Structure Factor of a Solution of Charged Rodlike Macromolecules in the Isotropic Phase

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ABSTRACT: A theory of the static and dynamical structure factor of a solution of charged rodlike polymers for the isotropic and VH-depolarized scattering was developed as an extension of our previous theory for uncharged rods. The potential of mean force was approximated with a sum of hard-rod and screened Coulomb interaction potentials. In the limit of zero polymer charge or zero Debye length, the theory reduces to the previous one for uncharged rods. The following are the major conclusions: (i) The isotropic dynamical structure factor, $g(\mathbf{k},t)$, and VH-depolarized one, $g_{VH}(\mathbf{k},t)$, were given as functions of the scattering vector $\mathbf{k}$, delay time t, rod length L and diameter b, polymer number concentration ν, the Debye length κ^{-1}, and polymer charge density σ. The static structure factors $g(\mathbf{k})$ and $g_{VH}(\mathbf{k})$ were also given in an approximate but analytical form. It is very easy and straightforward to evaluate the structure factors for arbitrary values of the parameters. (ii) The structure factor of a suspension of charged rods can be approximated with that of equivalent uncharged rods having an effective diameter b_{eff}. The approximation holds very well within a few percent of relative error, if a smaller value of the effective diameter b_{eff} is used for the depolarized scattering than the one used for the isotropic scattering. (iii) The present theory is applicable to suspensions of rods, the effective axial ratio L/b_{eff} of which is much larger than unity.

1. Introduction

There is increasing interest in the structural and dynamic properties of suspensions of interacting charged rodlike particles,[1,2] i.e., in connection with the initial stage of rodlike growth of ionic micells and scattering experiments on polyelectrolytes and filamentous viruses in aqueous solutions. For simpler systems like spherical particles, whether they are charged or not, methods of liquid-state theory were applied to derive the radial distribution function $g(r)$, from which all thermodynamic properties can be calculated.

We have presented a theory of the static and dynamical structure factors[3-5] of a solution of uncharged rodlike polymers in the isotropic phase. For charged rodlike polymers, however, theoretical results are available only for weakly interacting systems[6,7] or for a limiting case where the rod length L is much longer than the mean interaxial distance.[8] Another limiting case was studied by the Monte Carlo simulation,[9,10] where the rod length L is much shorter than or at most of the order of the mean distance between the center of mass of the rods. Studies on these limiting cases alone are clearly insufficient, and theories having wider applicability are to be developed.

The biggest trouble in theoretically treating a charged rod system is that we have not an exact expression for the electrostatic potential of mean force $w^e(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ between two rods in configurations $(\mathbf{r},\mathbf{u})$ and $(\mathbf{r}',\mathbf{u}')$, where $\mathbf{r}$ and $\mathbf{r}'$ are the position vectors of the center of the two rods and $\mathbf{u}$ and $\mathbf{u}'$ the orientation unit vectors of the long axis of the rods. Let us imagine the electrostatic potential around a charged rod of length L in an aqueous solution, in which the Debye screening length is κ^{-1}. If $\kappa L \gg 1$, the electrostatic potential near the charged rod would be well approximated by the one around an infinite line of charge, but when we see the rod from a distance, it should appear as a point charge. This intuitive view was proved to be the case by a numerical computation based on the Debye-Hückel approximation,[11] and the characteristic length at which the potential crosses over from the near-field one to the one created by a point charge seems to slightly increase with increasing the κL value. Though the electrostatic potential around a charged rod can be easily imagined, no analytical form is available for the potential $w^e(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$.

Let us think about the relationship between the electrostatic interaction among charged rods and the isotropic-nematic phase transition of a solution of the rods. Even when the rods have no charge, there exists the hard-rod interaction, which not only gives the excluded volume but also tends to orient the rods.[3] If they are highly charged, the rod diameter would effectively increase above the bare diameter b by as much as the Debye screening length κ^{-1} on the order of magnitude. In fact, the osmotic second virial coefficient A_2 of a solution of charged rodlike polymers[12,13] is equivalent to the one due to the hard-core interactions of *uncharged* rigid rods having an effective diameter b_{eff} larger than b. Though the increased effective diameter b_{eff} seems to strengthen the hard-rod interaction and enhance the rod orientation, we also have to take into consideration the fact that the electrostatic interaction between two charged rods would disorient the rods, because the charge-charge repulsion between two rods is stronger when they are placed parallel with each other than when they are placed perpendicular.[16,32] There thus remains a question whether and how the electrostatic interaction affects the isotropic-nematic phase transition of a solution of charged rodlike polymers.

The aim of this paper is first to extend our previous theory to charged rod systems. A reasonable starting point would be an approximation of the potential of mean force $w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ with a sum of the hard-rod term $w^h(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ and the electrostatic one $w^e(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$. We expect the potential w would naturally include the tendency that two charged rods avoid the parallel configuration. The second aim of the paper is, therefore, to give an answer to the question posed in the above. Since the present theory differs from the previous one only in the interrod interactions, we shall first begin with the potential of mean force $w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ between two charged rods. Second, we shall derive from $w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ the interaction potential $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$ for $f_{\mathbf{k}}(\mathbf{u},t)$, where $\mathbf{k}$ is the scattering vector, and $f_{\mathbf{k}}(\mathbf{u},t)$, the spatial Fourier transform of the average number density $f(\mathbf{r},\mathbf{u},t)$ of rods in the configuration $(\mathbf{r},\mathbf{u})$ at time

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t. Third, we shall give approximate but analytical forms of the static structure factors $g(\mathbf{k})$ and $g_{VH}(\mathbf{k})$ for the isotropic and VH-depolarized scattering, respectively, and show that a charged rod can be modeled as an *uncharged* rod having an effective diameter b_{eff}, the value of which must be taken differently according to whether the scattering is isotropic or depolarized. Fourth, we shall give the dynamical structure factors $g(\mathbf{k},t)$ and $g_{VH}(\mathbf{k},t)$ in the matrix representation, give results of numerical computation, and discuss the validity of the uncharged rod approximation. Finally, we compare the solution structure factor $S(\mathbf{k})$ with the ones experimentally observed and discuss the applicability of the present theory.

2. Interaction among Charged Rods

Since our theory for uncharged rods is already described in refs 3–5, we shall at first focus our attention on the potential of mean force between two charged rods.

2.1. Potential of Mean Force $w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$. We approximate a charged rod with a rigid rod of length L and diameter b having a line segment of charge on the long axis of the rod. We assume the potential of mean force $w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ is given by a sum of the hard-rod term w^h and electrostatic one w^e

$$w(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = w^h + w^e \tag{1}$$

$$w^h(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = \infty \quad \text{if the rods at } (\mathbf{r},\mathbf{u}) \text{ and } (\mathbf{r}',\mathbf{u}') \text{ overlap}$$
$$= 0 \quad \text{otherwise} \tag{2}$$

$$w^e(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = \int_{-L/2}^{L/2} ds \int_{-L/2}^{L/2} ds'\, U^e(|\mathbf{r}-\mathbf{r}'+s\mathbf{u}+s'\mathbf{u}'|) \tag{3}$$

where s and s' are the contour coordinates on the rod $(\mathbf{r},\mathbf{u})$ and $(\mathbf{r}',\mathbf{u}')$, respectively, and $U^e(r)\,ds\,ds'$ stands for the screened Coulomb potential energy between charged line elements ds and ds' separated at distance r

$$U^e(r)\,ds\,ds' = \sigma^2 L_B \frac{\exp(-\kappa r)}{r}\,ds\,ds' \tag{4}$$

where σ is the number of elementary charges on the unit length line segment and L_B the Bjerrum length defined by the following expression for a solvent of relative permittivity ϵ:

$$L_B = q^2/\epsilon k_B T \tag{5}$$

where k_B is the Boltzmann constant, T the absolute temperature, and q the charge of a proton. The Bjerrum length L_B is 0.7136 nm in water at 25 °C, and we shall put k_BT to unity hereafter. The Debye screening length κ^{-1} is given by

$$\kappa^{-1} = (8\pi L_B \nu_s)^{-1/2} \tag{6}$$

where ν_s is the number concentration of mono-mono valent salt.[14]

2.2. Interaction Potential $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$. Let us define the interaction potential $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ as

$$W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') \equiv 1 - \exp(-w) = 1 - \exp[-(w^h + w^e)] \tag{7}$$

The quantity $W(\mathbf{r},\mathbf{u},\mathbf{u}')$ is actually a complement of the probability density function for the center-of-mass distance $\mathbf{r}$ and the orientation $\mathbf{u}$ and $\mathbf{u}'$ of two rods, but we shall call W the interaction potential,[3] because the quantity $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$ works as a potential function in a kinetic equation for the average number density $f(\mathbf{r},\mathbf{u},t)$ of rods in the configuration $(\mathbf{r},\mathbf{u})$ at time t.

We assume that there extends a zone out of the hard core of a charged rod, where the electrostatic potential is approximated with the one around an infinite line of charge. We also assume that the electrostatic part w^e of the potential of mean force is much less than unity unless the extended zones of the two rods overlap each other. The shape of the zone is assumed to be a cylinder[15] of length L and radius r^E. The r^E value seems to gradually increase with κL (cf. Figure 3 of ref 11), but, as long as $\exp(-2\kappa r^E) \ll 1$, the precise r^E value is not important in our treatment. The extended zone, of course, includes the hard-core overlap region. Let W^H and W^E be the windowing functions, which are respectively unity in the hard-core and extended-zone overlap regions but otherwise zero:

$$W^H(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = 1 \quad \text{if the rod } (\mathbf{r},\mathbf{u}) \text{ and } (\mathbf{r}',\mathbf{u}') \text{ overlap}$$
$$= 0 \quad \text{otherwise} \tag{8}$$

$$W^E(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = 1 \quad \text{if the extended zones of the rods overlap}$$
$$= 0 \quad \text{otherwise} \tag{9}$$

where W^H is formally written as $W^H = 1 - \exp(-w^h)$, which we call the hard-core interaction potential. We have from eq 7

$$W = W^H \exp(-w^e) + W^E[1 - \exp(-w^e)] + (1 - W^E)w^e$$
$$= W^H + \sum_{n=1}^{\infty} \frac{(-w^{e,H})^n}{n!} - \sum_{n=1}^{\infty} \frac{(-w^{e,E})^n}{n!} + w^e - w^{e,E} \tag{10}$$

where $w^{e,*} \equiv w^e W^*$ with asterisk = "H" or "E", and we used $W^E W^H = W^H$. Putting $W^H = W^E$ for the low charge limit, we write W as

$$W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}') = W^H + w^e - w^{e,H} \tag{11}$$

Note that $w^{e,H}$ and $w^{e,E}$ are respectively the electrostatic potentials truncated in the hard-core or extended-zone overlap regions. Neglecting the end effect in the truncated electrostatic potential, we approximate the potential with the one between two infinitely long line charges.[8]

$$w^{e,*} = \frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\exp(-\kappa r)W^* \quad \text{(asterisk = H or E)} \tag{12}$$

$$Y = 2\pi\sigma^2 L_B \kappa^{-1} e^{-\kappa b} \tag{13}$$

where r is the shortest distance between the two line charges and a nondimensional parameter Y characterizes the strength of the electrostatic repulsion between two charged rods.[16] Note that $|\mathbf{u}\times\mathbf{u}'|$ is in the denominator, which makes the two rods avoid the parallel configuration.[17] We consider eq 12 holds well for $w^{e,H}$ but is not so good for $w^{e,E}$, because the infinitely long line-charge approximation becomes progressively worse with the increase of the rod separation.

2.3. Spatial Fourier Transform of $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$. Let $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$ be the spatial Fourier transform[30] of $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$, where $\mathbf{k}$ is the scattering vector. The computation of $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$, being easy but tedius, is described in section A of the Appendix. Using eqs A.2, A.4, and A.7–9 and neglecting the k terms, we finally have $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$ as

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = 2bL^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}')|\mathbf{u}\times\mathbf{u}'| \times \left[1 + \frac{1}{\kappa b}\left\{\gamma + \ln\left(\frac{Y}{|\mathbf{u}\times\mathbf{u}'|}\right) + E_1\left(\frac{Y}{|\mathbf{u}\times\mathbf{u}'|}\right)\right\}\right] \tag{14}$$

where $s_{\mathbf{k}}(\mathbf{u})$ is defined by eq A.3, $E_1(x)$ stands for the exponential integral, and γ is Euler's constant.

In the low charge limit, we have from eqs 11, A.4, and A.5

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = 2bL^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \left[1 + \frac{1}{\kappa b}\frac{Y}{|\mathbf{u}\times\mathbf{u}'|}\right] \tag{15}$$

Equation 14 agrees with eq 15 for the low-charge limit $Y \to 0$, as it should. When $Y \gg 1$, we may put $E_1(Y/|\mathbf{u}\times\mathbf{u}'|) = 0$ in eq 14, irrespective of the $|\mathbf{u}\times\mathbf{u}'|$ value, and have an asymptotic form for large Y as

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = 2bL^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \times \left[1 + \frac{1}{\kappa b}\left\{\gamma + \ln\left(\frac{Y}{|\mathbf{u}\times\mathbf{u}'|}\right)\right\}\right] \tag{16}$$

The terms enclosed by braces in eqs 14 and 16 agree with each other within 1% of relative accuracy for $Y > 2$ and within 0.1% for $Y > 3$.

Equation 14 has a number of desirable features required for the interaction potential of charged rod systems.

1. When $Y \to 0$ or $\kappa b \to \infty$, $W_{\mathbf{k}}$ reduces to the interaction potential previously derived for uncharged rods.
2. The interaction potential $W_{\mathbf{k}}$ is an increasing function of Y and κ^{-1}.
3. When the two rods are placed parallel with each other, the potential $W_{\mathbf{k}}$ logarithmically diverges in its ratio against the hard-rod potential and thus makes the two rods avoid the parallel configuration.
4. Let us define the effective diameter b_{eff} by

$$b_{\text{eff}} \equiv b[1 + (\kappa b)^{-1}\{\gamma + \ln(Y/|\mathbf{u}\times\mathbf{u}'|) + E_1(Y/|\mathbf{u}\times\mathbf{u}'|)\}] \tag{17}$$

Equation 17 agrees with our previous expectation that the effective diameter b_{eff} would be a sum of the hard-core value b and the Debye length κ^{-1} with a numerical coefficient of the order of unity.

Equation 14 is the basis of our theory, but the orientational weighting factor $1/|\mathbf{u}\times\mathbf{u}'|$ included in the exponential integral $E_1(x)$ prevents us from widely using the equation in our theory. Though eqs 15 and 16 respectively hold for $Y \ll 1$ and $Y \gtrsim 2$, they are mathematically tractable and, what is more important, retain most of the desirable features noted above. We shall mainly use eqs 15 and 16 hereafter.

3. Structure Factors

We shall give in this section structure factors in two representations; one is based on the procedure recently given by van der Schoot and Odijk,[18] and the other is written in the matrix representation.

Using the interaction potential $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$, we easily have static structure factors $g(\mathbf{k})$ and $g_{\text{VH}}(\mathbf{k})$ as follows.[4,5] Let $\Phi_{\mathbf{k}}$ be an operator that expresses the mean-field rod–rod interaction:[3]

$$\Phi_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{u}) = \int d\mathbf{u}' \left[\delta(\mathbf{u}-\mathbf{u}') + \frac{\nu}{4\pi} W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')\right] f_{\mathbf{k}}(\mathbf{u}') \tag{18}$$

where $f_{\mathbf{k}}(\mathbf{u})$ denotes an arbitrary function of the orientation unit vector $\mathbf{u}$. The static structure factors $g(\mathbf{k})$ and $g_{\text{VH}}(\mathbf{k})$ are given by[4,5,19]

$$g(\mathbf{k}) = L\langle s_{\mathbf{k}}(\mathbf{u}) \Phi_{\mathbf{k}}^{-1} s_{\mathbf{k}}^*(\mathbf{u})\rangle \tag{19}$$

$$g_{\text{VH}}(\mathbf{k}) = g_{\text{VH}}^{(\text{c})}(\mathbf{k}) \cos^2(\vartheta/2) + g_{\text{VH}}^{(\text{s})}(\mathbf{k}) \sin^2(\vartheta/2) \tag{20}$$

$$g_{\text{VH}}^{(\xi)}(\mathbf{k}) = L\langle d_{\mathbf{k}}^{(\xi)}(\mathbf{u}) \Phi_{\mathbf{k}}^{-1} d_{\mathbf{k}}^{(\xi)*}(\mathbf{u})\rangle \quad (\xi = \text{"c" or "s"}) \tag{21}$$

where $\langle\ldots\rangle$ denotes the orientational average $(4\pi)^{-1}\int d\mathbf{u}$, and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$, with ξ = "c" and "s" respectively the cosine and sine components of the depolarized structure factor $g_{\text{VH}}(\mathbf{k})$ with respect to the scattering angle ϑ. Function $s_{\mathbf{k}}(\mathbf{u})$ stands for the $\mathbf{k}$ component of the normalized electric field of the light scattered from a rod with orientation $\mathbf{u}$, and $d_{\mathbf{k}}^{(\xi)}(\mathbf{u})$ denotes the angular component of the electric field $d_{\mathbf{k}}(\mathbf{u})$ of the VH-depolarized scattered light; $d_{\mathbf{k}}(\mathbf{u}) = d_{\mathbf{k}}^{(\text{c})}(\mathbf{u}) \cos(\vartheta/2) + d_{\mathbf{k}}^{(\text{s})}(\mathbf{u}) \sin(\vartheta/2)$. The asterisk of $s_{\mathbf{k}}^*(\mathbf{u})$ and $d_{\mathbf{k}}^{(\xi)*}(\mathbf{u})$ stands for the complex conjugate. Function $s_{\mathbf{k}}(\mathbf{u})$ is given by eq A.3 and $d_{\mathbf{k}}^{(\xi)}(\mathbf{u})$ by[5]

$$d_{\mathbf{k}}^{(\xi)}(\mathbf{u}) = \sin\theta\cos\theta\sin\phi\, s_{\mathbf{k}}(\mathbf{u}) \quad (\text{for } \xi = \text{c})$$
$$= \sin^2\theta\sin\phi\cos\phi\, s_{\mathbf{k}}(\mathbf{u}) \quad (\text{for } \xi = \text{s}) \tag{22}$$

where θ and ϕ are respectively the polar and azimuthal angles of the orientation unit vector $\mathbf{u}$ in a polar coordinate system, the polar axis of which is the scattering vector $\mathbf{k}$.

Since we have no analytical form of the inverse of operator $\Phi_{\mathbf{k}}$, eqs 19 and 21 are not usable as they are. Rewriting the structure factors in terms of vectors and matrices is the method we adopted in our previous papers.[4,5] Since matrix Φ that corresponds to operator $\Phi_{\mathbf{k}}$ is real and symmetrical, it is an easy task to compute the inverse matrix Φ^{-1} and the structure factors $g(\mathbf{k})$ and $g_{\text{VH}}(\mathbf{k})$. (An explicit form of matrix Φ for the present problem is given in section D of the Appendix.) In order to see the physical meaning of eqs 19 and 21, however, we shall at first use an approximate but much easier method.

3.1. Structure Factors in the van der Schoot–Odijk Representation. van der Schoot and Odijk[18] recently derived a closed form for $g(\mathbf{k})$ using the Schwinger-type variational principle.[20] Applying their procedure to eqs 19 and 21, we easily have

$$g(\mathbf{k}) = L\frac{\langle |s_{\mathbf{k}}(\mathbf{u})|^2\rangle^2}{\langle s_{\mathbf{k}}(\mathbf{u}) \Phi_{\mathbf{k}} s_{\mathbf{k}}^*(\mathbf{u})\rangle} \tag{23}$$

$$g_{\text{VH}}^{(\xi)}(\mathbf{k}) = L\frac{\langle |d_{\mathbf{k}}^{(\xi)}(\mathbf{u})|^2\rangle^2}{\langle d_{\mathbf{k}}^{(\xi)}(\mathbf{u}) \Phi_{\mathbf{k}} d_{\mathbf{k}}^{(\xi)*}(\mathbf{u})\rangle} \quad (\xi = \text{c or s}) \tag{24}$$

We compute eqs 23 and 24 in the following way. Expanding $|\mathbf{u}\times\mathbf{u}'|$ and $|\mathbf{u}\times\mathbf{u}'|\ln(|\mathbf{u}\times\mathbf{u}'|)$ with spherical harmonics $Y_{lm}(\mathbf{u})$ and $Y_{lm}(\mathbf{u}')$ and truncating at $l = 2$, we approximate eq 16 as

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = 2bL^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') \times \left[\frac{\pi}{4} c_0 - 2\pi^2 c_2 \sum_m Y_{2m}(\mathbf{u}) Y^*_{2m}(\mathbf{u}')\right] \tag{25}$$

$$c_0 = 1 + (\kappa b)^{-1}(\gamma + \ln Y - 1/2 + \ln 2) \tag{26}$$

$$c_2 = \{1 + (\kappa b)^{-1}(\gamma + \ln Y - 5/4 + \ln 2)\}/16 \tag{27}$$

(See eqs C.1 and C.3 in the Appendix.) Using eqs 18 and 25, we have from eqs 23 and 24

$$g(\mathbf{k}) = L\frac{G(K)^2}{G(K) + (\pi\nu bL^2/2)c_0[G(K)^2 - (5c_2/2c_0)\{3G_2(K) - G(K)\}^2]} \tag{28}$$

$$g_{\text{VH}}^{(\xi)}(\mathbf{k}) = L\frac{G_{\text{VH}}^{(\xi)}(K)}{1 - 15\pi\nu bL^2 c_2 G_{\text{VH}}^{(\xi)}(K)} \quad (\xi = \text{c or s}) \tag{29}$$

where $K \equiv kL/2$. Functions $G(K)$, $G_2(K)$, and $G_{\text{VH}}^{(\xi)}(K)$ for ξ = c and s are given in section E of the Appendix.

Equations 28 and 29 suggest that we may approximate charged rods with uncharged ones. Consider replacing c_0 and c_2 in eq 28 with the zero-charge coefficients c_0^z (≡1) and c_2^z (≡1/16). Since the second term within the bracket in the denominator of eq 28 is at most a few percent as large as the first one, this replacement does not appreciably change the $g(\mathbf{k})$ value, if the bare diameter b is simultaneously replaced with an effective diameter $b_{\text{eff},0} \equiv (c_0/c_0^z)b$. Likewise replacement of c_2 and b in eq 29 with c_2^z and $b_{\text{eff},2} \equiv (c_2/c_2^z)b$ does not affect the $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ value at all. Equations 28 and 29 after the replacement express the structure factors for the equivalent uncharged rods.

3.2. Structure Factors in the Matrix Representation. Using results in our previous papers,[4,5] we have the dynamical structure factors $g(\mathbf{k},t)$ and $g_{\text{VH}}(\mathbf{k},t)$ in the matrix representation as

$$g(\mathbf{k},t) = L\mathbf{s}^{\text{T}}\mathbf{U}\exp[-\mathbf{\Lambda}t]\mathbf{U}^{-1}\mathbf{\Phi}^{-1}\mathbf{s} \tag{30}$$

$$g_{\text{VH}}(\mathbf{k},t) = g_{\text{VH}}^{(\text{c})}(\mathbf{k},t)\cos^2(\vartheta/2) + g_{\text{VH}}^{(\text{s})}(\mathbf{k},t)\sin^2(\vartheta/2) \tag{31}$$

$$g_{\text{VH}}^{(\xi)}(\mathbf{k},t) = 2L\{\hat{\mathbf{d}}^{\text{T}}\mathbf{U}\exp[-\mathbf{\Lambda}t]\mathbf{U}^{-1}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$$
$$(m = 1 \text{ for } \xi = \text{c, and } m = 2 \text{ for } \xi = \text{s}) \tag{32}$$

where $\mathbf{s}$ and $\hat{\mathbf{d}}$ are column vectors derived from function $s_k(u)$ and $d_k^{(\xi)}(\mathbf{u})$ with ξ = c and s, respectively, superscript T of $\mathbf{s}^{\text{T}}$ and $\hat{\mathbf{d}}^{\text{T}}$ denotes transposition, $\mathbf{U}$ and $\mathbf{\Lambda}$ are respectively the eigenvector and eigenvalue matrices of matrix $\mathbf{\Omega}$ that expresses the translational–rotational diffusion of a rod under the influence of other polymers, and $\{...\}^{(m)}$ stands for the operation that extracts the mth subvector or submatrices placed between the braces. The numerical factor 2 in the right-hand side of eq 32 comes from the symmetry of the subvectors and submatrices[5] with respect to $\pm m$.

Putting $t = 0$ in eqs 30 and 32, we easily have the static structure factors

$$g(\mathbf{k}) = L\mathbf{s}^{\text{T}}\mathbf{\Phi}^{-1}\mathbf{s} \tag{33}$$

$$g_{\text{VH}}^{(\xi)}(\mathbf{k}) = 2L\{\hat{\mathbf{d}}^{\text{T}}\mathbf{\Phi}^{-1}\hat{\mathbf{d}}\}^{(m)}$$
$$(m = 1 \text{ for } \xi = \text{c, and } m = 2 \text{ for } \xi = \text{s}) \tag{34}$$

The following is noteworthy. When we discuss the angular dependence of the depolarized structure factors $g_{\text{VH}}(\mathbf{k})$ and $g_{\text{VH}}(\mathbf{k},t)$, we shall deal with only their angular components $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k},t)$, because eqs 20 and 31 for the angular average are so simple and because the angular components $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k},t)$ scale[5] with kL. Suppose one wants to compute the depolarized dynamic light scattering spectrum of a suspension of length L rods at a particular scattering angle ϑ. Equation 31 tells us that the procedure for computing is (1) to get the kL value from ϑ and L, (2) to compute the angular components $g_{\text{VH}}^{(\xi)}(\mathbf{k},t)$ with ξ = c and s for the kL, and (3) to compute an angular average of the components by using eq 31. Since steps 1 and 3 are nothing but trivial, it is sufficient for us to know the kL dependence of the angular components of the depolarized structure factors.

4. Numerical Computation

In this section, we shall numerically compute structure factors for charged rods and equivalent uncharged ones, and show that the latter structure factor is a good approximation of the former.

4.1. Parameter Values Used. Having the van der Schoot–Odijk representation and matrix one, we are now able to numerically compute both static and dynamical structure factors, which are functions of six adjustable parameters; ν, $\mathbf{k}$, L, b, κ^{-1}, and σ. Six being too many, we shall use only typical parameter values chosen in the following way:

In order to see the charge effect clearly, we assume that our polymer molecules are highly charged, for which we determine the charge density σ by the counterion condensation theory:[21,22] $\sigma = 1/L_{\text{B}}$.

A very thin polymer cannot be rigid enough. We assume the polymer diameter is larger than that of α helix: $b \gtrsim 1.4$ nm.

Our theory requires the effective axial ratio L/b_{eff} be much larger than unity.[23] Assuming $L/b = 150$ and rather arbitrarily taking 10 as the lower limit of L/b_{eff}, the lowest ionic strength, for which our theory is expected to work, would be ~1 mM.

Equation 16 requires that $Y \geq 2$, which determines the upper limit of the ionic strength to be ~100 mM. Our previous theory will serve above 100 mM of the ionic strength.

Based on these considerations, we numerically computed the structure factors of a solution of charged rods and equivalent uncharged ones of the size of fd virus particles (L = 895 nm, b = 6.8 nm) suspended in a 1 mM ionic strength solvent. We shall compare in the next two sections results of numerical computation for charged rods with those for uncharged ones and discuss whether the uncharged rod model is a valid approximation for the structure factors of charged rod suspensions.

4.2. Static Structure Factors. We shall consider in this section relative accuracies of various approximate forms of the static structure factors, each of which is classified according to whether it is for charged rods or equivalent uncharged ones and whether it is written in the matrix representation (eqs 30–34) or van der Schoot–Odijk one (eqs 28 and 29). There are four approximate forms of the structure factors: (1) $g(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ for charged rods in the matrix representation (the most exact one in the framework of our theory); (2) $g(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ for equivalent uncharged rods in the matrix representation (which we shall call $g^{(\text{z})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{z})}(\mathbf{k})$, superscript z denoting zero charge); (3) $g(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ for charged rods in the van der Schoot–Odijk representation (which we shall call $g^{(\text{SO})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{SO})}(\mathbf{k})$); (4) $g(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ for equivalent uncharged rods in the van der Schoot–Okijk representation (which we shall call $g^{(\text{zSO})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{zSO})}(\mathbf{k})$).

These structure factors are computed in the following way:

$g(\mathbf{k})$ and $g_{\text{VH}}^{(\xi)}(\mathbf{k})$ are computed by eqs 33 and 34.

$g^{(\text{z})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{z})}(\mathbf{k})$ are computed by eqs 33 and 34 after matrix $\mathbf{\Phi}$ is replaced with the one for zero-charge rods.

$$\mathbf{\Phi}^{(\text{z})} = \mathbf{E} + \pi\nu b_{\text{eff},0}L^2\mathbf{W}^{(\text{z})} \quad (\text{for } g^{(\text{z})}(\mathbf{k}))$$
$$= \mathbf{E} + \pi\nu b_{\text{eff},2}L^2\mathbf{W}^{(\text{z})} \quad (\text{for } g_{\text{VH}}^{(\xi,\text{z})}(\mathbf{k})) \tag{35}$$

where matrix $\mathbf{W}^{(\text{z})}$ is the interaction matrix for equivalent uncharged rods[4,5] given by eq D.5.

$g^{(\text{SO})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{SO})}(\mathbf{k})$ are computed by eqs 28 and 29.

$g^{(\text{zSO})}(\mathbf{k})$ and $g_{\text{VH}}^{(\xi,\text{zSO})}(\mathbf{k})$ are computed by eqs 28 and 29 after b, c_0, and c_2 in eq 28 are replaced with $b_{\text{eff},0}$, c_0^z, and c_2^z, respectively, and b and c_2 in eq 29 are replaced with $b_{\text{eff},2}$ and c_2^z, respectively. Note that there is no need to compute $g_{\text{VH}}^{(\xi,\text{zSO})}(\mathbf{k})$, which exactly agrees with $g_{\text{VH}}^{(\xi,\text{SO})}(\mathbf{k})$.

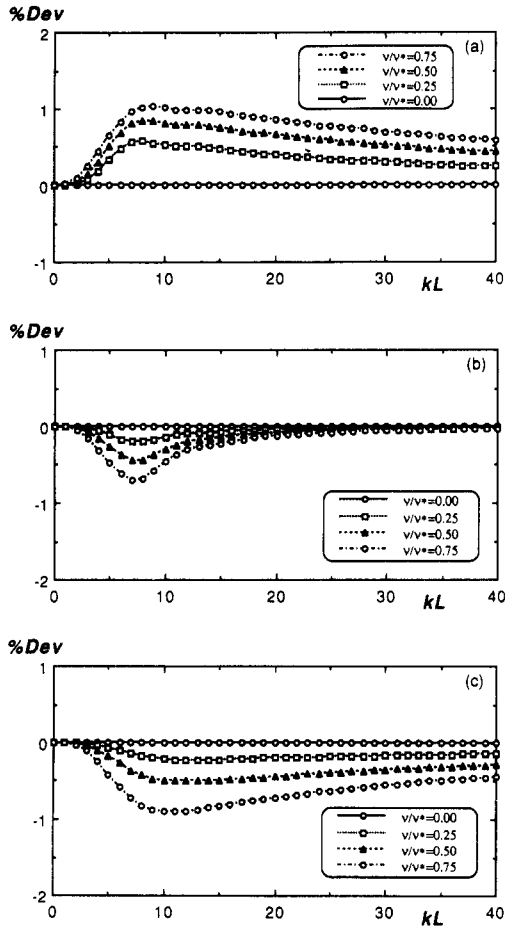

Figure 1. Percent deviation of the static structure factors for equivalent uncharged rods. Percent deviation is measured from the structure factors $g(\mathbf{k})$ and $g_{VH}^{(\xi)}(\mathbf{k})$ of charged rod suspensions. (a) $g^{(z)}(\mathbf{k})$; (b) $g_{VH}^{(c,z)}(\mathbf{k})$; (c) $g_{VH}^{(s,z)}(\mathbf{k})$.

When we numerically compare structure factors computed for equivalent uncharged rods with those for charged ones, we scale the number concentration ν of the former to keep a nondimensional product νbL^2 constant; replacement of b with $b_{eff,0}$ or $b_{eff,2}$ is accompanied by that of ν with $\nu_{eff,0}$ ($\equiv(c_0^{(z)}/c_0)\nu$) or $\nu_{eff,2}$ ($\equiv(c_2^{(z)}/c_2)\nu$). We measure the goodness of an approximation by the percent deviation of an approximate structure factor from $g(\mathbf{k})$ or $g_{VH}^{(\xi)}(\mathbf{k})$ for ξ = c or s.

Figure 1 shows percent deviation of the static structure factors $g^{(z)}(\mathbf{k})$ and $g_{VH}^{(\xi,z)}(\mathbf{k})$ of equivalent uncharged rods as functions of kL and ν. The maximum deviation occurs at around kL = 7–10, but the relative error never exceeds 1.1% for $\nu/\nu^* \leq 0.75$ where $\nu/\nu^* = \pi\nu bL^2/16 = \pi\nu_{eff,0}b_{eff,0}L^2/16 = \pi\nu_{eff,2}b_{eff,2}L^2/16$. Note the relationship[4,5] between the static structure factor $g(\mathbf{k})$ and initial decay rate $\Gamma_{\mathbf{k}}$ of the dynamical structure factor $g(\mathbf{k},t)$.

$$\Gamma_{\mathbf{k}} = \Gamma_{self}S^{-1}(\mathbf{k}) \propto g^{-1}(\mathbf{k}) \tag{36}$$

where Γ_{self} ($=\mathbf{s}^T\Theta\mathbf{s}/\mathbf{s}^T\mathbf{s}$, Θ being a matrix that describes the translational–rotational diffusion of a rod) is a weight average of the translational and rotational self-diffusivities of a rod in units of s^{-1} and $S(\mathbf{k})$ the solution structure factor defined by $S(\mathbf{k}) \equiv \mathbf{s}^T\Phi^{-1}\mathbf{s}/\mathbf{s}^T\mathbf{s}$. The positive deviation of $g^{(z)}(\mathbf{k})$ from $g(\mathbf{k})$ therefore means smaller $\Gamma_{\mathbf{k}}^{(z)}$ than $\Gamma_{\mathbf{k}}$ or slower decay of $g^{(z)}(\mathbf{k},t)$ than $g(\mathbf{k},t)$. Likewise we expect from the negative deviation of $g_{VH}^{(\xi,z)}(\mathbf{k})$ that $g_{VH}^{(z)}(\mathbf{k},t)$ would decay more quickly than $g_{VH}(\mathbf{k},t)$. It will be shown later in Figure 4 that the above expectation is the case.

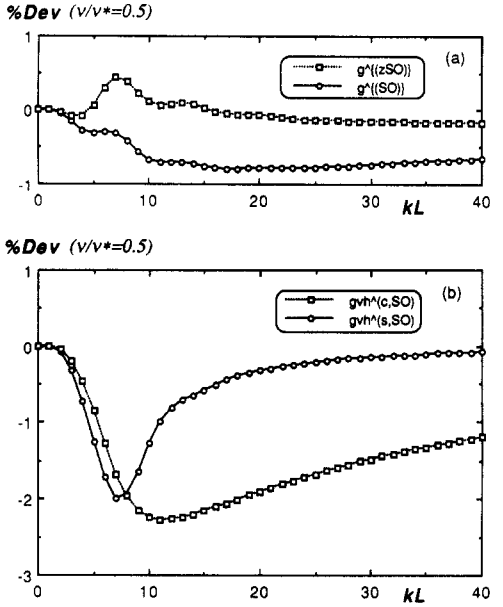

Figure 2. Percent deviation of the static structure factors in the van der Schoot–Odijk representation. (a) $g^{(SO)}(\mathbf{k})$ and $g^{(zSO)}(\mathbf{k})$. (b) $g_{VH}^{(c,SO)}(\mathbf{k})$ and $g_{VH}^{(s,SO)}(\mathbf{k})$.

Figure 2 shows that the van der Schoot–Odijk representation is a good approximation of the static structure factors within a few percent of relative error. Figure 2a shows the percent deviation of $g^{(SO)}(\mathbf{k})$ and $g^{(zSO)}(\mathbf{k})$ at $\nu/\nu^* = 0.5$, and Figure 2b shows that of $g_{VH}^{(\xi,SO)}(\mathbf{k})$ with ξ = c and s. Considering its simplicity, van der Schoot and Odijk's method works quite well for the static structure factors.

4.3. Correlation Function Profiles. Using the dynamical structure factors written in the matrix form (eqs 30 and 31 with eq D.2 or D.5), we compared the correlation function profiles of suspensions of charged rods and equivalent uncharged ones of the size of fd virus. Parts a and b of Figure 3 respectively show the normalized profiles and percent deviations of $g^{(z)}(\mathbf{k},t)$ and $g_{VH}^{(z)}(\mathbf{k},t)$ at $kL = 10$ for $\nu/\nu^* = 0.6$. Positive deviation shown in Figure 3a means slightly slower decay of $g^{(z)}(\mathbf{k},t)$ than $g(\mathbf{k},t)$ and negative deviation in Figure 3b quicker decay of $g_{VH}^{(z)}(\mathbf{k},t)$ than $g_{VH}(\mathbf{k},t)$, which conforms with the results shown in Figure 1. The relative error shown in the figures linearly increases with the delay time t. Except for the change in the initial decay rate, nothing anomalous happens in the correlation function profiles of equivalent uncharged rods. A note previously made[4,5] is given here again; our theory does not predict the appearance of a slow tail in the correlation function, which has been experimentally observed.

4.4. Solution Structure Factors. Let $S(\mathbf{k})$ and $S_{VH}^{(\xi)}(\mathbf{k})$ be the solution structure factors defined by

$$S(\mathbf{k}) = \mathbf{s}^T\Phi^{-1}\mathbf{s}/\mathbf{s}^T\mathbf{s} \tag{37}$$

$$S_{VH}^{(\xi)}(\mathbf{k}) = \{\hat{\mathbf{d}}^T\Phi^{-1}\hat{\mathbf{d}}/\hat{\mathbf{d}}^T\hat{\mathbf{d}}\}^{(m)}$$

(m = 1 for ξ = c, m = 2 for ξ = s) (38)

Figure 4 shows $S(\mathbf{k})$ and $S_{VH}^{(\xi)}(\mathbf{k})$ for $\kappa b = 0.25$ and $\nu/\nu^* = 0.5$. Experiments on TMV and fd virus gave oscillations in $S(\mathbf{k})$ in salt-free solutions,[24,25] but Figure 4 does not show any oscillations. The cause of this discrepancy is in the value of the apparent axial ratio L/b_{eff}; in salt-free

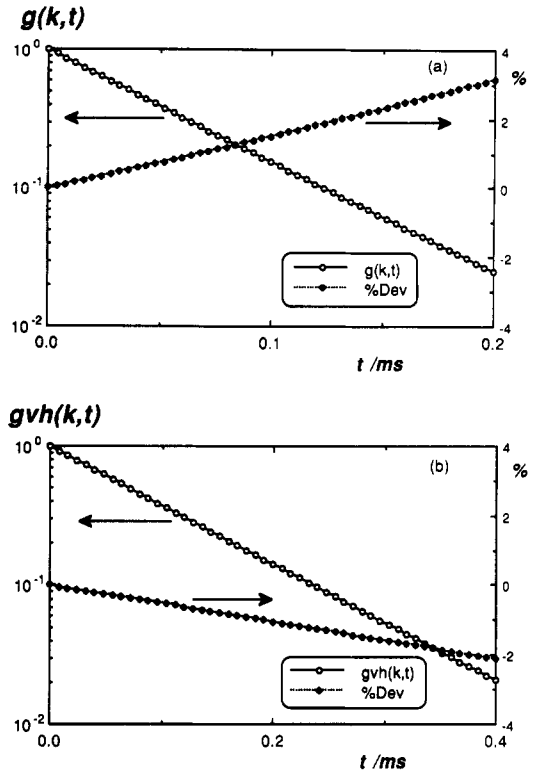

Figure 3. Normalized profiles and percent deviation of the dynamical structure factors at $kL = 10$ and $\nu/\nu^* = 0.5$. The size of the rod is the same as that of fd virus. The diffusion coefficient values were taken from ref 31. (a) $g^{(z)}(\mathbf{k},t)/g^{(z)}(\mathbf{k},0)$; (b) $g^{(z)}_{VH}(\mathbf{k},t)/g^{(z)}_{VH}(\mathbf{k},0)$.

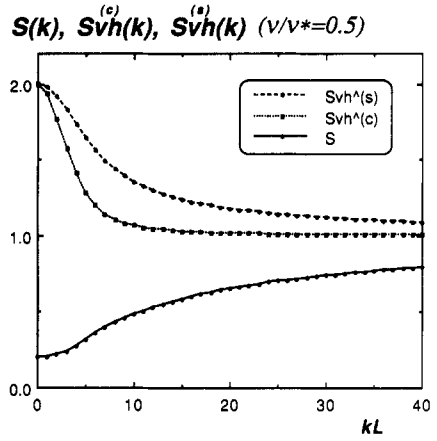

Figure 4. Solution structure factors $S(\mathbf{k})$ and $S^{(\xi)}_{VH}(\mathbf{k})$ of a charged rod suspension at $\nu/\nu^* = 0.5$.

solutions the effective diameter of the virus particles becomes so large that we can no longer consider them very slender rods, for which our theory is expected to work.

5. Discussion

A comparison of structure factors for charged rods and equivalent uncharged ones revealed that the both structure factors agree with each other within a few percent of relative error in the entire range of kL and ν and the ionic strength down to 1 mM. This good agreement, however, was obtained by using two effective diameters, $b_{eff,0}$ and $b_{eff,2}$, for the isotropic and VH-depolarized scattering, respectively. It should be noted that $b_{eff,2} \leq b_{eff,0}$, where the equality holds only in the zero-charge limit, but what does this inequality mean?

While the effective diameter $b_{eff,0}$, being the same as the one for the osmotic second virial coefficient A_2 of charged rod suspensions,[13] characterizes the excluded volume of a charged rod, it is $b_{eff,2}$ that gives the strength of the nematic interaction among rods.[23] The inequality $b_{eff,2} \leq b_{eff,0}$ means that nematic interaction among charged rods is weaker than expected from the increase of the excluded volume. The characteristic concentration ν^* for the isotropic–nematic phase transition of an uncharged hard-rod suspension is determined by a relationship $\nu^* \sim 1/bL^2$, and it is $b_{eff,2}$ that should be used in determining ν^* of charged rod suspensions. Use of $b_{eff,2}$ in $\nu^* \sim 1/bL^2$ gives higher ν^* values than using $b_{eff,0}$. The inequality therefore stands for the tendency that the electrostatic repulsion hinders parallel orientation of charged rods. Since the depolarized scattering sensitively detects fluctuation in the rod orientation, it is quite natural that $b_{eff,2}$ appears in the depolarized structure factors $g^{(z)}_{VH}(\mathbf{k})$ and $g^{(z)}_{VH}(\mathbf{k},t)$ of equivalent uncharged rods.

Though our theory does not take into consideration the coupling of small ion and macro ion fluctuations,[26] it at least includes the tendency that two charged rods avoid the parallel orientation. Knowing well the very simple nature of our theory, we shall draw three conclusions here: The first one is that we may approximate a charged rod with an equivalent uncharged rod, the effective diameter of which is $b_{eff,0}$ for the isotropic scattering and $b_{eff,2}$ for the depolarized one. The second is that, considering its simplicity, the accuracy of the static structure factors written in the van der Schoot–Odijk representation is very good within a few percent of relative error. The last is that our theory is applicable only to slender rods, the effective axial ratio L/b_{eff} of which is much larger than unity.

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Appendix

A. Computation of $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$. We shall compute in this Appendix the spatial Fourier transform of $W(\mathbf{r}-\mathbf{r}',\mathbf{u},\mathbf{u}')$. We obtain $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$ by computing the Fourier transform of each term in the right-hand side (rhs) of eq 10.

$$W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') = \mathcal{F}[W^{H}] + \sum_{n=1}^{\infty}\frac{(-1)^n\mathcal{F}[(w^{e,H})^n]}{n!} - \sum_{n=1}^{\infty}\frac{(-1)^n\mathcal{F}[(w^{e,E})^n]}{n!} + \mathcal{F}[w^e] - \mathcal{F}[w^{e,E}] \quad (A.1)$$

where $\mathcal{F}[...]$ stands for the spatial Fourier transform.

We already have an explicit form of $\mathcal{F}[W^H]$ as[3]

$$\mathcal{F}[W^{H}] = 2bL^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}')|\mathbf{u}\times\mathbf{u}'| \quad (A.2)$$

where $s_{\mathbf{k}}(\mathbf{u})$ is defined by

$$s_{\mathbf{k}}(\mathbf{u}) = \frac{1}{L}\int_{-L/2}^{L/2}\exp(i\mathbf{k}\cdot\mathbf{u}s)\,ds \quad (A.3)$$

It is very easy to compute the fourth term in the rhs of eq A.1. Using eqs 3 and 4, we have $\mathcal{F}[w^e]$ as

$$\mathcal{F}[w^e] = \int_{-L/2}^{L/2}ds\int_{-L/2}^{L/2}ds'\exp[-i\mathbf{k}\cdot(\mathbf{u}s+\mathbf{u}'s')]\int d\mathbf{r}\times \exp(i\mathbf{k}\cdot\mathbf{r})U^e(r)$$

$$= 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}')|\mathbf{u}\times\mathbf{u}'|\frac{\kappa}{\kappa^2+k^2}\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|} \quad (A.4)$$

The second and third terms (the infinite sums) in the rhs of eq A.1 can be computed as follows. Using eq 12, we compute $\mathcal{F}[(w^{e,H})^n]$ as (see details in section B)

$$\mathcal{F}[(w^{e,H})^n] = 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \times \frac{n\kappa - e^{-n\kappa b}[n\kappa - (\mathbf{k}\cdot\mathbf{v})^2 b]}{(n\kappa)^2 + (\mathbf{k}\cdot\mathbf{v})^2} \left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right)^n \quad (A.5)$$

where $\mathbf{v}$ is a unit vector perpendicular to both $\mathbf{u}$ and $\mathbf{u}'$. Replacing b with $2r^E$ and assuming $\exp(-2\kappa r^E) \ll 1$, we have an approximate form of $\mathcal{F}[(w^{e,E})^n]$ as

$$\mathcal{F}[(w^{e,E})^n] \simeq 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \frac{n\kappa}{(n\kappa)^2 + (\mathbf{k}\cdot\mathbf{v})^2} \times \left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right)^n \quad (A.6)$$

It should be noted that, except for the first few terms in the infinite sums in the rhs of eq A.1, we may always neglect $(\mathbf{k}\cdot\mathbf{v})^2$. It is evident that we may do so in the forward scattering ($k \simeq 0$ nm^{-1}), but we may neglect them even in the backward scattering ($k \simeq 3.4 \times 10^{-2}$ nm^{-1} for the refractive index $n = 1.33$ and the wavelength $\lambda = 488$ nm). Let us compare typical values of κ and b^{-1} with the maximum length of the scattering vector $\mathbf{k}$. As eq 6 shows, the κ value at room temperature in water ranges from 3×10^0 to 3×10^{-2} nm^{-1} when the ionic strength decreases from 10^0 to 10^{-4} mol. If we take the structural diameter of DNA as a typical b value, we have the b^{-1} value as 0.4 nm^{-1}. The $(\mathbf{k}\cdot\mathbf{v})^2$ term in eqs A.5 and A.6 is therefore negligible for $n \geq 10$.

Neglecting the $(\mathbf{k}\cdot\mathbf{v})^2$ term,[27] we can easily compute the infinite sums in the rhs of eq A.1:

$$\sum_{n=1}^{\infty} \frac{(-1)^n \mathcal{F}[(w^{e,H})^n]}{n!} \simeq 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \times \kappa^{-1} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{1 - e^{-n\kappa b}}{n} \left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right)^n = 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \times \kappa^{-1}\left[-E_1\left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right) + E_1\left(\frac{Y}{|\mathbf{u}\times\mathbf{u}'|}\right) - \kappa b\right] \quad (A.7)$$

$$\sum_{n=1}^{\infty} \frac{(-1)^n \mathcal{F}[(w^{e,E})^n]}{n!} \simeq 2L^2 s_{\mathbf{k}}(\mathbf{u}) s_{\mathbf{k}}(\mathbf{u}') |\mathbf{u}\times\mathbf{u}'| \times \kappa^{-1}\left[-E_1\left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right) - \gamma - \ln\left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right)\right] \quad (A.8)$$

where $E_1(x)$ is the exponential integral defined by[28]

$$E_1(x) = \int_x^{\infty} \frac{e^{-t}}{t}\, dt = -\gamma - \ln x - \sum_{n=1}^{\infty} \frac{(-x)^n}{n!n} \quad (A.9)$$

with Euler's constant $\gamma = 0.577\,21\ldots$ Using eqs A.2, A.4, and A.7–9 and neglecting the k terms, we finally have eq 14 for $W_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$.

B. Computation of $\mathcal{F}[(w^{e,H})^n]$. In order to compute $\mathcal{F}[(w^{e,H})^n]$ we use the oblique coordinate (ξ,η,ζ) introduced by Straley:[3,29]

$$\mathbf{r} = \mathbf{u}\xi + \mathbf{u}'\eta + \mathbf{v}\zeta \quad (B.1)$$

where vector $\mathbf{v}$ is a unit vector perpendicular to both $\mathbf{u}$ and $\mathbf{u}'$

$$\mathbf{v} = \frac{\mathbf{u}\times\mathbf{u}'}{|\mathbf{u}\times\mathbf{u}'|} \quad (B.2)$$

In this coordinate system, the two rods overlap when $|\xi| < L/2$, $|\eta| < L/2$, and $|\zeta| < b$. The volume element $d\mathbf{r}$ is expressed as

$$d\mathbf{r} = |\mathbf{u}\times\mathbf{u}'|\, d\xi\, d\eta\, d\zeta \quad (B.3)$$

Using eq 12 and Straley's oblique coordinate system, we write $\mathcal{F}[w^{e,H}]$ as

$$\mathcal{F}[(w^{e,H})^n] = \int_{-L/2}^{L/2} d\xi \int_{-L/2}^{L/2} d\eta \int_{-b}^{b} d\zeta \exp[i\mathbf{k}\cdot(\mathbf{u}\xi + \mathbf{u}'\eta + \mathbf{v}\zeta)] |\mathbf{u}\times\mathbf{u}'| \left(\frac{Ye^{\kappa b}}{|\mathbf{u}\times\mathbf{u}'|}\right) \exp(-n\kappa|\zeta|) \quad (B.4)$$

Integration of eq B.4 and use of $kb \ll 1$ give eq A.5.

C. Expansion of $|\mathbf{u}\times\mathbf{u}'|$ and $|\mathbf{u}\times\mathbf{u}'| \ln (1/|\mathbf{u}\times\mathbf{u}'|)$ with Spherical Harmonics. Expansion of $|\mathbf{u}\times\mathbf{u}'|$ is already given in ref 4.

$$|\mathbf{u}\times\mathbf{u}'| = \frac{\pi}{4} - 2\pi^2 \sum_{l=1}^{\infty} a_l \sum_m Y^*_{lm}(\mathbf{u}') Y_{lm}(\mathbf{u}) \quad (C.1)$$

$$a_l = 0 \quad \text{(for odd } l\text{)}$$

$$= \frac{l-1}{l+2}\left\{\frac{(l-3)!!}{l!!}\right\}^2 \quad \text{(for even } l\text{)} \quad (C.2)$$

Using the Legendre polynomial $P_l(\mathbf{u}\cdot\mathbf{u}')$, we expand $|\mathbf{u}\times\mathbf{u}'| \ln (1/|\mathbf{u}\times\mathbf{u}'|)$ as[32]

$$(1-x^2)^{1/2} \ln (1/(1-x^2)^{1/2}) = \frac{\pi}{4} b_0 - 2\pi^2 \sum_{l=1}^{\infty} \frac{2l+1}{4\pi} b_l P_l(x) = \frac{\pi}{4} b_0 - 2\pi^2 \sum_{l=1}^{\infty} b_l \sum_m Y^*_{lm}(\mathbf{u}') Y_{lm}(\mathbf{u}) \quad (C.3)$$

where we used the relationship $P_l(\mathbf{u}\cdot\mathbf{u}') = [4\pi/(2l+1)]\sum_m Y_{lm}(\mathbf{u}) Y^*_{lm}(\mathbf{u}')$. The expansion coefficient b_l is given by

$$b_0 = \ln 2 - 1/2 \quad (C.4)$$

$$b_l = 0 \quad \text{(for odd } l\text{)}$$

$$= \left\{\frac{(l-1)!!}{l!!}\right\}^2 \frac{\ln 2 - (l^2+l+4)/8}{(l-1)(l+2)} + \sum_{\substack{r=0 \\ \text{even}}}^{l-4} \frac{4}{(l-r-2)(l-r)(l-r+2)} \frac{(r-1)!!(2l-r-1)!!}{r!!(2l-r)!!}$$

(for even l) (C.5)

where the summation with respect to r is set to zero unless $l \geq 4$ and we have used the formulas

$$P_{2n}(\cos\theta) = 2\sum_{r=0}^{n-1} \frac{(2r-1)!!(4n-2r-1)!!}{(2r)!!(4n-2r)!!} \cos 2(n-r)\theta + \left[\frac{(2n-1)!!}{(2n)!!}\right]^2 \quad (C.6)$$

$$\int_0^{\pi} \ln (\sin\theta)\, d\theta = -\pi \ln 2 \quad (C.7)$$

$$\int_0^{\pi} \cos 2n\theta \ln (\sin\theta)\, d\theta = -\frac{\pi}{2n} \quad (C.8)$$

D. Matrix Representation of $\Phi_{\mathbf{k}}(\mathbf{u},\mathbf{u}')$. Let W be an operator

$$W f_{\mathbf{k}}(\mathbf{u}) = (1/4\pi^2 bL^2) \int d\mathbf{u}'\, W_{\mathbf{k}}(\mathbf{u},\mathbf{u}') f_{\mathbf{k}}(\mathbf{u}') \quad (D.1)$$

We have from operator W matrix $\mathbf{W}$, the $(lm,l'm')$th element of which we compute by $\langle lm|\mathbf{W}|l'm'\rangle = \int d\mathbf{u}\, Y^*_{lm}(\mathbf{u}) W Y_{l'm'}(\mathbf{u})$. Using eqs C.1 and C.3, we have $\mathbf{W}$ as

$$\mathbf{W} = \left(1 + \frac{\gamma + \ln Y}{\kappa b}\right)\left(\frac{1}{2}\mathbf{s}\mathbf{s}^{\mathrm{T}} - \mathbf{P}\mathbf{Q}\mathbf{P}\right) + \frac{1}{\kappa b}\left(\frac{b_0}{2}\mathbf{s}\mathbf{s}^{\mathrm{T}} - \mathbf{P}\mathbf{Q}^{\mathrm{E}}\mathbf{P}\right) \quad \text{(D.2)}$$

where $\mathbf{s}$ is a column vector, $\mathbf{P}$ a symmetrical matrix, and $\mathbf{Q}$ a diagonal matrix. Explicit forms for $\mathbf{s}$,$\mathbf{P}$, and $\mathbf{Q}$ are given in refs 4 and 5. $\mathbf{Q}^{\mathrm{E}}$ is a diagonal matrix, the $(lm,l'm')$-th element of which is given by

$$\langle lm|\mathbf{Q}^{\mathrm{E}}|l'm'\rangle = b_l\delta_{ll'}\delta_{mm'} \quad \text{(D.3)}$$

We use eq 15 to compute matrix $\mathbf{W}$ for the low charge limit:

$$\mathbf{W} = \left(\frac{1}{2} + \frac{2}{\pi}\frac{Y}{\kappa b}\right)\mathbf{s}\mathbf{s}^{\mathrm{T}} - \mathbf{P}\mathbf{Q}\mathbf{P} \quad \text{(D.4)}$$

It is evident from eqs D.2 and D.4 that the interaction matrix $\mathbf{W}$ for charged rod systems reduces to the zero-charge one in the limit $\kappa b \to \infty$ or $Y \to 0$

$$\mathbf{W}^{(z)} = \frac{1}{2}\mathbf{s}\mathbf{s}^{\mathrm{T}} - \mathbf{P}\mathbf{Q}\mathbf{P} \quad \text{(D.5)}$$

Matrix Φ that corresponds to operator $\Phi_{\mathbf{k}}$ is simply given by[4,5]

$$\Phi = \mathbf{E} + \pi\nu bL^2\mathbf{W} \quad \text{(D.6)}$$

where $\mathbf{E}$ is the identity matrix.

E. $\langle s_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}s^*_{\mathbf{k}}(\mathbf{u})\rangle$ and $\langle d^{(\xi)}_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}d^{(\xi)*}_{\mathbf{k}}(\mathbf{u})\rangle$. We shall give in this section explicit forms of eqs 28 and 29.

We have from eqs 18 and 25

$$\langle s_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}s^*_{\mathbf{k}}(\mathbf{u})\rangle = G(K) + \frac{\pi\nu bL^2}{2}\left[c_0G(K)^2 - \frac{5}{2}c_2\{3G_2(K) - G(K)\}^2\right] \quad \text{(E.1)}$$

$$\langle d^{(\xi)}_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}d^{(\xi)*}_{\mathbf{k}}(\mathbf{u})\rangle = G^{(\xi)}_{\mathrm{VH}}(K) - 15\pi\nu bL^2c_2\{G^{(\xi)}_{\mathrm{VH}}(K)\}^2 \quad (\xi = \mathrm{c\ or\ s}) \quad \text{(E.2)}$$

where $K \equiv kL/2$ and functions $G(K)$ and $G^{(\xi)}_{\mathrm{VH}}(K)$ are defined as

$$G(K) \equiv \langle|s_{\mathbf{k}}(\mathbf{u})|^2\rangle = \frac{\mathrm{Si}\,(2K)}{K} - \left(\frac{\sin K}{K}\right)^2 \quad \text{(E.3)}$$

$$G^{(\xi)}_{\mathrm{VH}}(K) \equiv \langle|d^{(\xi)}_{\mathbf{k}}(\mathbf{u})|^2\rangle = (1/2)[G_2(K) - G_4(K)] \quad (\text{for } \xi = \mathrm{c})$$
$$= (1/8)[G(K) - 2G_2(K) + G_4(K)] \quad (\text{for } \xi = \mathrm{s}) \quad \text{(E.4)}$$

where Si (x) is the sine integral and functions $G_2(K)$ and $G_4(K)$ in eqs E.1 and E.4 are as follows:

$$G_2(K) = \frac{1}{K^3}\left[-\frac{\sin 2K}{4} + \frac{K}{2}\right] \quad \text{(E.5)}$$

$$G_4(K) = \frac{1}{K^5}\left[\frac{K^3}{6} - \frac{2K^2 - 1}{8}\sin 2K - \frac{K}{4}\cos 2K\right] \quad \text{(E.6)}$$

References and Notes

(1) Hoffmann, H.; Kalus, J.; Thurn, H.; Ibel, K. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 1120.
(2) Drifford, M.; Dalbiez, J. P. *J. Phys. Chem.* **1984**, *88*, 5368.
(3) Doi, M.; Shimada, T.; Okano, K. *J. Chem. Phys.* **1988**, *88*, 4070.
(4) Maeda, T. *Macromolecules* **1989**, *22*, 1881.
(5) Maeda, T. *Macromolecules* **1990**, *23*, 1464.
(6) Benmouna, M.; Weill, G.; Renoit, H.; Akcasu, A. Z. *J. Phys. (Paris)* **1982**, *43*, 1679.
(7) Schneider, J.; Hess, W.; Klein, R. *J. Phys. A* **1985**, *18*, 1221.
(8) Stigter, D. *Biopolymers* **1977**, *16*, 1435.
(9) Schneider, J.; Hess, W.; Klein, R. *Macromolecules* **1986**, *19*, 1729.
(10) Schneider, J.; Karrer, D.; Dhont, J. K. G.; Klein, R. *J. Chem. Phys.* **1987**, *87*, 3008.
(11) Skolnick, J.; Grimmelmann, E. K. *Macromolecules* **1980**, *13*, 335.
(12) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
(13) Nicolai, T.; Mandel, M. *Macromolecules* **1989**, *22*, 438.
(14) It is assumed in eqs 1–3 that the probability of three-body interaction is negligible. Equations 3 and 4 also include two implicit assumptions that (1) the ion clouds surrounding a charged rod are always in their equilibrium distribution even when the rod moves around and (2) electrolyte friction due to the small ions is to be included in the rod self-diffusivities.
(15) The end effect on the electrostatic potential extends to a distance[13] of about $0.5\kappa^{-1}$, but, for simplicity, we put the cylinder length L^{E} of the extended zone equal to L.
(16) Stroobants, A.; Lekkerkerker, H. N. W.; Odijk, T. *Macromolecules* **1986**, *19*, 2232.
(17) Let L_{ov} be the overlap length between two rods placed parallel or nearly parallel with each other. For small angles $|\mathbf{u} \times \mathbf{u}'| < b/L_{\mathrm{ov}}$, the factor $1/|\mathbf{u} \times \mathbf{u}'|$ must be replaced by a smaller number of the order L_{ov}/b. See ref 12.
(18) van der Schoot; Odijk, T. *Macromolecules* **1990**, *23*, 4181.
(19) Since matrix Φ is diagonal[5] with respect to m, it is very easy to prove that $\langle d^{(\xi)}_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}{}^{-1}d^{(\xi')*}_{\mathbf{k}}(\mathbf{u})\rangle = 0$ unless $\xi = \xi'$. It follows that $\langle d_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}{}^{-1}d^*_{\mathbf{k}}(\mathbf{u})\rangle = \langle d^{(\mathrm{c})}_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}{}^{-1}d^{(\mathrm{c})*}_{\mathbf{k}}(\mathbf{u})\rangle \cos^2(\vartheta/2) + \langle d^{(\mathrm{s})}_{\mathbf{k}}(\mathbf{u})\Phi_{\mathbf{k}}{}^{-1}d^{(\mathrm{s})*}_{\mathbf{k}}(\mathbf{u})\rangle \sin^2(\vartheta/2)$
(20) Tait, J. H. *Neutron Transport Theory*; Longmans: London, 1964.
(21) Oosawa, F. *J. Polym. Sci.* **1957**, *23*, 421.
(22) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(23) Shimada, T.; Doi, M.; Okano, K. *J. Chem. Phys.* **1988**, *88*, 2815.
(24) Maier, E. E.; Schulz, S. F.; Weber, R. *Macromolecules* **1988**, *21*, 1544.
(25) Schulz, S. F.; Maier, E. E.; Weber, R. *J. Chem. Phys.* **1989**, *90*, 7.
(26) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; John Wiley & Sons: New York, 1976.
(27) Since $w^{\mathrm{e,E}}$ should agree with w^{e} for $r^{\mathrm{E}} \to \infty$ and since the relationship $\mathcal{F}[w^{\mathrm{e,E}}] = \mathcal{F}[w^{\mathrm{e}}]$ holds after neglecting the k^2 and $(\mathbf{k}\cdot\mathbf{v})^2$ terms in eqs A.4 and A.6, we expect the infintely long line-charge approximation for $w^{\mathrm{e,E}}$ is not so bad for forward scattering, in which the k^2 and $(\mathbf{k}\cdot\mathbf{v})^2$ terms are negligible.
(28) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover Publications: New York, 1978.
(29) Straley, J. P. *Phys. Rev. A* **1973**, *8*, 2181.
(30) In ref 7, the direct correlation function (=$-W$ in our case) was replaced in the spirit of the linear Debye–Hückel theory by $-w^{\mathrm{e}}$, and the Fourier transform of w^{e} was computed. In the present paper, however, we did not adopt this approximation because of the presence of the hard-rod term w^{h} in W and explicitly computed the Fourier transform of W. See the consequence of this in the difference between eq 22 of ref 7 and eq 28 of this paper.
(31) Maeda, T.; Fujime, S. *Macromolecules* **1985**, *18*, 2430.
(32) Vroege,G. J.; Odijk, T. *J. Chem. Phys.* **1987**, *87*, 4223.