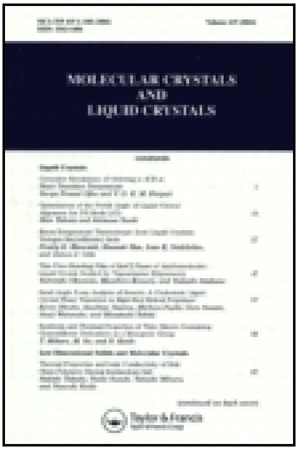

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Mean Field Theory for Semiflexible Nematic Polymers

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A general mean field equilibrium theory for multicomponent polymer systems is applied to the bulk state of semiflexible polymers which can undergo a first order nematic-isotropic phase transition. The polymers are taken as continuous chains whose aspect ratios are much greater than one. Local variations about unity in the absolute value of the tangent vector to the polymer curve are allowed, only the average of the square of the absolute value is constrained to unity. As a consequence the probability distribution for a single chain is taken to be the product of the Wiener measure and the Kratky-Porod term. The interaction between polymeric chains is included through the use of a mean field of the form similar to the Maier-Saupe expression. With this mean field we obtain an analytical expression (Feynman-Hibbs result) for the probability distribution from which the order parameter and the free energy are determined.

INTRODUCTION

Recently a mean field equilibrium theory[1] using the density functional integral method has been developed for semiflexible polymeric chains. In that work[1] the question of how best to describe semiflexible polymers was addressed. It is well known that biological and synthetic polymers are in most cases neither totally rigid nor totally flexible.[2] However, depending on the scale of observation one can perceive them as being flexible or rigid and then use the appropriate probability distribution[3] to describe the single chain (the Wiener measure[4] for flexible and extensible chains and the Kratky-Porod[5] distribution for stiff, inextensible chains). In the intermediate range of observation polymers are best thought of as semiflexible and the probability distribution for the single chain is taken as the product of the Wiener measure and the Kratky-Porod term. The general development presented in reference 1 led to a self-consistent solution of the differential equation for the probability distribution, $Q(\mathbf{r},\mathbf{u},L;\ \mathbf{r}_0,\mathbf{u}_0)$, for a chain of length L with the initial position $\mathbf{r}_0$ and orientation $\mathbf{u}_0$, ending at $\mathbf{r}$ with final orientation $\mathbf{u}$. In this work we focus on the application of the theory to the bulk state of nematic semiflexible polymers and find that with a quadratic mean field (of the Maier-Saupe[6] type) we obtain an analytical solution for the probability distribution.

There are a number of earlier works[7] that treat polymers as semiflexible. The main difference between our approach and these studies is that we relax the constraint that the absolute value of the tangent vector, $|\mathbf{u}|$, is identically equal to unity everywhere along the space curve that denotes the polymeric chain. This is done primarily for two reasons: (1) To avoid mathematical inconsistencies[1,8] that this constraint leads to and (2) relaxing this constraint gives rise to an analytical solution for the total probability distribution providing the effective mean field is approximated by a quadratic expression.

THEORY AND DISCUSSION

We consider a discrete chain consisting of N bonds of average length Δs such that the total length of the polymer is given by $L = N\Delta s$. Using the functional integral notation[8] (i.e., in the limit $\Delta s \to 0$, $N \to \infty$, $L = N\Delta s$) the polymeric chain can be thought of as a continuous space curve. Then the probability distribution, $P[\mathbf{u}(\cdot)]$, for an unperturbed single chain (semiflexible) can be taken as

$$P[\mathbf{u}\,(\cdot)]\alpha \exp\left\{-\frac{3}{2b^*}\int_0^L ds\,\mathbf{u}^2(s) - \frac{\beta\varepsilon}{2}\int_0^L ds\left(\frac{\partial \mathbf{u}(s)}{\partial s}\right)^2\right\} \tag{1}$$

where $\beta = 1/(k_B T)$ and $\mathbf{u}(s) = \partial \mathbf{r}(s)/\partial s$ is the tangent vector at a point s along the curve $(0 \leqslant s \leqslant L)$. Note in this model $\mathbf{u}^2(s)$ is not identically equal to unity[8] for all s. However it is still required that the average of square of the tangent vector, $\langle \mathbf{u}^2 \rangle$, is constraint to unity. In Equation (1) the first term is of the same form as the usual Wiener measure[4] and gives the probability distribution for the bond lengths. The second term represents the potential energy due to the bending of the chain, which is related to the intrinsic elasticity constant ε (in units of energy times length), and the inverse of the square of the radius of the curvature. In this model b^* and ε are related (see below).

In this work we consider a bulk nematic state that is composed of only one type of homopolymer. In general polymeric chains will interact with each other through long and short range intra- and inter-molecular interactions. The usual procedure for taking account of these interactions is to introduce an effective mean field. In this model the steric effects are not taken into account. However it is known[7] that the anisotropic part of the attractive Van der Waals force (Maier-Saupe mean field)[6] leads to a first order nematic-isotropic phase transition. When the constraint $\mathbf{u}^2(s) = 1$ is relaxed we find that for the semiflexible polymers the following form of the mean field, $w(\mathbf{u})$, gives rise to a first order phase transition

$$w(\mathbf{u}) = -\beta A\,\{f_z(S)u_z^2 + f_x(S)u_x^2 + f_y(S)u_y^2\} \tag{2}$$

with

$$f_z(S) = S + BS^2 + CS^3 \tag{3}$$

$$f_y(S) = f_x(S) = -\frac{1}{2}S + B'S^2 + C'S^3 \tag{4}$$

where S is the scalar orientational order parameter that accounts for the uniaxial symmetry of the nematic state. We show below that parameters: B' and C' are functions of S. Note that from the requirement that the nematic-isotropic phase transition is first order we must set the coefficient of S in Equation (4), $A' = -A/2$, since all terms linear in S must vanish in the free energy expression. The form of $w(\mathbf{u})$ as given by Equation (2) relates the mean field directly to the orientational order parameter S, given by

$$S = \frac{3}{2}\langle u_z^2\rangle - \frac{1}{2} \qquad \text{if } \hat{\mathbf{n}} = \hat{\mathbf{z}}. \tag{5}$$

It should be emphasized that of the five parameters: A, B, C, B', C' (we have let $A' = -(1/2)A$), introduced into $w(\mathbf{u})$ only two are independent, this will be shown below. Equation (2) is of similar form to the Maier-Saupe[6] expression of the mean field. The ansatz of Equation (2) can be motivated as follows. The intermolecular potential between rodlike molecules 1 and 2 can generally be written as an expansion in terms of spherical harmonics

$$V_{12}(r;\theta_1,\psi_1;\theta_2,\psi_2) = 4\pi \sum_{L_1L_2} u_{L_1L_2;n}(r)\, Y_{L_1,n}(\theta_1,\psi_1) Y_{L_2,n}(\theta_2,\psi_2). \tag{6}$$

For two polymeric chains separated by a distance $\mathbf{r}$, θ_1, ψ_1; θ_2, ψ_2 are the angles with respect to the intermolecular vector that intersects the chains at only two points s and s' i.e., $|\mathbf{r}_i(s) - \mathbf{r}_j(s')| = r$ (with $i \neq j$, $\{i,j\} = \{1, 2, \ldots \tilde{N}\}$). Orientational order in a nematic liquid crystal is defined in terms of the molecular orientation with respect to a space-fixed coordinate system which contains the director. Transforming Equation (6) from the coordinate system containing the intermolecular vector to this space-fixed coordinate system and following the procedure developed by Maier-Saupe[6] and others[9,10] one obtains the pseudo-potential for a single chain. There are a number of ways of obtaining the final form of this pseudo-potential. Most involve series expansion in terms of $P_L(\cos\theta)$ or $\cos^L\theta$ with the corresponding multiplicative coefficients that include averages with respect to P_L (i.e., $\langle P_L\rangle$) or $\cos^L\theta$ (i.e., $\langle\cos^L\theta\rangle$). The most commonly used approximation for polymer liquid crystals retains only the first term in this expansion i.e., $w(\mathbf{u})\alpha - \langle P_2\rangle P_2(\cos\theta)$ (where $S = \langle P_2\rangle$ if $\mathbf{u}^2(s) = \mathbf{1}$) or $w(\mathbf{u})\ \alpha - \Sigma_a c_a S u_a^2$ ($a = x,y,z$). In this work we require that the global average of the square of the tangent vector $\langle\mathbf{u}^2\rangle$ is equal to unity. This results in the need to generalize multiplicative factor of u_a^2 to include higher powers of S as shown in Equation (2).

A useful feature of the quadratic form for $w(\mathbf{u})$ is that the total probability distribution $Q(\mathbf{u}, L; \mathbf{u}_0)$ for a single chain of length L with initial and final orientations given by $\mathbf{u}_0$ and $\mathbf{u}$ respectively given by[1]

$$\begin{aligned} \mathbf{Q} &= \int \delta\mathbf{u}(\cdot)\, P[\mathbf{u}(\cdot)] \exp\left\{ - \int_0^L ds\, w[\mathbf{u}(s)]\right\} \\ &= \int d\mathbf{u} \int d\mathbf{u}_0\, Q(\mathbf{u},L;\mathbf{u}_0) \end{aligned} \tag{7}$$

becomes a functional integral of the harmonic oscillator type.[11] Thus one can solve for $Q(\mathbf{u},L;\mathbf{u}_0)$ in a closed form for an arbitrary polymer of length L,

$$Q(\mathbf{u},L;\mathbf{u}_0) = N\prod_a \left\{\frac{2\pi}{\Lambda_a}\sinh(2\Lambda_a L\lambda)\right\}^{-1/2}$$

$$\times \exp\left\{-\frac{1}{2}\Lambda_a \frac{(u_a^2 + u_{a0}^2)\cosh(2\Lambda_a L\lambda) - 2u_a u_{a0}}{\sinh(2\Lambda_a L\lambda)}\right\} \tag{8}$$

where

$$\lambda = \frac{1}{2\beta\varepsilon}, \quad \frac{1}{d_a} = \frac{3}{2b^*} - \beta A f_a(S), \qquad \Lambda_a = (d_a\lambda)^{-1/2}. \tag{9}$$

Given $Q(\mathbf{u},L;\mathbf{u}_0)$ one can calculate the averages of physical quantities as discussed in reference 8.

For example the mean-square end-to-end distance, $\langle \mathbf{R}^2\rangle$, using the spatial correlation function for $\mathbf{u}(s)$, $\langle \mathbf{u}(s')\cdot\mathbf{u}(s'')\rangle$, is given as follows

$$\langle \mathbf{R}^2\rangle = \int_0^L ds' \int_0^L ds'' \langle \mathbf{u}(s')\cdot\mathbf{u}(s'')\rangle \tag{10}$$

or

$$\langle \mathbf{R}^2\rangle = \sum_a \frac{1}{\Lambda_a}\left\{\frac{L}{2\Lambda_a\lambda} - \frac{1}{8(\Lambda_a\lambda)^2}\tanh(2\Lambda_a L\lambda)\right\}. \tag{11}$$

We determine the order parameter S as defined in equation (5). This requires the calculation of $\langle \mathbf{u}^2\rangle$ as follows:

$$\langle \mathbf{u}^2\rangle = \sum_a \frac{1}{2\Lambda_a}\left\{\tanh(2\Lambda_a L\lambda) + \operatorname{csch}(4\Lambda_a L\lambda) + \frac{1}{4\Lambda_a L\lambda}\right\}. \tag{12}$$

In the limit $\Lambda_a L\lambda \rightarrow \infty$ we obtain

$$\langle \mathbf{R}^2\rangle = \sum_a \frac{1}{2\Lambda_a}\left\{\frac{L}{\Lambda_a\lambda} - \frac{1}{4(\Lambda_a\lambda)^2}\left[1 - 2\exp(-4\Lambda_a L\lambda) + \ldots\right]\right\} \tag{13}$$

and

$$\langle \mathbf{u}^2\rangle = \sum_a \frac{1}{2\Lambda_a}\left\{1 + \frac{1}{4\Lambda_a L\lambda} + 2\exp(-8\Lambda_a L\lambda) + \ldots\right\} \tag{14}$$

with the requirement that $\langle \mathbf{u}^2 \rangle$ is equal to unity. With two conditions ($\Sigma_a \, 1/(2\Lambda_a) = 1$ and $\Lambda_a = \Lambda$ when $S = 0$) inserted into equation (13) we obtain an expression for $\langle \mathbf{R}^2 \rangle$ that is similar in form to the Kratky-Porod result.[4] Also in this limit we find that the effective segment length is given by $b^* = 1/(\Lambda\lambda)$ or $b^* = (4/3)\beta\varepsilon = 2/(3\lambda)$. This result again should be compared with $b^* = 2\beta\varepsilon = 1/\lambda$ for wormlike model.[4]

Next we illustrate how to determine the constraining conditions on the parameters A, B, C, B' and C'. As $T \to 0$ we must have $S \to 1$. This gives one relationship between B and C (in the limit $L\lambda \to \infty$ this is given by $1 + B + C = 0$). Also as $T \to 0$ we must have $S \to -1/2$, this gives a relationship between B', and C' (for $L\lambda \to \infty$, $1 + B' - C'/2 = 0$). In general we express B' and C' in terms of B, C and S from the requirement that at given T, the same S must satisfy two equations $S = 3/2 \, \langle u_z^2 \rangle - 1/2$ and $S = 1 - 3 \, \langle u_x^2 \rangle$ (note $\langle u_x^2 \rangle = \langle u_y^2 \rangle$). For example in the limit $L\lambda \to \infty$ C' expanded to first order in S satisfies the following relationship

$$C' = -\left(\frac{5}{2} + B\right) - \frac{3}{2}(1 + B)S + \mathrm{O}[S]^2. \tag{15}$$

Then the $f_a(S)$ functions in the mean field expression (see Equation (2)) can be written as

$$f_z(S) = S + BS^2 - (1 + B)S^3 \tag{16}$$

$$f_y(S) = f_x(S) = -\frac{1}{2}S - \left(\frac{9}{4} + \frac{B}{2}\right) S^2 - \left(\frac{13}{4} + \frac{7B}{4}\right) S^3. \tag{17}$$

Equations (2),(16) and (17) give $w(\mathbf{u})$ in terms of two unknown parameters: A and B. Using Equation (14) in the limit $L\lambda \to \infty$ the order parameter is given by

$$S = \frac{3}{4\Lambda_z} - \frac{1}{2} = \frac{3}{4}\left\{\frac{3}{2b^*\lambda} - \frac{\beta A}{\lambda}(S + BS^2 - (1 + B)S^3)\right\}^{-1/2} - \frac{1}{2} \tag{18}$$

Two more relationships between S and T are needed in order to specify the parameters A and B (and consequently C, B' and C') completely. The values of the single chain parameters (b^*, ε) can be determined semiempirically.[1]

The critical values of the temperature and the order parameter (T_c, S_c) are given by requirement that the free energies of the nematic and isotropic states are equal. In the limit $L\lambda \to \infty$ (with $w(\mathbf{u})$ given by Equations (2), (16) and (17)) the expressions for the nematic, F_N, and isotropic, F_1, free energies are given as follows

$$F_N = \tilde{N}L\lambda \left\{\frac{1}{6}\frac{\beta A}{\lambda}\left[-\frac{3}{2}S^2 - \left(3 + \frac{3B}{2}\right)S^3 + \left(\frac{9}{2} + \frac{3B}{2}\right)S^4\right]\right\}$$

$$+ \bar{N} \sum_{a} \left\{ \frac{1}{2} \ln \left[\cosh \left(2 \Lambda_a L\lambda\right)\right] \right\}, \tag{19}$$

$$F_I = F_N(S = 0). \tag{20}$$

In the limit $L\lambda \rightarrow \infty$ equation (19) further simplifies to the following expression

$$\frac{\Delta F}{\bar{N} L\lambda} = \frac{1}{6} \frac{\beta A}{\lambda} \left[- \frac{3}{2} S^2 - \left(3 + \frac{3B}{2}\right) S^3 + \left(\frac{9}{2} + \frac{3B}{2}\right) S^4 \right] + \sum_{a} \Lambda_a - 3\Lambda. \tag{21}$$

Since the mean field expression retains terms up to third order in S which in turn leads to terms up to fourth order in S in the expression for the free energy, we must expand the remaining part of ΔF (i.e., terms that contain Λ_a) up to fourth order in S. This is because series expansion of Λ_a contains terms to all orders in S. This results in the following expression for $\Delta F = F_N - F_I$,

$$\frac{\Delta F}{\bar{N} L\lambda} = - \frac{\nu(-45 + 2\nu)}{36} S^2 - \frac{\nu(-648 - 405B + 54\nu + 36B\nu + 2\nu^2)}{324} S^3 - \frac{\nu(-1458 - 486B + 1053\nu + 432B\nu + 108B^2\nu - 54\nu^2 + 36B\nu^2 + 5\nu^3)}{1944} S^4 + \mathrm{O}[S]^5 \tag{22}$$

where

$$\nu = \frac{\beta A}{\lambda}. \tag{23}$$

RESULTS

Using Equation (18) one can obtain a plot of S as a function of the reduced temperature $T/\tilde{T}$ ($\tilde{T} = (A\varepsilon)^{1/2}/k_B$) both for $L\lambda \rightarrow \infty$ and for finite length $L\lambda$ (= 0.1, 1, 5, 10). These plots for a typical value of $B = -1.135$ are illustrated in Figure 1. From this figure it is concluded that the S versus $T/\tilde{T}$ curves for finite length polymers converge rapidly to the asymptotic curve (when $L\lambda \rightarrow \infty$).

From the expansion of the free energy (Equation (22)) we obtain two solutions for S_c in terms of T and B when the condition $\Delta F = 0$ is satisfied (one of the solutions corresponds to an unstable state). The crossings of the $S(\Delta F = 0)$ versus $T/\tilde{T}$ curves with the S versus $T/\tilde{T}$ curves for different values of B determine the critical values of the temperature and the orientational order parameter (see Figure

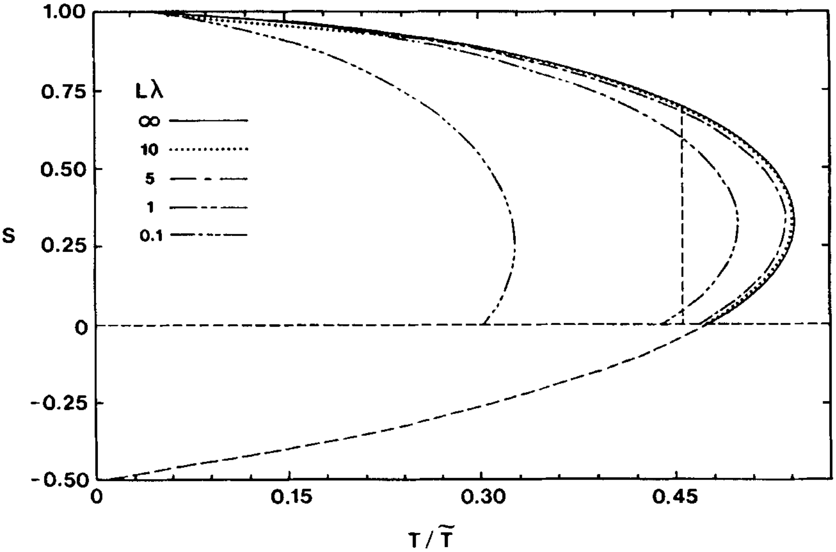

FIGURE 1 Variation of the orientational order parameter, S, (see equation (5)) with the reduced temperature $T/\tilde{T}$ ($\tilde{T} = (A\varepsilon)^{1/2}/k_B$) for $L\lambda \rightarrow \infty$ ($\lambda = 1/(2\beta\varepsilon)$) and finite length $L\lambda = \{10, 5, 1, 0.1\}$ polymer chains ($B = -1.135$). The critical value of $S_c = 0.70$ at $T_c = 0.45\ \tilde{T}$ for $L\lambda \rightarrow \infty$ is indicated by the vertical dashed line. Note that the lower part of the curve for $L\lambda \rightarrow \infty$ for negative values of S corresponds to the state where the chains align in the xy-plane.

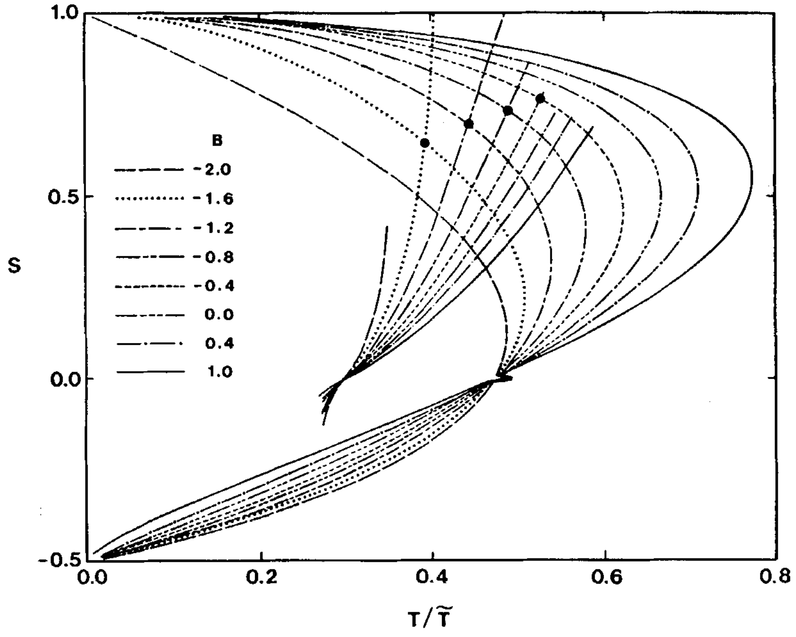

FIGURE 2 Crossing of the $S(\Delta F = 0)$ versus $T/\tilde{T}$ curves with the S versus $T/\tilde{T}$ curves for various values of B in the limit $L\lambda \rightarrow \infty$, giving the critical values of the temperature and the orientational order parameter.

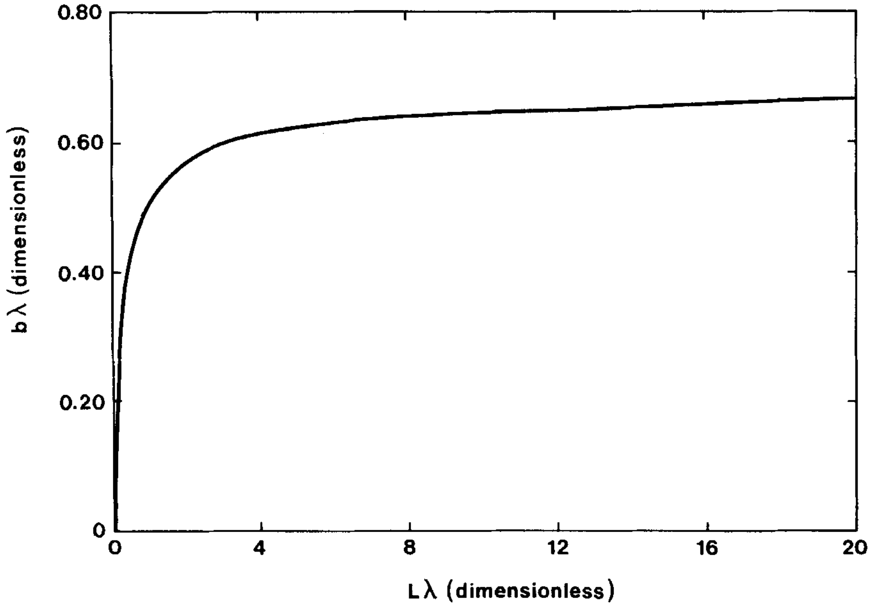

FIGURE 3 Variation of the reduced segment length $b^*\lambda$ ($\lambda = 1/(2\beta\varepsilon)$) with the reduced length $L\lambda$ of the polymer. ($b^*\lambda$ must be such that in the isotropic state $S = 3/(4\Lambda_z) - 1/2 = 0$ (see text) is satisfied self-consistently.)

(2). For example with $L\lambda \to \infty$ for $B = -1.135$ we find that $T_c = 0.45\ (A\varepsilon)^{1/2}/k_B$ and $S_c = 0.70$ (see Figure 1). Figure 3 shows how $b^*\lambda$ changes with the length, $L\lambda$, in order to satisfy the requirement that $S = 0$ in the isotropic state. Note that $b^*\lambda$ reaches the asymptotic value (2/3) as $L\lambda \to \infty$. In the zero temperature limit ($S \to 1$) one must take the limit $T \to 0$ and then $L\lambda \to \infty$ in the free energy expression (Equation (19)), which then leads to a different result for ΔF from Equation (22).

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