Statistical theory and structure factor of a semidilute solution of rodlike macromolecules interacting by van der Waals forces

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The second and third virial coefficients are estimated for a semidilute suspension of macromolecular rods interacting by van der Waals forces. Whenever the attractive interaction becomes strong enough to be noticeable, it is no longer quantitatively correct to adopt a second virial approximation. Nevertheless, the statistical properties of the second virial fluid are investigated because it is a very convenient idealization of strongly interacting molecular fluids. Sufficient conditions for the local thermodynamic stability of the isotropic phase are set up. The coupling of orientational with translational degrees of freedom which arises from the anisotropic van der Waals interaction between two rods is particularly manifest in the structure factor. This is calculated analytically with the help of a variational theorem.

I. INTRODUCTION

A semidilute suspension of slender rods interacting by hard core repulsion and van der Waals forces is an important prototype for fluids consisting of highly anisometric molecules. In such a solution, the translation of the macromolecules is coupled strongly to their orientational degrees of freedom. Whenever two rods approach each other, parallel configurations are weighted heavily by the attractive interaction which is effectively short ranged and hence markedly anisotropic. By contrast, the orientational bias exerted by the repulsive excluded volume is a great deal weaker.

Unfortunately, we lack a complete understanding of the van der Waals interaction between two rods in spite of intense research in the 1970s. In the next section, we propose two distinct approximations—a sticky potential of very short range and an intermediate interaction tentatively extrapolated down to zero separation. Both approximations give virtually identical sets of estimates of the second and third virial coefficients (Sec. III) which justifies our impression that we are focusing on universal features of the van der Waals force. Section IV shows that the interplay between attractive and repulsive interactions is unexpectedly subtle. Whenever the van der Waals interaction is thermodynamically nonnegligible, the third virial coefficient has to be taken into account. Therefore, the second virial fluid is a severe approximation. Nonetheless, we study it in some detail because it is an interesting example of a liquid of anisometric particles exhibiting marked orientation-translation coupling. We present a local analysis of the stability of the isotropic solution in Sec. V. Because of the orientation-translation coupling, the attractive forces should have an impact on the wave-vector dependence of the light scattered by the fluid, so we evaluate the structure factor in Sec. VI.

II. VAN DER WAALS INTERACTION BETWEEN TWO RODS

We consider an isotropic suspension of slender rodlike macromolecules of length L, width D, and aspect ratio

 $p \equiv L/D \gg 1$. The rods are impenetrable so they interact through a hard core repulsion which presumably defines the athermal limit of the interaction. In addition, the macromolecules attract each other by van der Waals or dispersion forces which we here approximate as a sum over pairs of rods only. We disregard three- and higher-order body forces.

In general, the van der Waals interaction $E(\mathbf{u},\mathbf{u}',\mathbf{R}_c)$ between two rods skewed at an angle γ is a very complex potential of mean force. It depends on their orientations \mathbf{u} and \mathbf{u}' and the vector distance \mathbf{R}_c between their centers of mass (see Fig. 1). When $L \gg R_c \equiv |\mathbf{R}_c| > D$, we can disregard end effects and the function E simplifies considerably becoming a function of γ and the distance R between the centerlines of the two cylinders. In Table I are compiled several limiting forms of $E(\gamma,R)$ which are discussed at length in Ref. 2. Furthermore, we want to keep in mind the following qualitative features of the van der Waals interaction:

- (1) For $R_c \gg L$, the interaction $E(\mathbf{u}, \mathbf{u}', \mathbf{R}_c)$ decays essentially as that between two pointlike particles, i.e., as R_c^{-6} , but this isotropic attraction is negligible for the purpose of our discussion focusing on slender rods.
- (2) In practice, the interaction is predominantly short ranged. This is borne out by the following example in which we set the aspect ratio p=50, the Hamaker constant $A'=10^{-20}$ J, and the temperature T=300 K. If the two rods are parallel and separated by a surface to surface distance of R-D=D/2, we have $-E/k_BT=O(10)$ which plunges to $O(10^{-1})$ upon increasing their separation to R-D=2D. A similar consideration holds when the rods are perpendicular.
- (3) If the rods are very close $(R D \leqslant D)$, the interaction is so strongly attractive that it may be regarded as sticky. Note that the divergence of E as R tends to D is spurious, for the continuum theory of dispersion forces breaks down at the atomic level.
- (4) The inverse $\sin \gamma$ dependence quantifies the tendency of the rods to align. It may be understood in terms of a "surface of interaction." For instance, let us consider the case $L \gg R \gg D$. The two cylindrical rods may be replaced by

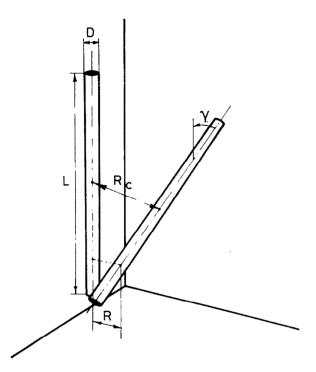


FIG. 1. The configuration of two rods of length L and diameter D skewed at an angle γ . The vector distance between the centerlines is denoted by \mathbf{R} ; \mathbf{R}_c is the vector distance between the centers of mass.

two infinite lines parametrized by the coordinates i and j along the respective contours. The van der Waals interaction is now an integral of r_{ij}^{-6} over i and j, where r_{ij} is the distance between i and j. The dominant term comes from the region where r_{ij} runs from R to several times R. Hence the surface of interaction is about R wide and $R \sin^{-1} \gamma \log$ so that the particular entry in Table I arises from multiplying the integrand of magnitude R^{-6} by the area of the surface.

Since the interaction is complicated and incompletely known anyway, we will employ two extreme approximations—one emphasizing the stickiness of the potential, the other stressing the R^{-4} decay at intermediate distances.

(i) This is an extension of a proposal by Grosberg and Khokhlov³ which we shall call a sticky potential

$$E_{S}/k_{B}T = \begin{cases} -\delta\epsilon \sin^{-1}\gamma & \gamma > \delta^{1/2}p^{-1} \\ -\delta^{1/2}\epsilon p(1 - |z/L|), & \gamma < \delta^{1/2}p^{-1} \end{cases}$$
(2.1)

for separations in the range $D < R < D(1+\delta)$, provided the rods overlap¹ (E_S is zero otherwise). Here ϵ is the depth of the potential (measured in units of the energy of attraction for two flat surfaces of area D^2) and δ is its width divided by the diameter of the rods ($\delta \le 1$). Note that E_S depends on δ because it is proportional to the "area of interaction." When $\gamma \le \delta^{1/2} p^{-1}$, the rods are essentially parallel to the z axis in a polar coordinate system and $R_c = |z|$. Note that the matching of the two expressions at $\gamma = \delta^{1/2} p^{-1}$ is imperfect for $z \ne 0$.

(ii) The intermediate potential, which supposes that the intermediate form of the van der Waals interaction may be extrapolated down to R = D (see Table I),

TABLE I. Van der Waals interaction between two cylinders. A' is the Hamaker constant, typically in the range 10^{-20} – 10^{-19} J. End effects have been neglected, i.e., $L \gg R_c$ and D. The entries in this table have been taken from Ref. 2.

	E	
	$R-D \triangleleft D$	$R \gg D$
$\gamma = 0$	$-\frac{1}{24\sqrt{2}}pA'\left(\frac{D}{R-D}\right)^{3/2}$	$-\frac{3\pi}{128}pA'\left(\frac{D}{R}\right)^5$
γ≯p ⁻¹	$-\frac{1}{12}A'\left(\frac{D}{R-D}\right)^{a}$	$-\frac{\pi}{32}A'\left(\frac{D}{R}\right)^4\sin^{-1}\gamma$

$$E_{I}/k_{B}T = \begin{cases} -\frac{\pi}{32}A\sin^{-1}\gamma\left(\frac{D}{R}\right)^{4}, & \gamma > p^{-1} \\ -\frac{3\pi}{128}Ap(1-|z/L|)\left(\frac{D}{R}\right)^{5}, & \gamma \leqslant p^{-1} \end{cases} (2.2)$$

for overlapping rods¹ $(A = A'/k_BT)$. Equation (2.2) underestimates the magnitude of the attraction at very close separations.

III. VIRIAL COEFFICIENTS

A. The second virial coefficient

The second virial coefficient in a system of rods of uniform density reads

$$B = -\frac{1}{2} \int \int \psi(\mathbf{u}) \psi(\mathbf{u}') \beta_1(\mathbf{u}, \mathbf{u}') d\mathbf{u} d\mathbf{u}',$$

$$\beta_1 = \int \Phi(\mathbf{r} - \mathbf{r}', \mathbf{u}, \mathbf{u}') d(\mathbf{r} - \mathbf{r}').$$
(3.1)

Here, the orientation of a test rod is described by the unit vector $\mathbf{u} = \mathbf{u}(\theta,\phi)$ along its axis, which is given in terms of the polar coordinates θ and ϕ defined with respect to the z axis in our Cartesian coordinate system ($\mathbf{r} = x,y,z$). In the isotropic state, the angular distribution function ψ of the test rod equals $(4\pi)^{-1}$ and the position of its center of mass is denoted by \mathbf{r} . The primed variables specify the generalized coordinates of another test rod so that $\mathbf{R}_c = \mathbf{r} - \mathbf{r}'$. In view of the discussion in Sec. II, the Mayer function has the approximate form

$$\Phi(\mathbf{R}_c, \mathbf{u}, \mathbf{u}') = \begin{cases} -1, & R \leq D \\ \exp(-E/k_B T) - 1, & R > D \end{cases}$$
(3.2)

when the rods overlap and $\Phi = 0$ otherwise. Therefore, both the cluster integral $\beta_1(\mathbf{u},\mathbf{u}') = \beta_1(\gamma)$ and the virial coefficient B consist of separate contributions from the hard core repulsion (denoted by the subscript "R") and the van der Waals attraction (denoted by the subscript "A")

$$\beta_1(\gamma) = \beta_{1,R}(\gamma) + \beta_{1,A}(\gamma), \quad B = B_R + B_A.$$
 (3.3)

Following Onsager,⁵ we have for slender rods

$$\beta_R = -2L^2D\sin\gamma + O(LD^2), \quad B_R = \frac{1}{4}\pi L^2D + O(LD^2).$$
(3.4)

We now discuss the contribution from the dispersion force in terms of the two extremes proposed in Sec. II, which we denote by the subscripts "S" and "I" instead of "A."

(i) The sticky potential yields

$$\beta_{1,s} = \begin{cases} -4\pi L D^2 \delta \{1 + [1 - \exp(\epsilon \delta^{1/2} p)] / \epsilon \delta^{1/2} p \}, & \gamma \leqslant \delta^{1/2} p^{-1} \\ -2L^2 D \delta \sin \gamma [1 - \exp(\epsilon \delta / \sin \gamma)], & \gamma > \delta^{1/2} p^{-1} \end{cases}$$
(3.5)

In these expressions, we neglect terms of relative magnitude p^{-1} . We write the contribution to the second virial coefficient as⁴

$$B_{S} \cong \pi L D^{2} p^{-2} \delta^{2} \{1 + [1 - \exp(\epsilon \delta^{1/2} p)] / \epsilon \delta^{1/2} p\}$$

$$+ L^{2} D \delta \int_{\delta^{1/2} p^{-1}}^{\pi/2} d\gamma \sin^{2} \gamma$$

$$\times [1 - \exp(\epsilon \delta / \sin \gamma)]. \tag{3.6}$$

At this stage, it is convenient to introduce the variable $\xi_S = -B_S/B_R$ which is accessible experimentally, at least in principle. When $\epsilon \delta^{1/2} p \le 1$, $\xi_S \simeq \epsilon \delta^2 [1 + O(p^{-2}\delta)]$, so the contribution from the van der Waals forces is entirely negli-

gible. This is also true when $\epsilon \delta^{1/2} p = O(1)$, since then $\xi_S \simeq \delta^2 p^{-3}$. The case of experimental interest is $\epsilon \delta^{1/2} p \gg 1$, for which the term originating from the parallel configurations dominates

$$\xi_s \simeq 4\delta^2 p^{-3} (\epsilon \delta^{1/2} p)^{-1} \exp(\epsilon \delta^{1/2} p). \tag{3.7}$$

Unfortunately, it is impossible to take the limit $\epsilon \to \infty$, $\delta \to 0$ in such a way that $\xi_S = \xi_S(p)$ is well defined for all p, so that we cannot introduce the analog of Baxter's model for sticky spheres.⁶

(ii) The cluster integral of the van der Waals interaction in the intermediate range is given by

$$\beta_{1,I} = \begin{cases} -4\pi LD^{2} \left[\frac{1}{2}M(-\frac{7}{3} - \frac{2}{3}, Hp) - \frac{1}{7} - \frac{1}{2}Hp \right] / Hp \\ -2L^{2}D\sin\gamma \left[\exp(\frac{4}{3}H\sin^{-1}\gamma) - 1 - \frac{4}{3}H\sin^{-1}\gamma M(\frac{3}{4}, \frac{7}{4}, \frac{4}{3}H\sin^{-1}\gamma) \right] \end{cases}$$
(3.8)

in the respective ranges $\gamma \leqslant p^{-1}$ and $\gamma > p^{-1}$. Here M(a,b,x) is the Kummer function and $H \equiv 3\pi A/128$. The integrals leading to Eq. (3.8) are evaluated in Appendix A. For $Hp \gtrsim 1$, the parallel configurations again dominate and we approximate the ratio of the virial coefficients $\xi_I \equiv -B_I/B_R$ by

$$\xi_I \cong 4H^{-2}p^{-5}\exp(Hp).$$
 (3.9)

B. The third virial coefficient

Unlike B, the third virial coefficient

$$C = -\frac{2}{3} \int \int \int \beta_2({\bf u},{\bf u}',{\bf u}'') \psi({\bf u}) \psi({\bf u}') \psi({\bf u}'') d{\bf u} d{\bf u}' d{\bf u}'',$$

$$\beta_2(\mathbf{u},\mathbf{u}',\mathbf{u}'') = \frac{1}{2} \int \int \Phi(\mathbf{r}',\mathbf{u},\mathbf{u}') \Phi(\mathbf{r}'',\mathbf{u},\mathbf{u}'')$$

$$\times \Phi(\mathbf{r}' - \mathbf{r}'',\mathbf{u}',\mathbf{u}'') d\mathbf{r}' d\mathbf{r}''$$
(3.10)

is not separable into purely hard core and dispersion terms

$$C = C_R + C_A + C_{RA}. (3.11)$$

The first two terms represent the three body analog of B_R and B_A . The third term C_{RA} involves an integration over generalized coordinates in such a way that hard core and van der Waals contributions are intermingled. Scaling arguments and numerical computations reveal that^{5,8-10}

$$C_R \simeq B_R^2 p^{-1}$$
. (3.12)

A qualitative analysis for C_A and C_{RA} is also possible in the regime where attraction becomes significant. We know

that the largest contribution to the second virial coefficient B_A stems from the parallel configurations of two test rods. A similar dominance of the exponential term occurs for C_A . We therefore need to evaluate the cluster integral $\beta_{2,A}$ for only those configurations of virtually parallel rods in which each rod almost touches the other two. For the sticky potential, we have

$$\beta_{2,S} \simeq \delta (LD^2 \delta)^2 (\epsilon \delta^{1/2} p)^{-2} [\exp(\epsilon \delta^{1/2} p)]^3$$
(parallel rods). (3.13)

Equation (3.13) is obtained as follows:

- (1) One rod serves as a reference and is placed along the z axis with its center of mass at the origin of our coordinate system. The other two rods have their respective centers of mass at \mathbf{r}' and \mathbf{r}'' , and also point in the z direction. The double volume integral of Eq. (3.10) is carried out in such a way that the hard cores never overlap. It is convenient to introduce cylindrical coordinates $d\mathbf{r}' \to R' dR' d\phi' dz'$ and analogously for \mathbf{r}'' . The length scales D, δD , and L correspond to R', dR', and dz', respectively, so the two volume integrations produce the factor $(\delta D^2 L)^2$.
- (2) The integration over ϕ'' gives a factor δ because we must have three pairs of touching cylinders.
- (3) The Mayer function $\Phi \simeq \exp[\epsilon \delta^{1/2} p(1 |z'/L|)]$ has a maximum at z' = 0 leading to the $[\exp(\epsilon \delta^{1/2} p)]^3$ term because there are three Mayer functions.
- (4) The two z integrations of the remaining $\exp(-\epsilon \delta^{1/2}pz/L)$ terms provide the factor $(\epsilon \delta^{1/2}p)^{-2}$.

Equation (3.13) then yields⁴

$$C_S \simeq -\delta (LD^2 \delta)^2 (\epsilon \delta^{1/2} p)^{-2} [\exp(\epsilon \delta^{1/2} p)]^3 (\delta p^{-2})^2$$

$$\simeq -\delta B_S^2 \exp(\epsilon \delta^{1/2} p), \qquad (3.14)$$

where B_S is given by Eq. (3.6) in the case $\epsilon \delta^{1/2} p \gg 1$.

We only briefly sketch the estimation of the cross coefficient C_{RS}

- (1) Rod 1 acts as the reference. It intersects rod 2 and (almost) touches rod 3. Rods 2 and 3 must then either intersect or touch.
- (2) Attraction between a pair of rods is only significant when the rods are practically parallel.
- (3) We distinguish two leading contributions to C_{RS} . The first stems from configurations in which rods 1 and 2 intersect at an angle $\gamma \gtrsim p^{-1}$, while rod 3 is roughly parallel to rod 1. This leads to a contribution proportional to $B_R B_S$.
- (4) The second contribution is connected with configurations in which all three rods are almost parallel. The overlap of rods 2 and 3 gives a term proportional to $B_R B_S p^{-3}$, which we disregard since $p \ge 1$. The tiny number of configurations with rods 2 and 3 touching [equivalent⁴ to a "phase volume" of $\simeq (\delta p^{-2})^2$] does however introduce a term $\simeq -B_S^2$.

To sum up, we have

$$C_{RS} \simeq -B_R^2 \xi_S [1 + X(\xi_S)], \quad X(\xi_S) \simeq \xi_S.$$
 (3.15)

The intermediate van der Waals potential gives very similar results, of which we only cite

$$C_I \simeq -B_I^2 \exp(Hp). \tag{3.16}$$

IV. ATTRACTION VERSUS REPULSION

The conditions under which attraction and repulsion balance ($\xi = 1$) may be loosely called a θ state. It follows from Eqs. (3.7) and (3.9) that in that case

$$H = 3p^{-1} \ln p [1 + O(\ln \ln p / \ln p)],$$

$$\epsilon \delta^{1/2} = 3p^{-1} \ln p [1 + O(\ln \ln p / \ln p)]$$
(4.1)

as $p \to \infty$ with ϵ and δ fixed. The common leading order term results from the dominance of the exponentials in the expres-

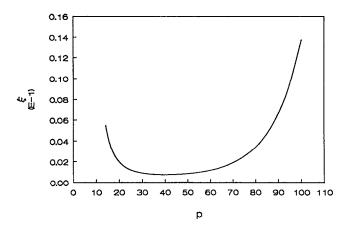


FIG. 2. Relative contribution ξ_I of attraction to the second virial coefficient as a function of the aspect ratio p. Intermediate potential H=0.125.

sions for ξ . By setting $\delta = 1$, we obtain a previous result by Grosberg and Khokhlov.³

The relative strength of the van der Waals interaction as expressed by the parameter ξ shows a peculiarity in its dependence on the aspect ratio p. For example, in Fig. 2, we have plotted ξ_I as a function of p for a typical value of H which clearly shows a minimum. This minimum is located at $p = 4/\epsilon \delta^{1/2}$ and p = 5/H in the respective approximations, assuming that δ is a fixed parameter. We come back to a possible implication of this feature below.

The relative importance of three-body interactions in the virial expansion of the free energy is expressed by the parameter

$$\tau \equiv |C| \nu B_R^{-1}, \tag{4.2}$$

where ν is the number density of the rods. The second virial approximation is applicable if $\tau \leqslant 1$. We know that for hard slender rods, the three-body interactions may indeed be neglected^{5,8,9} for we have

$$\tau_R \equiv C_R \nu B_R^{-1} \simeq p^{-1} c, \tag{4.3}$$

which tends to zero as $p \to \infty$; the dimensionless concentration $c \equiv B_R \nu$ is smaller than 3.29 in the isotropic phase. ¹¹ For the sticky potential, we have

$$\tau_{RS} \equiv |C_{RS}| \nu B_R^{-1} \simeq \xi_S [1 + O(\xi_S)] c,$$

$$\tau_S \equiv |C_S| \nu B_R^{-1} \simeq \delta \xi_S^2 c \exp(\epsilon \delta^{1/2} p)$$

$$\simeq (\epsilon \delta^{1/2} p) (\xi_S p)^3 c \delta^{-1}. \tag{4.4}$$

We may neglect the cross term when attraction becomes significant and set $\tau \simeq \tau_S$. Even for quite small values of ξ , τ may be of order unity since $p \gg 1$ and $\epsilon \delta^{1/2} p \gg 1$. The presumably small prefactor that we have left unspecified will not alter this fact. Note also that τ_S diverges if one were to attempt the formal limit $\delta \to 0$, $\epsilon \to \infty$ keeping ξ_S fixed.

Our qualitative analysis implies that the second virial approximation could become invalid when rods start to exhibit a more than marginal attraction (except of course at very low concentrations). The intermediate approximation

$$\tau_I \simeq (\xi_I p)^3 H^2 p^2 c \tag{4.5}$$

leads to the same conclusion.

We cannot exclude a breakdown of the virial expansion at temperatures above θ in view of the tendency of τ to become larger than unity with increasing attraction. This does not mean, however, that the suspension should necessarily phase separate. Macroscopic phase separation may be prevented by the formation of finite aggregates ("bundles" of rods). One rationale for this scenario lies in the decrease of the aspect ratio of the particles with aggregation and the concomitant diminishing of ξ and τ . Conceivably, the aggregates may stay finite because of the existence of an optimum value of the aspect ratio (see Fig. 2). Our reasoning is of course speculative, but the aggregation of rods merits further investigation.

In summary, when the dispersion forces between rods start influencing the thermodynamics, the second virial approximation will lose its quantitative validity. Nevertheless, it is of methodological interest to investigate a second virial fluid of attracting rods. The marked effect of the coupling of orientational and translational degrees of freedom on, for instance, the scattering of light can then be analyzed quantitatively. This will be important in understanding real systems.

V. STABILITY OF THE SECOND VIRIAL FLUID

Because the van der Waals forces may induce phase transitions of various types, it is important to investigate the thermodynamic stability of the second virial fluid. The isotropic suspension of rods is (locally) stable if infinitesimal fluctuations of the density away from equilibrium are accompanied by an increase in the free energy. We look at fluctuations involving both the translation and orientation of the rods.

The total free energy F of the suspension is a functional of the local rod density $f(\mathbf{r},\mathbf{u})$, which is normalized to the total number of macromolecules

$$\int \int f(\mathbf{r}, \mathbf{u}) d\mathbf{r} d\mathbf{u} = N. \tag{5.1}$$

It is convenient to abbreviate (r,u) by q and drdu by dq. The relation between F and f is then given by a straightforward extension of the Onsager analysis⁵

$$F[f] = \text{constant} + k_B T \int f(\mathbf{q}) \ln f(\mathbf{q}) d\mathbf{q}$$
$$-\frac{1}{2} k_B T \int \int \Phi(\mathbf{q}, \mathbf{q}') f(\mathbf{q}) f(\mathbf{q}') d\mathbf{q} d\mathbf{q}' \quad (5.2)$$

and consists of a constant we leave unspecified, an ideal entropy term, and a second virial term with Mayer function $\Phi(q,q') = \Phi(r - r',u,u')$. Now write the local rod density as a sum of the equilibrium value $f_{eq}(\mathbf{q})$ and a presumably small perturbation $\delta f(\mathbf{q})$, i.e., $f = f_{eq} + \delta f$. After its insertion in Eq. (5.2) and subsequent expansion of the resulting expression in powers of δf , the free energy becomes

$$F[f]/k_BT$$

$$= F \left[f_{eq} \right] / k_B T + \int \delta f(\mathbf{q}) \left[1 + \ln f_{eq}(\mathbf{q}) - \int f_{eq}(\mathbf{q}') \right]$$

$$\times \Phi(\mathbf{q}, \mathbf{q}') d\mathbf{q}' d\mathbf{q}' + \frac{1}{2} \int \int \delta f(\mathbf{q}) \delta f(\mathbf{q}')$$

$$\times f_{eq}^{-1}(\mathbf{q}) \left[\delta(\mathbf{q} - \mathbf{q}') - f_{eq}(\mathbf{q}) \Phi(\mathbf{q}, \mathbf{q}') \right]$$

$$\times d\mathbf{q} d\mathbf{q}' + \text{higher order terms.}$$
(5.3)

The equilibrium distribution minimizes F subject to condition (5.1). Hence we have

$$\ln f_{\rm eq}(\mathbf{q}) = \lambda - 1 + \int f_{\rm eq}(\mathbf{q}') \Phi(\mathbf{q}, \mathbf{q}') d\mathbf{q}', \qquad (5.4)$$

where λ is a Lagrange multiplier. This is an extension of the integral equation proposed by Onsager, used to analyze the isotropic to nematic transition in hard rod systems.^{5,8} If we omit higher-order terms, Eq. (5.3) reduces to

$$F[f]/k_B T = F[f_{eq}]/k_B T$$

$$+ \frac{1}{2} \int \int \delta f(\mathbf{q}) \delta f(\mathbf{q}') f_{eq}^{-1}(\mathbf{q})$$

$$\times [\delta(\mathbf{q} - \mathbf{q}') - f_{eq}(\mathbf{q}) \Phi(\mathbf{q}, \mathbf{q}')] d\mathbf{q} d\mathbf{q}'. (5.5)$$

We restrict ourselves to the isotropic phase $f_{eq}(\mathbf{q}) = \nu/4\pi$. Next we write Eq. (5.5) in terms of the Fourier trans-

$$\delta f(\mathbf{k}, \mathbf{u}) = \int \exp(-i\mathbf{k} \cdot \mathbf{r}) \delta f(\mathbf{q}) d\mathbf{r},$$

$$\delta f(\mathbf{q}) = (2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{r}) \delta f(\mathbf{k}, \mathbf{u}) d\mathbf{k},$$
 (5.6)

etc., yielding

$$F[f]/k_BT$$

=
$$F[f_{eq}]/k_BT + \frac{1}{2}(2\pi)^{-3}(\nu/4\pi)^{-1}\int A(\mathbf{k})d\mathbf{k}$$
,

$$A(\mathbf{k}) \equiv \int \int \delta f(-\mathbf{k}, \mathbf{u}') \delta f(\mathbf{k}, \mathbf{u}) \{ \delta(\mathbf{u} - \mathbf{u}') - \nu(4\pi)^{-1} \Phi(\mathbf{k}, \mathbf{u}, \mathbf{u}') \} d\mathbf{u} d\mathbf{u}'.$$
 (5.7)

The free energy fluctuation $F[f] - F[f_{eq}]$ is thus cast into the form of a summation of Fourier components A(k). For the suspension to be (locally) stable, any small fluctuation should increase the free energy, implying that A(k) > 0 is a sufficient condition (see also Ref. 12 for a more general expression involving the direct correlation function). It is shown in Appendix B that if the rods exhibit a weak attraction ($\xi \leq 1$), the stability against small perturbations is governed by the sufficient condition $c < 4/(1 + 8\xi)$.

In the above, we have analyzed the effect of an arbitrary yet small fluctuation of the local rod density on the total free energy which results in the general equation (5.7). A specific result of interest is obtained if we have in mind a certain type of concentration fluctuation. Then, the increase of the free energy is linked to the structure factor.

To show this, let a hypothetical external field $\phi(q)$ act on each rod. We now add a term $\int \phi(\mathbf{q}) f(\mathbf{q}) d\mathbf{q}$ to Eq. (5.2) and a term $-\phi(\mathbf{q})$ to Eq. (5.4). The choice $\phi(\mathbf{k},\mathbf{u}) = -\epsilon j_0(\mathbf{K}\cdot\mathbf{u})$, where $\phi(\mathbf{k},\mathbf{u})$ is the Fourier transform of $\phi(\mathbf{q})$, ϵ is a small number, and $j_0(\mathbf{K} \cdot \mathbf{u})$ is the spherical Bessel function defined in Eq. (6.2) couples directly to the relevant type of concentration fluctuation (see Ref. 13). The change in the distribution function δf due to the external field is then given by

$$(1 + \nu \widehat{W}) \delta f(\mathbf{k}, \mathbf{u}) = (4\pi)^{-1} \nu \epsilon j_0(\mathbf{K} \cdot \mathbf{u}), \tag{5.8}$$

where

(5.3)

$$\widehat{W}(\cdots) \equiv -(4\pi)^{-1} \int \Phi(\mathbf{k}, \mathbf{u}, \mathbf{u}')(\cdots) d\mathbf{u}' \qquad (5.9)$$

denotes an integral operator. Equation (5.8) can be obtained by linearization and subsequent Fourier transformation of the modified equation (5.4). Next we note that both $\delta f(-\mathbf{k},\mathbf{u})$ and $\delta f(\mathbf{k},\mathbf{u})$ obey Eq. (5.8), thus allowing us to eliminate δf from Eq. (5.7). After comparing the final result

with Eqs. (6.3) and (6.4) for the structure factor $S(\mathbf{k})$ given in the next section, we arrive at

$$F[f]/k_B T = F[f_{eq}]/k_B T + \frac{1}{2} \nu \epsilon^2 (2\pi)^{-3} \int S(\mathbf{k}) d\mathbf{k}.$$
(5.10)

A sufficient condition for (local) stability is if $S(\mathbf{k})$ is greater than zero for all wave numbers. In the next section, we show that this must be the case when $c < [2\xi(1-1/\epsilon\delta^{1/2}p)]^{-1}$ [$S(\mathbf{k})$ diverges when the opposite inequality holds; at the same time, it is negative for a certain range of k]. This condition is less restrictive than the previous one, as we would expect.

VI. STRUCTURE FACTOR OF THE SECOND VIRIAL FLUID

In this section, we calculate the static structure factor pertaining to isotropic light scattering by the second virial fluid. In order to describe both inter- and intramolecular interference, the rods are divided into L/D "segments" which act as the basic scattering units. The structure factor is then given by the autocorrelation function ^{14,15}

$$S(\mathbf{k}) = \langle c(-\mathbf{k})c(\mathbf{k}) \rangle_{s} / vV, \tag{6.1}$$

where k is the usual scattering vector, V is the scattering volume, $c(\mathbf{k})$ is the Fourier transform of the local segment density $c(\mathbf{r})$, and $\langle \cdots \rangle_s$ denotes a statistical average. There is a simple relation between the local segment density and the local number density f, or rather their Fourier transforms¹³

$$c(\mathbf{k}) = \int j_0 (\mathbf{K} \cdot \mathbf{u}) f(\mathbf{k}, \mathbf{u}) d\mathbf{u},$$

$$j_0 (\mathbf{K} \cdot \mathbf{u}) \equiv \sin \mathbf{K} \cdot \mathbf{u} / \mathbf{K} \cdot \mathbf{u}$$
 (6.2)

with $K = \frac{1}{2}kL$ a dimensionless scattering vector. It is straightforward to show that the analysis of Doi et al.¹³ and van der Schoot and Odijk¹⁶ holds for any second virial fluid. We therefore write the structure factor

$$S(\mathbf{k}) = \langle j_0(\mathbf{K} \cdot \mathbf{u}) g(\mathbf{k}, \mathbf{u}) \rangle \tag{6.3}$$

in terms of the unknown function g, the solution of the integral equation

$$(1 + \nu \widehat{W})g(\mathbf{k}, \mathbf{u}) = j_0(\mathbf{K} \cdot \mathbf{u}). \tag{6.4}$$

Here $\langle \cdots \rangle$ now denotes the orientational average $(4\pi)^{-1} \int d\mathbf{u}(\cdots)$. An integral equation such as Eq. (6.4) can be attacked with the help of a variational principle, ^{16,17} leading to

$$S(\mathbf{k}) \simeq \frac{\langle j_0^2(\mathbf{K} \cdot \mathbf{u}) \rangle^2}{\langle j_0^2(\mathbf{K} \cdot \mathbf{u}) \rangle + \nu \langle j_0(\mathbf{K} \cdot \mathbf{u}) \widehat{W} j_0(\mathbf{K} \cdot \mathbf{u}) \rangle}.$$
 (6.5)

Equation (6.5) compares well with numerical evaluations of integral equations such as Eq. (6.4) pertaining to suspensions of hard rods and suspensions of rodlike polyelectrolytes. 17-19

We now proceed to specify the Fourier transformed Mayer function $\Phi(\mathbf{k}, \mathbf{u}, \mathbf{u}')$ which acts as the kernel of the integral operator W. As in the calculation of the second virial coefficient B, Φ separates in contributions from repulsion and attraction

$$\Phi(\mathbf{k},\mathbf{u},\mathbf{u}') = \Phi_R(\mathbf{k},\mathbf{u},\mathbf{u}') + \Phi_A(\mathbf{k},\mathbf{u},\mathbf{u}'). \tag{6.6}$$

Provided $|\mathbf{k}|D \equiv kD \leqslant 1$, one has

$$\Phi_{R}(\mathbf{k},\mathbf{u},\mathbf{u}') = \beta_{1,R}(\gamma)j_{0}(\mathbf{K}\cdot\mathbf{u})j_{0}(\mathbf{K}\cdot\mathbf{u}')$$
(6.7)

with $\gamma = \gamma(\mathbf{u}, \mathbf{u}')$, as shown in Ref. 13. Employing the sticky potential approximation (2.1), we get

$$\Phi_{S}(\mathbf{k},\mathbf{u},\mathbf{u}') \simeq -4\pi L D^{2} \delta \left\{ \frac{j_{0} (2\mathbf{K} \cdot \mathbf{u}) - (\epsilon \delta^{1/2} p)^{-1} [\exp(\epsilon \delta^{1/2} p) - \cos 2\mathbf{K} \cdot \mathbf{u}]}{1 + [2(\epsilon \delta^{1/2} p)^{-1} \mathbf{K} \cdot \mathbf{u}]^{2}} \right\}, \quad \gamma \leqslant \delta^{1/2} p^{-1}$$

$$\simeq -2L^{2} D \delta \sin \gamma [1 - \exp(\epsilon \delta / \sin \gamma)] j_{0} (\mathbf{K} \cdot \mathbf{u}) j_{0} (\mathbf{K} \cdot \mathbf{u}'), \quad \gamma > \delta^{1/2} p^{-1}. \tag{6.8}$$

Equation (6.8) is simplified considerably by noting that

$$\Phi_{S}(\mathbf{k}, \mathbf{u}, \mathbf{u}') \cong \begin{cases}
\beta_{1,S}(\gamma) \left[1 + (2\mathbf{K} \cdot \mathbf{u}/\epsilon \delta^{1/2} p)^{2} \right]^{-1}, & \gamma \leq \delta^{1/2} p^{-1} \\
\beta_{1,S}(\gamma) j_{0}(\mathbf{K} \cdot \mathbf{u}) j_{0}(\mathbf{K} \cdot \mathbf{u}'), & \gamma > \delta^{1/2} p^{-1}
\end{cases}$$
(6.9)

is an accurate description in the regime of interest $\epsilon \delta^{1/2} p \gtrsim 1$ [cf. Eq. (3.5)]. Again, to a good approximation, we may neglect the large angle part of Eq. (6.9) in the calculation of the double integral appearing in Eq. (6.5)

$$\nu \langle j_0(\mathbf{K} \cdot \mathbf{u}) \widehat{W} j_0(\mathbf{K} \cdot \mathbf{u}) \rangle \cong 8\pi^{-1} c \langle \langle j_0^2(\mathbf{K} \cdot \mathbf{u}) j_0^2(\mathbf{K} \cdot \mathbf{u}') \sin \gamma \rangle \rangle' - 2c \xi_s \langle j_0^2(\mathbf{K} \cdot \mathbf{u}) / 1 + (2\mathbf{K} \cdot \mathbf{u} / \epsilon \delta^{1/2} p)^2 \rangle.$$

$$(6.10)$$

One of the terms has been calculated previously¹⁷

$$8\pi^{-1}c\langle\langle j_0^2(\mathbf{K}\cdot\mathbf{u})j_0^2(\mathbf{K}\cdot\mathbf{u}')\sin\gamma\rangle\rangle' \cong 2cF^2(K) - \frac{5}{4}cG^2(K), \quad F(K) \equiv \langle j_0^2(\mathbf{K}\cdot\mathbf{u})\rangle = K^{-1}Si(2K) - j_0^2(K),$$

$$G(K) \equiv \frac{3}{4}K^{-2}[1 - j_0(2K)] - \frac{1}{4}F(K)$$
(6.11)

with Si(x) the sine integral and F(K) the so-called single rod form factor. ¹⁴ The other term may be expressed as

$$\langle f_0^2(\mathbf{K} \cdot \mathbf{u})/1 + (2\mathbf{K} \cdot \mathbf{u}/\epsilon \delta^{1/2} p)^2 \rangle \equiv [F(K) - I(K,\epsilon \delta^{1/2} p)], \tag{6.12}$$

where the correction term

$$I(K,\epsilon\delta^{1/2}p) = 4 \int_0^1 \left[\frac{\sin^2 Kx}{(2Kx)^2 + (\epsilon\delta^{1/2}p)^2} \right] dx$$
 (6.13)

vanishes in the limit $K/\epsilon\delta^{1/2}p\to 0$ and is of the order $(K\epsilon\delta^{1/2}p)^{-1}$ for $K\gtrsim \epsilon\sigma^{1/2}p$. The structure factor is thus simplified to a form amenable to interpretation

$$S(K) = \frac{F^{2}(K)}{(1 - 2c\xi_{S})F(K) + 2cF^{2}(K) - (5/4)cG^{2}(K) + 2c\xi_{S}I(K,\epsilon\delta^{1/2}p)}.$$
(6.14)

This expression has the following features:

- (1) In the case where attractive forces are absent, setting $\xi_S = 0$ yields a result¹⁷ very similar to the random phase approximation, ^{13,20-22} except for the correction term involving G(K). As shown elsewhere, ¹⁷ G(K) vanishes for $K \leqslant 1$, but does contribute significantly if $K \gtrsim 1$.
- (2) The influence of the van der Waals interaction $(\xi_s > 0)$ on the scattering is markedly different from that of the repulsive forces (see below). This is caused by the fact that for the sticky interaction, almost parallel configurations of rods are weighted much more heavily than strongly skewed configurations. Equation (6.14) exhibits strong coupling of the orientational and translational degrees of freedom.
- (3) At zero scattering angle, Eq. (6.14) reduces to $S(0) = [1 + 2(1 \xi_S)c]^{-1} = (1 + 2Bv)^{-1}$ (6.15) giving the usual relation between the structure factor and the osmotic compressibility.
- (4) The limit $K/\epsilon\delta^{1/2}p \gg 1$ yields to leading order in powers of K^{-1}

$$S(K) \approx (\pi/2K)\{1 - 2\xi_S c[1 - (\epsilon \delta^{1/2} p)^{-1}]\}^{-1}.$$
 (6.16)

Apparently the structure factor diverges (and becomes negative in some range of K) when $2\xi_S c[1 - (\epsilon \delta^{1/2} p)^{-1}] \geqslant 1$,

C=0.5

FIG. 3. The structure factor of the second virial fluid of dimensionless concentration c=0.5 according to Eq. (6.14). Results are shown for various levels of attraction. To evaluate the small correction $I(K,\epsilon\delta^{1/2}p)$, we set p=100 and $\delta=1$. This choice of δ might seem to contradict the condition $\delta < 1$ of Sec. II, but in fact does not because it only affects inessential prefactors which are left unspecified anyway.

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0.00

indicating a transition to a different phase which we leave unspecified here. Although this may occur in the regime where the second virial approximation is not strictly valid, the given bound does provide a sufficient condition for phase separation to set in since we have underestimated the effect of attraction.

- (5) If we increase ξ_s , the van der Waals contribution to the second virial coefficient, at a fixed concentration c, for instance by decreasing the temperature of the system, the structure factor shifts towards higher values over the entire K range. This is illustrated in Fig. 3.
- (6) Attraction has a strong effect on the wave vector dependence of the structure factor. In a suspension of hard rods ($\xi_S = 0$), an increase of the concentration causes a decrease of S(K), most noticeably at small K. The situation is decidedly different when $\xi_S > 0$, because then an increase of the concentration causes the structure factor to decrease only at small K, but to *increase* beyond some value of K. This inflection shifts towards lower K with increasing attraction, as can be seen from Figs. 4–7. It is estimated to occur at $K \approx (27/64) \pi \xi_S^{-1} (1 1/\epsilon \delta^{1/2} p)$ valid for $K \gtrsim 1$.

The above results will be very similar if we apply the intermediate approximation. A straightforward calculation shows that

$$\Phi_{I}(\mathbf{k},\mathbf{u},\mathbf{u}') \simeq \begin{cases}
\beta_{1,I}(\gamma) [1 + (2\mathbf{K}\cdot\mathbf{u}/Hp)^{2}]^{-1}, & \gamma \leq p^{-1} \\
\beta_{1,I}(\gamma) j_{0}(\mathbf{K}\cdot\mathbf{u}) j_{0}(\mathbf{K}\cdot\mathbf{u}'), & \gamma > p^{-1}
\end{cases}$$
(6.17)

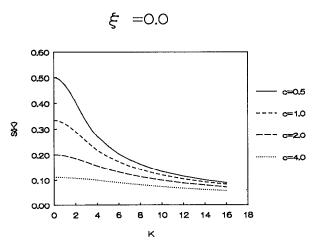


FIG. 4. The structure factor of the second virial fluid for various concentrations. Attractive forces are absent, so the parameter ξ_S is set equal to zero, in which case, the second virial approximation should be quite accurate.

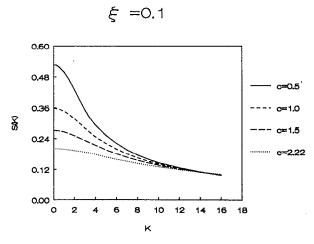


FIG. 5. The same as in Fig. 4, but now with attractive forces $[\xi_s = 0.1, p = 100, \text{ and } \delta = 1 \text{ (see the caption to Fig. 3)}].$

if $Hp \gtrsim 1$. Hence, after replacing ξ_S by ξ_I and $I(K, \epsilon \delta^{1/2}p)$ by I(K, Hp) in Eq. (6.14), we obtain an analogous expression for the structure factor in the intermediate approximation. Note that the condition $kD \ll 1$ ensures that interference effects within the range of the potential may be neglected.

VII. CONCLUDING REMARKS

For a semidilute solution of slender rods, the second virial approximation is quite reasonable provided the interactions are repulsive. If there are van der Waals interactions present of sufficient magnitude to perturb the thermodynamics of the suspension, the same approximation is no longer accurate and higher-order virials have to be accounted for.

Although the second virial fluid of attracting rods is of little use in a quantitative comparison with experiments, it may serve as an important model displaying excessive orientation—translation coupling. For instance, we have given an

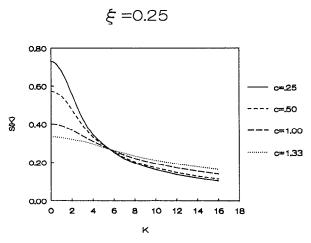


FIG. 6. The same as Fig. 5, except for $\xi_S = 0.25$ [p = 100 and $\delta = 1$ (see the caption to Fig. 3)].

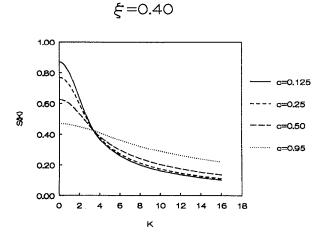


FIG. 7. The same as Fig. 5, for $\xi_S = 0.4$ [p = 100 and $\delta = 1$ (see the caption to Fig. 3)].

analytic expression for the structure factor which depends strongly on the van der Waals interaction. This may be useful in gaining a qualitative understanding of future experiments on rodlike biopolymers in which the temperature is varied.

APPENDIX A

Here we evaluate the cluster integral $\beta_{1,I}(\gamma)$ in the intermediate approximation to the van der Waals potential. Let us start with the small angle limit and insert Eqs. (2.2) and (3.2) into Eq. (3.1)

$$-\beta_{1,I}(\gamma < p^{-1}) \cong \int_0^{2\pi} d\phi \int_D^{\infty} dR \int_{-L}^L dz R$$

$$\times \{1 - \exp[Hp(1 - |z/L|)D^5R^{-5}]\}$$
(A1)

in cylindrical coordinates and $H = 3\pi A/128$. We have neglected a small contribution from end effects. The ϕ and z integrations are carried out after scaling $z/L \rightarrow z$ and $R/D \rightarrow R$, which results in

$$J \equiv -\beta_{1,I} (\gamma < p^{-1})/4\pi L D^{2}$$

$$\cong \int_{1}^{\infty} dR R \left[1 + H^{-1} p^{-1} R^{5} - H^{-1} p^{-1} R^{5} \exp(H \rho R^{-5}) \right]. \tag{A2}$$

Integral J may be approximated in the limits $Hp \leqslant 1$ and $Hp \geqslant 1$.

$$J \cong \begin{cases} -\frac{1}{6}Hp[1 + O(Hp)], & Hp \ll 1 \\ -\frac{1}{3}H^{-2}p^{-2}\exp(Hp)[1 + O(H^{-1}p^{-1})], & Hp \gg 1. \end{cases}$$
(A3)

In the intermediate range, it is possible to use several exact relations. We have

$$d^{2}(HpJ)/d(Hp)^{2} = -\frac{1}{5} \int_{0}^{1} t^{-2/5} \exp(Hpt) dt$$
$$= -\frac{1}{5} M(\frac{3}{5}, \frac{8}{5}, Hp)$$
(A4)

The Kummer function M(a,b,x) has the following property:⁷

$$\partial M(a,b,x)/\partial x = ab^{-1}M(a+1,b+1,x).$$
 (A5)

From Eq. (A5) it follows that Eq. (A4) has the particular solution

$$HpJ = \frac{1}{2}M(-\frac{7}{2}, -\frac{2}{3}, Hp).$$
 (A6)

The complete solution now reads

$$HpJ = \frac{1}{2}M(-\frac{7}{5}, -\frac{2}{5}, Hp) + Q_1 + Q_2Hp,$$
 (A7)

where Q_1 and Q_2 are constants left to be determined. Even without knowing the values of these constants, we have already recovered the correct limiting behavior⁷ for large Hp,

$$HpJ = -\frac{1}{2}(Hp)^{-1}\exp(Hp)\left[1 + O(H^{-1}p^{-1})\right]$$
 (A8)

owing to dominance of the exponential. Next we expand Eq. (A7) for small Hp,

$$J \cong (\frac{1}{2} + Q_1)H^{-1}p^{-1} + (\frac{1}{2} + Q_2) - \frac{1}{2}Hp.$$
 (A9)

Since J = 0 when Hp = 0, we find that the first two terms of Eq. (A9) should vanish, i.e., $Q_1 = -1/7$ and $Q_2 = -1/2$. Note that we have automatically recovered the correct limit $Hp \le 1$.

The large angle limit $\beta_{1,I}(\gamma > p^{-1})$ is determined more easily. Upon using Straley's oblique coordinates²³ and neglecting end effects we rewrite Eq. (3.1) as

$$-\beta_{1,I}(\gamma > p^{-1}) \cong 2 \int_{D}^{\infty} d\zeta \int_{-L/2}^{L/2} d\zeta \int_{-L/2}^{L/2} d\eta$$

$$\times \sin \gamma \left\{ 1 - \exp\left[\frac{4}{3}H\sin^{-1}\gamma(D/\zeta)^{4}\right] \right\}$$

$$\cong 2L^{2}D\sin \gamma \int_{1}^{\infty} dx \left[1 - \exp\left(\frac{4}{3}H\right) + \exp\left(\frac{4}{3}H\right) \right]$$

$$\times \sin^{-1}\gamma x^{-4} \right]. \tag{A10}$$

Partial integration and the subsequent transformation $t = x^{-4}$ then lead to⁷

$$-\beta_{1,I}(\gamma > p^{-1}) \approx 2L^{2}D \sin \gamma [\exp X - 1 - XM(\frac{3}{4}r_{A}^{2},X)]$$
(A11)

with $X = 4H \sin^{-1} \gamma$. This reduces to

$$-\beta_{1,I}(\gamma > p^{-1})/2L^{2}D\sin\gamma$$

$$\cong \begin{cases} -\frac{1}{3}X[1 + O(X)] \\ -\frac{1}{4}X^{-1}\exp X[1 + O(X^{-1})] \end{cases}$$
(A12)

in the respective limits $X \le 1$ and $X \ge 1$.

APPENDIX B

To derive a sufficient condition for which

$$A(\mathbf{k}) = \int \int \delta f(-\mathbf{k}, \mathbf{u}) \delta f(\mathbf{k}, \mathbf{u}') \{ \delta(\mathbf{u} - \mathbf{u}') - \nu(4\pi)^{-1} \Phi(\mathbf{k}, \mathbf{u}, \mathbf{u}') \} d\mathbf{u} d\mathbf{u}'$$
(B1)

is positive for all wave numbers, we make use of orthogonal expansions. First we set the vector k parallel to the z axis of a

Cartesian coordinate system. We define \mathbf{u} in terms of the usual polar coordinates θ and ϕ . We assume the fluctuations to be a function of scalar quantities so that $\delta f(\mathbf{k},\mathbf{u}) = \delta f(k,x)$ with $x = \cos \theta$. Equation (B1) is written as

$$A(\mathbf{k}) = 2\pi \int_{-1}^{1} \int_{-1}^{1} \delta f(-k,x) \delta f(k,x') \{ \delta(x-x') - \nu(4\pi)^{-1} \Phi(k,x,x') \} dx dx'$$

$$\Phi(k,x,x') = \int_{0}^{2\pi} \Phi(\mathbf{k},\mathbf{u},\mathbf{u}') d\phi.$$
(B2)

If the rods interact solely via a hard core repulsion 13,24

$$\Phi_{R}(k,x,x') = -2L^{2}Dj_{0}(Kx)j_{0}(Kx')\int_{0}^{2\pi}\sin\gamma\,d\phi$$

$$= -4\pi L^{2}Dj_{0}(Kx)j_{0}(Kx')\left[\frac{\pi}{4} - \sum_{n=1}^{\infty}D_{2n}\right]$$

$$\times P_{2n}(x)P_{2n}(x'), \qquad (B3)$$

where $P_{2n}(x)$ are Legendre polynomials and the coefficients are defined as $D_{2n} \equiv C_{2n}F_{2n}$ with $C_{2n} = (4n + 1)/2$ and

$$F_2 = \frac{\pi}{16}, \quad F_{2n} = \left(\frac{\pi}{2^{2n}}\right) \frac{(2n-3)!!(2n-1)!!}{n!(n+1)!}, \quad n > 1.$$
 (B4)

Since $F_{2n+2} < F_{2n}$, one has $D_{2n} < C_{2n}F_2$ for n > 1 and accordingly

$$\sum_{n=1}^{\infty} D_{2n} P_{2n}(x) P_{2n}(x')$$

$$< F_2 \delta(x - x') - F_2 \sum_{n=0}^{\infty} C_{2n+1} P_{2n+1}(x)$$

$$\times P_{2n+1}(x'). \tag{B5}$$

Inequality (B5) is established with the help of the closure relation²⁵

$$\delta(x - x') = \sum_{n=0}^{\infty} C_n P_n(x) P_n(x').$$
 (B6)

From Eqs. (B5) and (B6), we find $(c = B_R \nu)$

$$\delta(x - x') - \nu(4\pi)^{-1} \Phi_{R}(k, x, x')$$

$$> \delta(x - x') + 4c\pi^{-1} j_{0}(Kx) j_{0}(Kx')$$

$$\times \left[\frac{\pi}{4} - F_{2} \delta(x - x') + F_{2} \sum_{n=0}^{\infty} C_{2n+1} P_{2n+1}(x) \right]$$

$$\times P_{2n+1}(x') . \tag{B7}$$

Insertion of Eq. (B7) into Eq. (B2) gives

$$A(k) > 2\pi \int_{-1}^{1} \int_{-1}^{1} \left[1 - 4c\pi^{-1} F_{2} j_{0}(Kx) j_{0}(Kx') \right] \\ \times \delta(x - x') \delta f(-k, x) \delta f(k, x') dx dx' \\ + \text{non-negative terms.}$$
 (B8)

The "non-negative terms" are of the form

$$\left[\int_{-1}^{1} \delta f(-k,x) j_0(Kx) P_n(x) dx\right] \times \left[\int_{-1}^{1} \delta f(k,x) j_0(Kx) P_n(x) dx\right],$$

which are indeed real and non-negative because $\delta f(-k,x)$ and $\delta f(k,x)$ are complex conjugates. If we insert $F_2 = \pi/16$ and perform one integration, Eq. (B8) becomes

$$A(k) > \text{non-negative terms} + 2\pi \int_{-1}^{1} \left[1 - \frac{1}{4} c f_0^2(Kx) \right] \times \delta f(-k, x) \delta f(k, x) dx.$$
 (B9)

Since $1 - 4^{-1}cj_0(Kx)^2 \ge 1 - 4^{-1}c$, a sufficient condition for A(k) to be positive for arbitrary k and $\delta f(k,x)$ is

$$c < 4.$$
 (B10)

Clearly this bound is exact for k=0, but conservative for k>0. Equation (B10) is modified when the rods exhibit an additional attractive interaction. The contribution to $\Phi(k,x,x')$ stemming from attraction is dominated by configurations of (almost) parallel rods (see Sec. VI), allowing us to write $(\alpha \equiv 2\epsilon^{-1}\delta^{-1/2}p^{-1}>0)$

$$\Phi_{S}(k,x,x') \simeq -4\pi B_{S}[\delta(x-x') + \delta(x+x')] \times [1 + (\alpha K x)^{2}]^{-1}$$
(B11)

for the sticky potential [cf. Eqs. (6.9) and (6.10)]. Symmetry demands that $\delta f(k,x) = \delta f(k,-x)$. Insertion of Eq. (B11) in Eq. (B2) thus yields

$$A(k) > 2\pi \int_{-1}^{1} \left[1 - 4^{-1} c f_0^2 (Kx) - 2c \xi_S / 1 + (\alpha Kx)^2 \right] \\ \times \delta f(-k,x) \delta f(k,x) dx + \text{non-negative terms.}$$
(B12)

The inequality

$$1 - 4^{-1}cj_0(Kx)^2 - 2c\xi_S[1 + (\alpha Kx)^2]^{-1}$$

> 1 - 4^{-1}c - 2c\xi_S (B13)

helps to determine a sufficient condition for which A(k) is positive

$$c < 4/(1 + 8\xi_S)$$
. (B14)

Use of the intermediate instead of the sticky potential leads to a similar relation.

- ¹ As usual, the distance between the two centerlines is defined as the shortest distance between the first centerline and the plane through the second which is parallel to the first. Overlap is defined as the condition that two rods cross. In that case, the projection of the first rod onto the same plane must touch the second rod.
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