the noninteracting regime where the exponent is exactly 0.5 as given by mean-field theory and by Eq. (28). Finally, another prediction of mean-field theory, also confirmed by simulation, is that the Lifshitz point (which separates the high-temperature isotropic ordinary fluid from the low-temperature isotropic structured fluid) occurs at $E/4$.

Despite the fact that Rouault and Milchev [37] did not compare the absolute values of their mean chain lengths with theoretical predictions, the agreement between mean-field theory and simulation appears to be much better than the comparison of our results for the dipole chains with simulation, discussed in Sec. II, seems to suggest. We believe that the main reason for this discrepancy is that in Rouault and Milchev's simulations care was taken to ensure equilibrium conditions at all temperatures. This was implemented by restricting the lowest temperature studied for a given system size, in order to guarantee the presence of monomers in the simulation box. Although for the smallest system sizes this condition severely restricts the range of temperatures that can be studied, it does allow equilibrium to be reached among chains of all sizes. The same, however, cannot be said of the published simulations of dipole chains [24,26], which may be affected by strong finite-size effects, and therefore no firm conclusions on the validity of the living polymer approach to describe the behavior of the low-density strongly dipolar fluid may be drawn at present.

In our treatment of the dipolar fluid we have also included the effects of the excluded volume of the semiflexible chains and of additional isotropic interactions between DHSs. Our study of the model with attractive interactions was restricted to the effects of these interactions on chain dissociation. We have not discussed the liquid-vapor condensation that is observed in these systems when the relative strength of the isotropic attraction (with respect to the dipole-dipole interaction) exceeds a critical threshold or the order-disorder-polymerization transition that was investigated (extensively) in a recent computer simulation of a different (lattice) model of semiflexible (living) polymers with nonbonding attractive interactions [55]. These interactions cause the system to phase separate into dense and rarefied phases. The nature and location of the transitions depend on the relative strengths of the energies that characterize the chain: the bonding energy, the chain bending rigidity, and the nonbonding interaction between monomers. In the dipole chain, however, the bonding and bending energies are not independent. Although a systematic computer simulation study of the condensation transition of the Stockmayer fluid has been carried out recently by van Leeuwen and Smit [22], the global phase diagrams of the DHS and DSS fluids remain, to a large extent, unexplored.

We conclude by making some remarks on the phase transitions that are expected to occur in strongly dipolar fluids, based on computer simulation studies of living polymers and recent theories of chain formation. It was shown some years ago that long-ranged orientational order is absent in (lattice) models of living polymers if the nonbonding interaction is set to zero [43] or if the chains are totally flexible [56]. A more recent study [55] of a simple (lattice) model of semiflexible living polymers with nonbonding (monomer-monomer) interactions revealed the existence of a first-order polymerization order-disorder transition between a low-temperature ordered state of stiff parallel rods and a high-temperature disordered state due to disorientation of the chains. This research also confirms the expected exponential form of the equilibrium chain length distribution, although the density and temperature dependence of the mean chain length deviate from their expected behavior. The situation for dipole chains with additional attractions is much less clear, but it is likely that a fluid phase with long-range orientational order is preempted by the solid.

A better understood phase diagram obtains when the liquid-vapor critical point occurs in the neighborhood of the Lifshitz point. In that regime, isotropic interactions may inhibit the formation of chains, and consequently clustering of the particles is driven by the usual energy-entropy mechanism. This mechanism is ultimately responsible for the condensation of the gas at a critical density and temperature. The competition between chain formation and clustering was addressed recently by van Roij [50] within a free-energy ansatz that combines the original van der Waals theory of liquid condensation and the association theory of ideal particles. The resulting phase diagrams indicate that liquid-vapor condensation becomes metastable if the tendency to form weakly interacting chains is sufficiently strong [57]. In his treatment van Roij assumes the chains to be noninteracting on the basis of plausible intuitive arguments, but without a supporting quantitative estimate. Moreover, his estimation of the semiphenomenological parameters in his theory on the basis of separating the dipole-dipole interaction into an average isotropic attraction and a remaining anisotropic contribution is, in our view, not correct. Indeed, the unweighted average of the dipole-dipole interaction over the orientations of the intermolecular vector is zero and therefore, in the low-temperature (isotropic) phase of chains, the net isotropic attraction of the dipolar fluid vanishes. Only at higher temperatures can the dipoles rotate freely and the Boltzmann-averaged isotropic interaction then becomes nonzero, while the bonding (directional) energy vanishes. Although in van Roij's work both condensation and chaining are treated in qualitative terms, the ansatz does capture the two competing mechanisms. A connection with the underlying model interactions is nevertheless missing.

An approach that is very close to ours, but does not explicitly address the issue of phase transitions, is that of Sear [58]. This author has proposed an explanation for the failure to find liquid-vapor condensation in simulations of DSS [24] and DHS [26] fluids. His argument is based on the observation that chains form in low-density dipolar fluids, which then by assumption interact only weakly. In this theory, the configurational energy and the mean chain length of a low-density DHS fluid are calculated from the equation of state obtained from the activity expansion of the pressure. Sear neglected all interactions between monomers beyond nearest neighbors and assumed that the pressure of a fluid of noninteracting chains is given by the infinite sum of linear chain graphs containing f bonds (where f is the Mayer function) between successive spheres. His derivation is very simple and elegant because the chain integrals factorize, yielding a closed-form expression, but whether this is a realistic approximation for the pressure of a fluid of chains is, in our view, an open theoretical question. It actually amounts to replacing a chain by a collection of pairs of monomers, since all steric effects involving more than two nearest neighbors are lost. For the present model and large dipole moments, Sear's predictions are very similar to ours, but we do not see why this should be the case in general. In particular, he does recover mean-field results such as the $(\rho^*)^{1/2}$ dependence of the mean chain length. This can be understood by noting that Eq. (5) in [58] can be rewritten in terms of our variables, as

$$\beta P=\frac{e^{\nu}}{1-\dfrac{e^{\nu+S_0}}{1-e^{\nu+S_0}}},\tag{51}$$

which coincides with our Eq. (30) in the limit of small $\alpha=\nu+S_0$ (large λ).

By contrast, the main advantage of our treatment is that it can be easily generalized; in this paper we have discussed two such generalizations. The most straightforward describes an orientationally ordered fluid and is elaborated in the Appendix. This allows a more detailed treatment of the ferroelectric phase transition by taking chains into account, as will be presented elsewhere. The second generalization is the inclusion of interactions between chains: excluded-volume and attractive interactions were considered in Sec. III, which allowed us to delimit the noninteracting chain regime. We have been able to describe chain dissociation, and in future work we hope to address the condensation and polymerization transitions in a more realistic (and self-consistent) manner.

Finally, Stevens and Grest have performed Gibbs ensemble simulations of the DSS fluid in a field and found a coexistence between two very low-density phases of long, polarized chains aligned along the field [23]. As discussed in previous paragraphs, at such low densities as considered in this work ($\rho^*\sim 10^{-2}$), no ordinary liquid-vapor separation is seen in zero field: instead, DSSs associate into chains that are entangled and thus exhibit no global orientational order. When a field is applied the chains become more or less straight; in an infinite system at zero temperature, or in an infinite field, they would be infinitely long. Since the dipolar interaction between two parallel, infinitely long, dipolar chains is zero, no phase separation would ensue. Now the longest chains seen in the simulations actually span the system and thus are ''infinite'' by virtue of the periodic boundary conditions used (there are also a number of shorter chains). This suggests that the dipolar interactions between two chains in the field are very weak and can be neglected. Then (apart from excluded-volume effects), we are left with a model of noninteracting semiflexible polymers, which do not phase separate in the absence of a field [55]. So the usual excluded-volume argument that drives the orientational phase transition in nematic polymers does not seem to be applicable to the system of dipole chains: at these very low packing fractions, semiflexible rods would only order nematically (i.e., separate into paranematic and nematic phases) if they were straight on the length scale of the simulation box size (see [46] and references cited therein), which is not the case. Note that mixtures of long and short *rigid* rods may separate into two nematic phases [59] due to competition between orientational entropy and entropy of mixing. It is tempting to suggest a connection between the transition in the field and nematic demixing, but as argued above we cannot identify the mechanism that drives the phase transition in the field, at least for a system with no additional isotropic attractions, and thus for the moment we feel that this transition remains to be understood.

ACKNOWLEDGMENTS

M.A.O. acknowledges support of the Portuguese Government in the form of Grant No. PRAXIS XXI/BCC/4387/94. P.I.C.T. and M.M.T.d.G. have been partially supported by Portuguese Government Grant No. PRAXIS XXI/2/2.1/FIS/181/94. The work of the FOM Institute is part of the research program of FOM and is supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek. P.I.C.T. gratefully acknowledges the hospitality of the Centro de Física da Matéria Condensada, where part of this work was performed. Interactions with Jean-Jacques Weis have been greatly appreciated. We thank René van Roij and Richard Sear for communicating their results prior to publication and, together with Bela Mulder and Daan Frenkel, for a critical reading of the manuscript.

APPENDIX: DENSITY-FUNCTIONAL THEORY OF A FLUID OF DIPOLE CHAINS

In Sec. II we derived the free energy of a single long dipole chain and in Sec. III that of the isotropic phase of a fluid of interacting long dipole chains. In this appendix we generalize our theory to allow for orientational order of the chains. This order can either be induced by an external field or appear self-consistently if the system undergoes a transition to the ferroelectric state.

The fluid of partially ordered chains is characterized by the one-particle ODF $\hat{f}(\mathbf{a},\mathbf{r})$ of a sphere in a chain. It can be written as

$$\hat{f}(\mathbf{a},\mathbf{r})=\frac{\mathcal{Z}_k(\mathbf{a},\mathbf{r})\mathcal{Z}_{N-k+1}(\mathbf{a},\mathbf{r})}{\mathcal{Z}_{\mathrm{ch}}}.\tag{A1}$$

The same principle of ground-state dominance then leads to

$$\hat{f}(\mathbf{a},\mathbf{r})\approx\psi_1^2(\mathbf{a},\mathbf{r}),\tag{A2}$$

where $\psi_1(\mathbf{a},\mathbf{r})=\mathcal{Z}^{(1)}(\mathbf{a})\mathcal{Z}^{(1)}(\mathbf{r})$ is the ground-state eigenfunction of the operator $\nabla_{\mathbf{a}}^2+\sigma^2\nabla_{\mathbf{r}}^2$ (we assume all spheres in a chain to be equivalent).

Consider now a dipole chain in an aligning external potential $U_e(\mathbf{a},\mathbf{r})$. We require the free energy of the chain in the field as a functional of the ODF. This was first derived by Lifshitz [60], and the resulting functional is called Lifshitz entropy [61]. From Eqs. (13) and (14) we get

$$\lambda_{11}=\Omega\int \hat{f}(\mathbf{a},\mathbf{r})\frac{(\nabla_{\mathbf{a}}^2+\sigma^2\nabla_{\mathbf{r}}^2)\psi_1(\mathbf{a},\mathbf{r})}{\psi_1(\mathbf{a},\mathbf{r})}d\mathbf{a}\,d\mathbf{r}. \tag{A3}$$

If the ground state gives the predominant contribution, $\hat{f}(\mathbf{a},\mathbf{r})$ is related to $\psi_1(\mathbf{a},\mathbf{r})$ via Eq. (53), whence the entropy of a chain is

$$\begin{aligned}S_{\mathrm{ch}}=&-\frac{N\Omega k_B}{4}\int d\mathbf{a}\,d\mathbf{r}\frac{[\boldsymbol{\nabla}_{\mathbf{a}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}\\&-\frac{N\Omega k_B\sigma^2}{4}\int d\mathbf{a}\,d\mathbf{r}\frac{[\boldsymbol{\nabla}_{\mathbf{r}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}.\end{aligned} \tag{A4}$$

We finally obtain, for the free-energy functional of one long dipole chain in an external field,

$$\begin{aligned}\frac{1}{V}\mathcal{F}_{\mathrm{ch}}[\hat{f}(\mathbf{a},\mathbf{r})]=&-(N-1)k_BTS_0+N\int d\mathbf{a}\,d\mathbf{r}U_e(\mathbf{a},\mathbf{r})\hat{f}(\mathbf{a},\mathbf{r})\\&+\frac{N\Omega k_BT}{4}\int d\mathbf{a}\,d\mathbf{r}\\&\times\left\{\frac{[\boldsymbol{\nabla}_{\mathbf{a}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}+\sigma^2\frac{[\boldsymbol{\nabla}_{\mathbf{r}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}\right\},\end{aligned} \tag{A5}$$

where, as before, the first term is the intrachain energy [cf. discussion following Eq. (24)].

Combining these results with those of Sec. III A, we arrive at the expression for the free-energy density of a fluid of long, interacting dipole chains at low density. It will, however, depend on the nature of the external field U_e. If this is not an electric field and the average electric field $\mathbf{E}=\mathbf{0}$, the free-energy functional reads

$$\begin{aligned}\frac{1}{V}\mathcal{F}[\rho_{\mathrm{ch}},\hat{f}(\mathbf{a},\mathbf{r})]=&-(N-1)\rho_{\mathrm{ch}}k_BTS_0\\&+N\rho_{\mathrm{ch}}\int d\mathbf{a}\,d\mathbf{r}U_e(\mathbf{a},\mathbf{r})\hat{f}(\mathbf{a},\mathbf{r})\\&+\frac{3\rho_{\mathrm{ch}}Nk_BT}{8\lambda}\int d\mathbf{a}\,d\mathbf{r}\\&\times\left\{\frac{[\boldsymbol{\nabla}_{\mathbf{a}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}+\sigma^2\frac{[\boldsymbol{\nabla}_{\mathbf{r}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}\right\}\\&+\rho_{\mathrm{ch}}^2k_BTN^2\sigma^3\int\hat{f}(\mathbf{a}_1)|\sin\gamma_{12}|\\&\times\hat{f}(\mathbf{a}_2)d\mathbf{a}_1d\mathbf{a}_2,\end{aligned} \tag{A6}$$

where the first term is the sum of (average) bond energies, the second is the energy associated with the external field, the third is the orientational entropy from Eq. (A4), and the last one the excluded-volume contribution from Eq. (35). It follows from Sec. III A that the dipolar contribution is negligibly small. When the system is in the external electric field $\mathbf{E}_e$, one has to include also the electrostatic energy $-\mathbf{E}\cdot\mathbf{P}$. The external field term in Eq. (A6) should then be replaced by

$$-\int\mathbf{E}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})d\mathbf{r}, \tag{A7}$$

where $\mathbf{P}(\mathbf{r})=N\rho_{\mathrm{ch}}\int\boldsymbol{\mu}\hat{f}(\mathbf{a},\mathbf{r})d\mathbf{a}$ and $\mathbf{E}$ is the average electric field in the medium. For a spherical sample, $\mathbf{E}=(4\pi/3)\mathbf{E}_e$.

We now allow for chains of different lengths. Let $\rho(N)$ be the density of chains of length N (cf. Sec. II B); we then have

$$\begin{aligned}\frac{\mathcal{F}[\hat{f}(\mathbf{a},\mathbf{r}),\rho(N)]}{V}=&k_BT\sum_{N=1}\rho(N)[\ln\rho(N)-1]-k_BT\sum_{N=1}\rho(N)(N-1)S_0+\sum_{N=1}N\rho(N)\int d\mathbf{a}\,d\mathbf{r}U_e(\mathbf{a},\mathbf{r})\hat{f}(\mathbf{a},\mathbf{r})\\&+\frac{3k_BT}{8\lambda}\sum_{N=1}N\rho(N)\int d\mathbf{a}\,d\mathbf{r}\left\{\frac{[\boldsymbol{\nabla}_{\mathbf{a}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}+\sigma^2\frac{[\boldsymbol{\nabla}_{\mathbf{r}}\hat{f}(\mathbf{a},\mathbf{r})]^2}{\hat{f}(\mathbf{a},\mathbf{r})}\right\}\\&+k_BT\sigma^3\sum_{N,N'=1}N\rho(N)N'\rho(N')\int\hat{f}(\mathbf{a}_1)|\sin\gamma_{12}|\hat{f}(\mathbf{a}_2)d\mathbf{a}_1\,d\mathbf{a}_2.\end{aligned} \tag{A8}$$

Likewise, if the system is in an external electric field, the term containing U_e should be replaced by

$$-\sum_{N=1}N\rho(N)\int\boldsymbol{\mu}\cdot\mathbf{E}(\mathbf{r})\hat{f}(\mathbf{a},\mathbf{r})d\mathbf{a}\,d\mathbf{r}. \tag{A9}$$

Equation (A8) is the free-energy functional of a fluid of long chains at low density, corresponding to $\lambda\gg1$ and $\Delta^{-1}\ll\rho^*\ll1$. Note that it is a functional of two distribution functions $\hat{f}(\mathbf{a},\mathbf{r})$ and $\rho(N)$, both of which are determined by minimization. In the absence of any external field U_e, the system is isotropic and characterized by the chain length distribution $\rho(N)$ alone; the latter is subject to the constraint Eq. (22) that the total number of particles per unit volume, in chains of all lengths, must equal the particle number density.

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