Molecular weight dependence of Soret coefficient of Rouse chains

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In dilute polymer solutions under temperature gradients, mass fluxes are induced by the Soret effect. According to earlier experimental works, the Soret coefficient, which characterizes the magnitude of the phenomenon, increases as increasing the molecular weight of polymers[1]. For this molecular weight dependence, the microscopic mechanism remains unclear, although theories based on (macroscopic) thermodynamic quantities have been proposed [2,3]. To tackle this problem theoretically, we discuss the dynamics of Rouse chains under temperature gradients.

The equation of motion for the i-th Rouse bead is written as follows:

$$\frac{d\boldsymbol{R}_i}{dt} = \frac{\boldsymbol{P}_i}{m} \quad \frac{d\boldsymbol{P}_i}{dt} = -\frac{\partial \Phi(\boldsymbol{R}_i)}{\partial \boldsymbol{R}_i} - \frac{\partial U}{\partial \boldsymbol{R}_i} - \zeta \frac{\boldsymbol{P}_i}{m} + \sqrt{2\zeta k_B T(\boldsymbol{R}_i)}\boldsymbol{w}_i(t) \tag{1}$$

Here $\boldsymbol{R}_i$ and $\boldsymbol{P}_i$ are the position and momentum of the i-th bead, ζ is the friction coefficient, m is the mass, $\Phi(\boldsymbol{R}_i)$ is the chemical potential, k_B is the Boltzmann constant, and $\boldsymbol{w}_i(t)$ is the Gaussian white noise which corresponds to the time derivative of the standard Wiener process. U is the harmonic potential defined as $U = \sum_i^{N-1} K \left(\boldsymbol{R}_{i+1} - \boldsymbol{R}_i\right)^2 /2$ with K being a constant. $T(\boldsymbol{R}_i)$ is the temperature which depends on the position. According to the average temperature $\bar{T}$, we choose units of length, energy, and time as $\left(k_B\bar{T}/K\right)^{1/2}$, ζ/K, and $k_B\bar{T}$. We consider a rectangular system and set the x-axis along the temperature gradient. For the simplest case with the bead number per chain $N = 2$, we have theoretically derived S_T of the center of mass of Rouse chains as follows:

$$S_T = \frac{1}{\bar{T}} + \frac{1}{k_B\bar{T}} \frac{\partial \Phi(x)}{\partial x} / \frac{\partial T(x)}{\partial x} \quad \left(\bar{T} = \frac{1}{L} \int_0^L T(x)dx\right) \tag{2}$$

Here L is the box size in the x-direction. This result demonstrates that S_T is independent of the choice of K. Meanwhile, with larger N values, the conformational dynamics become quite complicated because the coupling terms between the temperature gradient and conformational degrees of freedom are significant. These coupling terms imply that S_T can be N-dependent. Nevertheless, we are working to find the analytical expression of S_T and the numerical integration of eq. (1). The results will be shown on-site.

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[2] A. Würger, *Physical Review Letters* **102**, 078309 (2009).
[3] 3. M. Eslamian et al., *International Journal of Thermophysics* **32**, 652 (2011).