Notes

Comment on the Paper by Skolnick and Yaris, "Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 1. General Theory"

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In this short note, it is pointed out that the solution for the damped diffusion model of Skolnick and Yaris[1] is mathematically incorrect. The eigenfunction satisfying the eigenvalue eq III-2 has been found to be $\rho = e^{\alpha x}$, eq III-3a, but it does not satisfy the closure relation in the k space and, therefore, as it stands, cannot be used in eq III-4. Indeed, the solution given by eq III-4 does not satisfy the initial condition of eq II-6. The correct eigenfunction $\rho_y(x)$ belonging to the continuous eigenvalue $\lambda_y = -k^2$ with the "index" y is given by

$$\rho_y(x) = (2\pi)^{-1/2}e^{iyx} \tag{1}$$

where

$$y = (k^2 - \beta/D)^{1/2} \qquad \text{for } k \geq (\beta/D)^{1/2}$$

$$y = -(k^2 - \beta/D)^{1/2} \qquad \text{for } k < -(\beta/D)^{1/2} \tag{2}$$

and the integration over k should be replaced by that over y from $-\infty$ to $+\infty$ *without* the Jacobian. However, it should be recognized that the solution of the diffusion eq III-1 is simply given by $\rho = e^{-\beta t}\rho_1$, where ρ_1 is the solution of eq II-3. In any case, eq III-8 should be replaced by

$$\langle B_n(x,t)B_n^*(x,0)\rangle_x = \pi^{-1}B_n(0)^2e^{-\beta t}\int_0^{k_B} e^{-Dk^2t}\,dk \tag{3}$$

with $k_B = k_{max}$, so that all equations that follow for this model should be recalculated.

References and Notes

(1) Skolnick, J.; Yaris, R. *Macromolecules* **1982**, *15*, 1041.

Corrections

J. Skolnick* and Robert Yaris: Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 1. General Theory. Volume 15, Number 4, July–August 1982, page 1041.

As Yamakawa has correctly pointed out,[1] the integration over y in eq III-6, p 1042, should be done without the Jacobian in order for the k space to be complete.

The normalized autocorrelation function, eq III-15, p 1043, should be replaced by

$$\phi_{SY} = \frac{e^{-\beta t}}{2\omega_c}\left(\frac{\pi}{Dt}\right)^{1/2} \operatorname{erf}\,[(Dt\omega_c^2)^{1/2}] \tag{III-15}$$

The spectral density given by eq III-17 on p 1043 is in error, having omitted terms of order $\beta/(\beta^2 + \omega^2)^{1/2}$. Equation III-17 should be replaced by

$$J_{SY}(\omega) = \frac{1}{D\omega_c}\int_0^{\omega_c} dy\, \frac{(y^2 + \beta/D)}{\{(y^2 + \beta/D)^2 + \omega^2/D^2\}} \tag{III-17}$$

Equation III-18a on p 1043 should read

$$J_{SY}(\omega) = \delta^{-1}\int_0^1 dz\, \frac{(z^2 + \beta/\delta)}{\{(z^2 + \beta/\delta)^2 + \omega^2/\delta^2\}} \tag{III-18a}$$

and eq III-19a should be

$$J_{SY}(\omega) = \delta^{-1}\left\{\frac{c(\omega)}{4k(\omega)} \ln \frac{A(\omega)}{B(\omega)} + \frac{s(\omega)}{2k(\omega)} \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right]\right\} \tag{III-19a}$$

where $A(\omega)$, $B(\omega)$, $c(\omega)$, $k(\omega)$, and $s(\omega)$ remain as defined in eq III-19b–f of our paper.

Equation IV-11 on p 1045 should read

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \omega_c^{-1}\int_0^{\omega_c} dy\, \frac{(\beta + Dy^2)(\beta + Dy^2 - i\omega)}{(\beta + Dy^2)^2 + \omega^2} \tag{IV-11}$$

$\epsilon''/(\epsilon_0 - \epsilon_\infty)$ is still given by $\omega J_{SY}(\omega)$, with $J_{SY}(\omega)$ defined above in eq III-19a.

Equation IV-15 on p 1045 should be

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = 1 - \frac{\omega^2}{\delta^2}\left\{\frac{1}{8k^3(\omega)c(\omega)} \ln \frac{B(\omega)}{A(\omega)} + \frac{1}{4k^3(\omega)s(\omega)} \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right]\right\} \tag{IV-15}$$

Replace eq IV-18, p 1045, with

$$f(\omega) = -\frac{\omega'^2}{2}\left(\frac{1 + 2\beta'}{(1 + \beta')^2 + \omega'^2}\right) + \frac{1}{8k(\omega)c(\omega)}\left(\frac{2\beta'^2 + \omega'^2}{2} - \frac{\beta'^3}{k^2(\omega)}\right) \ln \frac{A(\omega)}{B(\omega)} + \frac{1}{4k(\omega)s(\omega)}\left(\frac{2\beta'^2 + \omega'^2}{2} + \frac{\beta'^3}{k^2(\omega)}\right) \tan^{-1}\left[\frac{2k(\omega)s(\omega)}{k^2(\omega) - 1}\right] \tag{IV-18}$$

with $\beta' = \beta/\delta$ and $\omega' = \omega/\delta$.

(1) Yamakawa, H. *Macromolecules*, preceding paper in this issue.

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