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# The static structure factor of a dilute system of charged rods in solution

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**Abstract.** For a solution of charged rods the static structure factor is derived in a weak-coupling expression. The interaction between the rods is assumed to be a superposition of screened Coulomb interactions between point charges distributed along the rod. Screening arises from the counter ions as well as from salt in the solvent. We treat the case of an isotropic solution as well as the nematically ordered state.

## 1. Introduction

The static structure factor of charged spherical macroparticles in solution as measured by light or neutron scattering is well understood according to the work of Hayter and Penfold (1981) and of Hansen and Hayter (1982). The situation is rather different for charged rod-like macroparticles. Here even the experimental situation is scarce. A detailed experimental study of the static structure factor and of related functions like the radial distribution function and the effective potential has been performed (Hoffmann *et al* 1983) on systems of rod-like micelles for different concentrations. The interpretation of these results is intricate to some extent because the length of the rod-like micelles is not fixed, but it may change with concentration in an unknown way. In systems of macroparticles the intensity of scattered light or neutrons depends on the form factor and structure factor, the latter being caused by interparticle correlations. For spherical particles which are much smaller than the wavelength of light or neutrons the form factor can be expressed by  $F(k=0)=1$ . Because of the large length of the rods this approximation is not allowed for systems of rods. Usually, biologists or physical chemists are more interested in the form of the particles, considering the appearance of the structure factor in the scattering signal as a mere nuisance, whereas physicists take the opposite point of view. Therefore it is desirable to obtain additional information on both quantities, either from separate experiments or by theoretical calculations.

So far there is no theory for the structure factor of rod-like systems comparable in standard to the above mentioned procedures for interacting spherical particles. The theory presented in this paper can only be considered as a first step in this direction. Similar to the theories employed for charged spherical particles, our starting point is the Ornstein-Zernike equation.

The latter equation is, however, much more complicated for rod-like particles, since the correlation functions also depend on the direction of two interacting rods in addition to the distance vector of their centres of gravity. So far we have only succeeded in

solving this equation in a weak-coupling limit, which is equivalent to the Debye-Hückel approximation for point-like particles. This approximation may be appropriate for weakly interacting systems which are sufficiently dilute, so that the mean distance between the centres of gravity of two rods is still larger or of the order of the length of the rods.

Recently a paper on the same subject has appeared by Benmouna and coworkers (Benmouna *et al* 1982) and will be discussed in § 5 of this paper. However, we want to stress here that their theory applies to a totally different concentration regime. This arises from the fact that these authors use an expression for the second virial coefficient of a system of infinitely long rods (Zimm 1946, Onsager 1949, Stigter 1977). Applied to systems of rods with finite length this can be only a sound approximation as long as the mean distance between the centres of gravity is much smaller than the length of the rods, although still much larger than their diameter.

## 2. The model

A system of  $N$  rigid rods of length  $L$  and vanishing diameter  $d$  is considered. The centres of gravity are situated at  $\mathbf{r}_j, j = 1, \dots, N$  and the  $j$ th rod has an orientation denoted by the unit vector  $\mathbf{u}_j$ .

Since we are interested in dilute systems of charged rods with  $L \gg d$ , where the concentrations are about  $L^{-3}$  or even smaller, we can neglect hard-core effects, which become important in concentration regimes of  $(dL^2)^{-1}$ . The total charge  $Q$  on each rod is assumed to be homogeneously distributed, and interactions between rods will be taken as a screened Coulomb interaction.

As an intermediate step each rod is represented by  $n+1$  point particles carrying the charge  $Q/(n+1)$ , which are equally distributed along the rod axis of length  $L$ . Later on, the number of point particles will be taken to infinity. The position of point particle  $\alpha$  of the  $j$ th rod is

$$\mathbf{r}_j^\alpha = \mathbf{r}_j + \alpha(L/n)\mathbf{u}_j, \quad -\frac{1}{2}n \leq \alpha \leq \frac{1}{2}n. \quad (1)$$

The concentration of particles is

$$c(\mathbf{r}) = \sum_{j=1}^N \frac{1}{n+1} \sum_{\alpha=-n/2}^{+n/2} \delta(\mathbf{r} - \mathbf{r}_j^\alpha). \quad (2)$$

Its Fourier components in the limit  $n \rightarrow \infty$  are

$$c(\mathbf{k}) = \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j) j_0(L\mathbf{k} \cdot \mathbf{u}_j/2) \quad (3)$$

where  $j_0(x) = (\sin x)/x$ .

The static structure factor is defined as

$$\begin{aligned} S(\mathbf{k}) &= N^{-1} \int d\Gamma c(\mathbf{k})c(-\mathbf{k}) \exp(-\beta U) \bigg/ \int d\Gamma \exp(-\beta U) \\ &\equiv N^{-1} \langle c(\mathbf{k})c(-\mathbf{k}) \rangle. \end{aligned} \quad (4)$$

Here,  $U$  is the interaction potential,  $\beta = (k_B T)^{-1}$  and the integrations are over the configuration space.

Without interactions ( $U = 0$ ) one obtains from (4) and (3) the form factor of an infinitely thin rod (Pecora 1968)

$$S_0(\mathbf{k}) \equiv F(k) = (2/kL) \int_0^{kL} dx j_0(x) - [(2/kL) \sin(kL/2)]^2. \quad (5)$$

The interaction potential for charged rods of infinite length is derived by Brenner and Parsegian (1974). However, we are interested in concentration regimes of the order of  $L^{-3}$  or smaller. Therefore, the distance between neighbouring rods is about  $L$  or even larger. In this case we have to consider rods with finite length. We therefore assume the interaction potential  $U(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$  of two charged rods, whose centres of gravity have the vector distance  $\mathbf{r}$  and which have orientations  $\mathbf{u}_1$  and  $\mathbf{u}_2$ , respectively, to arise from a screened Coulomb interaction between each of the  $n + 1$  point particles of charge  $Q/(n + 1)$  on the first rod with each of the  $n + 1$  point charges on the second one:

$$U(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \sum_{\alpha, \beta = -n/2}^{+n/2} \frac{1}{4\pi\epsilon\epsilon_0} \left( \frac{Q}{n+1} \right)^2 \frac{\exp(-q_0 |\mathbf{r}_1^\alpha - \mathbf{r}_2^\beta|)}{|\mathbf{r}_1^\alpha - \mathbf{r}_2^\beta|}. \quad (6)$$

Here,  $\epsilon$  is the dielectric constant of the solvent and

$$q_0^2 = (\beta / \epsilon\epsilon_0) \sum_{\sigma} \rho_{\sigma} q_{\sigma}^2 \quad (7)$$

is the Debye-Hückel screening parameter. The charge of a counter-ion of species  $\sigma$  is denoted by  $q_{\sigma}$  and their concentration by  $\rho_{\sigma}$ . The ansatz (6) assumes a spherical double layer around each point charge on the rod. This is obviously not correct, because the other point charges along the rod axis will disturb the counter-ion cloud around the charge under consideration. However, the ansatz is exact for the two limiting cases  $L \rightarrow 0$  and  $q_0 \rightarrow 0$ ; therefore we assume that (6) will approximate the real interaction potential in a reasonable manner for weakly screened systems.

Representing the screened Coulomb factor in (6) by its Fourier integral, one can perform the limit  $n \rightarrow \infty$  and obtain

$$U(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \frac{1}{(2\pi)^3} \int d^3k \exp(i\mathbf{k} \cdot \mathbf{r}) j_0(Lk u_1/2) j_0(Lk u_2/2) \frac{1}{\epsilon\epsilon_0} \frac{Q^2}{q_0^2 + k^2}. \quad (8)$$

### 3. Static structure factor in Debye-Hückel approximation

The aim is to establish the equivalent for rod-like particles of the well-known relation between the static structure factor and the radial distribution function for isotropic particles. Therefore the Ornstein-Zernike equation is written as (Stell 1977)

$$h(\mathbf{r}_{12}, \Omega_1, \Omega_2) = C(\mathbf{r}_{12}, \Omega_1, \Omega_2) + (\rho/4\pi) \int d^3r_3 d\Omega_3 C(\mathbf{r}_{13}, \Omega_1, \Omega_3) h(\mathbf{r}_{32}, \Omega_3, \Omega_2). \quad (9)$$

Here,  $h$  denotes the total correlation function and  $C$  is the direct correlation function. Both functions depend on the vector distance  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  of the centres of gravity and on the orientations  $\mathbf{u}_i$  and  $\mathbf{u}_j$  of particles  $i$  and  $j$ . Instead of  $\mathbf{u}_i$  we can also denote the orientation by the polar angles  $\Omega_i \equiv (\theta_i, \varphi_i)$ . The correlation functions in (9) are Fourier

transformed and developed in terms of spherical harmonics as

$$h(\mathbf{r}, \Omega_1, \Omega_2) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{r}) \sum_{l,l'=0}^{\infty} \sum_{m=-l}^l \sum_{m'=-l'}^{l'} Y_{lm}^*(\Omega_1) Y_{l'm'}(\Omega_2) h_{lm,l'm'}(\mathbf{k}) \tag{10}$$

where

$$h_{lm,l'm'}(\mathbf{k}) = \int d^3r \, d\Omega_1 \, d\Omega_2 \exp(i\mathbf{k} \cdot \mathbf{r}) Y_{lm}(\Omega_1) Y_{l'm'}(\Omega_2) h(\mathbf{r}, \Omega_1, \Omega_2) \tag{11}$$

and similarly for  $C(\mathbf{r}, \Omega_1, \Omega_2)$ . The oz equation (9) can then be rewritten as

$$h_{lm,l'm'}(\mathbf{k}) = C_{lm,l'm'}(\mathbf{k}) + \frac{\rho}{4\pi} \sum_{l''m''} C_{lm,l''m''}(\mathbf{k}) h_{l''m'',l'm'}(\mathbf{k}). \tag{12}$$

The main approximation in the present treatment is to replace the direct correlation function in the spirit of the linear Debye-Hückel theory by  $-\beta U(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ . This replacement is exact only in the limit  $r \rightarrow \infty$ , for potentials which vanish faster than  $r^{-3}$ , as discussed by Stell (1977). Since in our case the potential is of screened Coulomb type, this condition is fulfilled. The extension of the exact asymptotic result to all distances is in the spirit of the mean-field approximation. In Fourier components we therefore write

$$C_{lm,l'm'}(\mathbf{k}) = -\beta U_{lm,l'm'}(\mathbf{k}). \tag{13}$$

Here,  $U_{lm,l'm'}(\mathbf{k})$  is given in terms of  $U(\mathbf{r}_{12}, \mathbf{u}_1, \mathbf{u}_2)$ , (8), by a formula equivalent to (11). In the case of  $\mathbf{k}$  parallel to the  $z$  axis we get a simple expression for  $U_{lm,l'm'}(k\hat{z})$  by expanding the  $j_0$  in spherical harmonics. We get from (8)

$$U_{lm,l'm'}(k\hat{z}) = \delta_{m_0} \delta_{m'_0} a_l(k) a_{l'}(k) \frac{4\pi}{\epsilon\epsilon_0} \frac{Q^2}{q_0^2 + k^2} \tag{14}$$

where

$$a_l(k) = i^l (2l+1)^{1/2} \frac{2}{kL} \int_0^{kL/2} j_l(x) \, dx. \tag{15}$$

The index  $l$  takes the values  $l = 0, 2, 4, \dots$  and  $j_l(x)$  denotes spherical Bessel functions.

Equations (13) and (14) are used in (12). Iterating the resulting equation produces a geometric series which is summed up to give

$$\begin{aligned} h_{lm,l'm'}(k\hat{z}) &= \delta_{m_0} \delta_{m'_0} (-4\pi) \frac{a_l(k) a_{l'}(k) \nu(k)}{1 + \rho \cdot \nu(k) F(k)} \\ &\equiv h_{ll'}(k) \end{aligned} \tag{16}$$

where

$$\nu(k) = \frac{Q^2 / \epsilon\epsilon_0}{q_0^2 + k^2}. \tag{17}$$

In an isotropic system  $S(\mathbf{k})$  does not depend on the direction of  $\mathbf{k}$ . Therefore we can use  $\mathbf{k}$  parallel to the  $z$  axis without loss of generality. The structure factor  $S(\mathbf{k})$  (4) can now be related to  $h_{ll'}(k)$ . From (4) and (3) and the expansion of  $j_0$  in terms of

spherical harmonics, one obtains

$$S(\mathbf{k}) = \sum_{l,l'} a_l(\mathbf{k}) a_{l'}(\mathbf{k}) S_{ll'}(\mathbf{k}). \tag{18}$$

Here

$$\begin{aligned} S_{ll'}(\mathbf{k}) &= \frac{4\pi}{N} \left\langle \sum_{i,j} \exp[i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j) \hat{\mathbf{z}}] Y_{l0}(\Omega_j) Y_{l'0}(\Omega_i) \right\rangle \\ &= 4\pi \langle Y_{l0}(\Omega_1) Y_{l'0}(\Omega_1) \rangle + 4\pi(N-1) \langle \exp[i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_j) \hat{\mathbf{z}}] Y_{l0}(\Omega_1) Y_{l'0}(\Omega_2) \rangle \end{aligned} \tag{19}$$

where  $\hat{\mathbf{z}}$  denotes the unit vector in the direction of the  $z$  axis. Whereas the first term in (19) is just  $\delta_{ll'}$ , the second one is essentially the Fourier transform of the angle dependent generalisation of the radial distribution function for rods

$$g(\mathbf{r}_{12}, \Omega_1, \Omega_2) = (4\pi/\rho)^2 N(N-1) \int d^3r_3 \dots d^3r_N d\Omega_3 \dots d\Omega_N e^{-\beta U} / \int d\Gamma e^{-\beta U}. \tag{20}$$

The second term in (19) is then given by  $(\rho/4\pi)g_{ll'}(\mathbf{k})$ , where  $g_{ll'}(\mathbf{k})$  is given by a formula like (11) with  $\mathbf{k}$  parallel to the  $z$  axis and  $m = m' = 0$ . Since  $g = h + 1$ , one has  $g_{ll'}(\mathbf{k}) = h_{ll'}(\mathbf{k})$  for  $\mathbf{k} \neq 0$ , so that

$$S_{ll'}(\mathbf{k}) = \delta_{ll'} + (\rho/4\pi)h_{ll'}(\mathbf{k}) \tag{21}$$

then  $S(\mathbf{k})$  is given from (18) and (16) by

$$S(\mathbf{k}) = F(\mathbf{k}) / (1 + \rho\nu(\mathbf{k})F(\mathbf{k})). \tag{22}$$

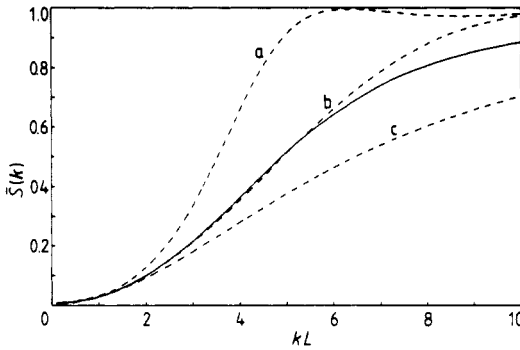
This result corresponds to the Debye-Hückel theory for point particles, but here the form factor  $F(\mathbf{k})$  for rods enters. The main difference from the Debye-Hückel treatment for spherical particles arises because the form factor of the point particles is 1, whereas  $F(\mathbf{k})$  for an infinitely thin rod is given by (5). The effect of the interactions between rods on the structure is described by  $\bar{S}(\mathbf{k}) \equiv S(\mathbf{k})/F(\mathbf{k})$ ,

$$\bar{S}(\mathbf{k}) = (1 + \rho\nu(\mathbf{k})F(\mathbf{k}))^{-1} = \left( 1 + \frac{\beta\rho Q^2/\epsilon\epsilon_0}{k^2 + q_0^2} F(\mathbf{k}) \right)^{-1}. \tag{23}$$

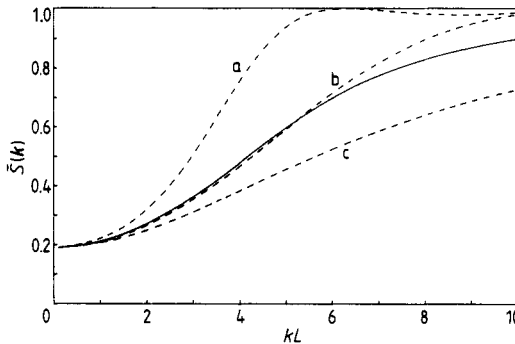
An interesting point of the result for  $\bar{S}(\mathbf{k})$  is the fact that, although this quantity stems entirely from correlations between rods, again the form factor enters in the denominator. This can be easily understood because the form of the particles enters the interaction law (8). In the mean-field approximation (23) the influence of the form is particularly simple; it enters the formula just as a factor, multiplying the direct correlation function between point particles of the same charge as the rods. If one goes beyond the mean-field approximation, also  $\nu(\mathbf{k})$  would depend on the form of the particles. Nevertheless, the simplicity of the result (23) suggests the following pragmatic improvement: use the general form of (23), but insert for  $\nu(\mathbf{k})$  a better approximation for the direct correlation function of spherical particles.

In figure 1 the result for  $\bar{S}(\mathbf{k})$  is shown for rods of length  $L = 3000 \text{ \AA}$  and a total charge of  $Q = 120$  elementary charges. The salt-free solution is assumed to be very dilute, the concentration being such that there are 0.1 rods per volume  $L^3$ . Due to the presence of the form factor  $F(\mathbf{k})$  in the denominator of (22) the structure factor  $\bar{S}(\mathbf{k})$

increases faster as a function of  $kL$  than the corresponding structure factor for point-like particles (which is the curve denoted by  $\cos \theta = 0$ ). In figure 2 salt has been added, which increases  $\bar{S}(k)$  at long wavelengths due to increased screening.



**Figure 1.** Static structure factor  $\bar{S}(k)$  for an isotropic system (full line) and for a nematic ordered system (dashed lines).  $\theta$  is the angle between director and scattering vector (a,  $\cos \theta = 1$ ; b,  $\cos \theta = 0.5$ ; c,  $\cos \theta = 0$ ).  $Q = 120e$ ,  $q_0 l = 0.593$ .



**Figure 2.** As figure 1 but for a system with added salt, leading to a stronger screening of the interaction (a,  $\cos \theta = 1$ ; b,  $\cos \theta = 0.5$ ; c,  $\cos \theta = 0$ ).  $Q = 120e$ ,  $q_0 l = 3.143$ .

#### 4. Static structure factor for fully aligned rods

If all rods are assumed to be parallel to each other without any ordering of their centres of gravity, the structure factor will depend not only on the magnitude of  $k$  but also on its direction relative to the rod axes. Let the  $z$  axis of a coordinate system be parallel to the rods and let  $\theta$  denote the angle between the scattering vector  $k$  and this  $z$  axis. If such order exists the single particle form factor  $F(k)$  and  $S(k)$  are anisotropic and they will depend on  $\theta$ .

The concentration fluctuation (3) becomes in this case

$$c_{\parallel}(k) = j_0 [Lk(\cos \theta)/2] \sum_j \exp(ik \cdot r_j) \quad (24)$$

and the form factor is

$$F_{\parallel}(k) = j_0^2 [Lk(\cos \theta)/2]. \quad (25)$$

In figure 3  $F_{\parallel}(\mathbf{k})$  is shown as a function of  $kL$  for three different angles. If  $\cos \theta = 0$ , so that  $\mathbf{k}$  is perpendicular to the rods, the system degenerates to a point particle system because of the assumption of infinitely thin rods.

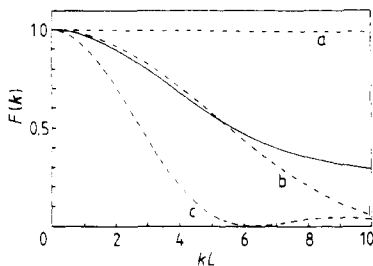


Figure 3. Form factor of rods in the nematic state (dashed lines) and in the isotropic state (full line) (a,  $\cos \theta = 0$ ; b,  $\cos \theta = 0.5$ ; c,  $\cos \theta = 1$ ).

The interaction potential (23) simplifies to

$$U_{\parallel}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3k \exp(i\mathbf{k} \cdot \mathbf{r}) j_0^2(Lk(\cos \theta)/2) \frac{Q^2/(\epsilon\epsilon_0)}{q_0^2 + k^2}. \tag{26}$$

In the Ornstein-Zernicke equation the integration over the directions can be performed since all rods are parallel. Proceeding as in the isotropic case leads to the structure factor

$$S_{\parallel}(\mathbf{k}) = F_{\parallel}(\mathbf{k}) / (1 + \rho\nu(\mathbf{k})F_{\parallel}(\mathbf{k})). \tag{27}$$

In figure 1 the quantity  $\bar{S}_{\parallel}(\mathbf{k}) = S_{\parallel}(\mathbf{k}) / F_{\parallel}(\mathbf{k})$  is plotted for three different angles  $\theta$ . If  $\mathbf{k}$  is parallel to the rods,  $\bar{S}_{\parallel}(\mathbf{k})$  increases much faster as a function of  $kL$  compared with the isotropic case and if  $\mathbf{k}$  has a finite angle with the  $z$  axis. For  $\theta = 60^\circ$ ,  $\bar{S}_{\parallel}(\mathbf{k})$  is similar to the isotropic case for  $kL \leq 6$ .

With the addition of salt the qualitative appearance of  $\bar{S}_{\parallel}(\mathbf{k})$  is similar, but the additional screening increases the values of  $\bar{S}_{\parallel}(\mathbf{k})$  at small  $kL$ .

### 5. Discussion

In this paper we have presented a theory for the static structure factor of charged rod-like macroparticles in solution. The interaction law of two rods was assumed to be a superposition of screened Coulomb interactions between point charges distributed along the rod. Although this superposition ansatz is exact for the unscreened Coulomb interaction, it is only an approximation for the screened case because it neglects correlations among the counterions and correlations between counterions and neighbouring point charges along the rod. Our main interest is weakly screened systems. Then, as long as the mean interparticle distance is not too small compared with the rod length, the above mentioned effects should be of minor importance. Also it has been found in the theory of simple liquids that such details of an interaction law bear little influence on the shape of the static structure factor and related quantities (see, e.g., figure 44 in Hansen and McDonald (1976)).

Much more restrictive with respect to the utility of our theory is the linear Debye-Hückel ansatz, which closes the Ornstein-Zernicke equation. Therefore, our results



are only valid for weakly coupled systems at low concentrations. As a consequence the static structure factor  $\bar{S}(\mathbf{k})$  is a monotonously increasing function of the wavevector and shows no correlation maximum, as was observed in experiments (Hoffmann *et al* 1983).

For a dilute system of infinitely long hard rods the static structure factor takes the following form (Zimm 1948)

$$\bar{S}(\mathbf{k}) = 1 - 2A_2 M \rho F(\mathbf{k}), \quad (28)$$

$M$  being the molecular weight and  $A_2$  the second virial coefficient. The latter depends on the diameter and the length of the rods (Zimm 1946, Onsager 1949, Stigter 1977). This expression can only be supposed to be valid if the diameter of the rods is much smaller but the length much larger than the mean distance between centres of gravity.

Benmouna and coworkers proposed (Benmouna *et al* 1982) using expression (28) also for systems of charged rods, approximating the screened Coulomb potential by an effective hard-core potential with charge- and screening length-dependent diameter. This can be only a reasonable approximation as long as the potential is sufficiently steep. Therefore, the theory of Benmouna and coworkers applies to strongly screened systems at concentrations where the mean distance between centres of gravity is much smaller than the length of the rods, which is just the opposite situation compared to the presuppositions of our work. Also the theory of Benmouna and coworkers fails to produce a correlation peak in the true structure factor  $\bar{S}(\mathbf{k}) = S(\mathbf{k})/F(\mathbf{k})$ .

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