

Hydrodynamic interactions in DNA thermophoresis: Supplemental Material

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The effect of hydrodynamic interactions in a dilute polyelectrolyte solution are studied in terms of a series expansion for the Oseen tensor. In other words, we theoretically evaluate the thermophoretic mobility $D_T^{(n)}$ of a stiff chain of n beads. Here we present a detailed calculation of the thermophoretic mobility.

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I. HYDRODYNAMIC INTERACTIONS

We deal with the hydrodynamic screening of DNA thermophoresis, and in particular the influence of the hydrodynamic interactions effect in a dilute polyelectrolyte solution. In other words, we study the molecular weight dependence of the thermophoretic D_T which is defined as

$$\mathbf{u} = -D_T \nabla T. \quad (1)$$

Consider a molecular chain consisting of n units, where each molecular bead of charge q results in the Debye-Hückel surface potential $\zeta = q/4\pi\epsilon a$. Throughout this paper we assume that the molecular size a is small compared to the Debye screening length λ . We find that hydrodynamic interactions enhance the thermophoretic mobility beyond the single particle value $D_T^{(1)}$. In terms of a simple model, we also account for the well-known effect of counterion condensation which occurs for long chains: Due to the strong attraction of the charged polymer, a fraction of the counterions condense onto the polymer until the effective charge density of the polymer is reduced to a certain critical value [3]. The remaining ions are treated within Debye-Hückel approximation.

In the polymer chain, a given molecular unit j creates a flow \mathbf{v} in the surrounding fluid, and drag its neighbor bead i . As a consequence, the overall velocity \mathbf{u} can be written as the sum of the velocity of single monomer and the advection flow engendered by the rest of the molecular chain,

$$\mathbf{u} = \mathbf{u}_1 + \frac{1}{n} \sum_{i,j \neq i} \langle \mathbf{v}(\mathbf{r}_{ij}) \rangle, \quad (2)$$

where the angular brackets $\langle \cdot \cdot \cdot \rangle$ indicate the configurational average with respect to the distance vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

The velocity field $\mathbf{v}(\mathbf{r}_{ij})$ is the solution of the stationary Stokes equation at low Reynolds number. It consists of the superposition of a term due to the thermodynamic force \mathbf{f} exerted by the bead j on the fluid, and the corresponding counterforce \mathbf{F} on the bead,

$$\mathbf{v}(\mathbf{r}_{ij}) = \mathbf{G}(\mathbf{r}_{ij}) \cdot \mathbf{F}_j + \int dV \mathbf{G}(\mathbf{r}_{ij} - \mathbf{r}) \cdot \mathbf{f}_j(\mathbf{r}), \quad (3)$$

where we introduce the Oseen tensor $\mathbf{G}(\mathbf{r}) = (1 + \widehat{\mathbf{r}}\widehat{\mathbf{r}})/8\pi\eta r$ with η the solvent viscosity and $\widehat{\mathbf{r}} = \mathbf{r}/r$ the radial unit vector [2].

In Eq. (3), the force density \mathbf{f} describes the interaction of a molecular unit with the surrounding water. Since there is no net force on the molecule, we need to account for the backreaction of the fluid on the monomer, in terms of the counterforce

$$\mathbf{F}_j = - \int dV \mathbf{f}_j, \quad (4)$$

exerted by the charged fluid on each monomer. These forces provide the source term in the Stokes equation. The general expression for the thermodynamic force density is evaluated within an approach based on linear response theory [4],

$$\mathbf{f} = -(\rho\psi + n_i k_B T) \frac{\nabla T}{T} - \frac{E^2}{2} \nabla \epsilon - n_i k_B T \frac{\nabla n_0}{n_0} + \rho \mathbf{E}_T, \quad (5)$$

where ϵ is the solvent permittivity, n_0 the bulk salinity, $n_i = n_+ + n_-$ the excess ion density and $\rho = e(n_+ - n_-)$ the charge density. All terms in \mathbf{f} are of comparable magnitude; for small molecules the fields \mathbf{E}_T and $\nabla \epsilon$ dominate,

whereas the gradients ∇T and ∇n_0 are negligible. This limit corresponds to the Hückel limit of electrophoresis, with the size of a molecular unit much smaller than the Debye length, $a \ll \lambda$. We simplify Eq. (5) by introducing the logarithmic permittivity derivative $\tau = -d \ln \epsilon / d \ln T$,

$$\frac{\nabla \epsilon}{\epsilon} = -\tau \frac{\nabla T}{T}. \quad (6)$$

In addition, we treat the electrostatic potential in Debye-Hückel approximation, where $e\psi$ is assumed small as compared to the thermal energy $k_B T$. Then the series of the excess ion density n_i and the charge density ρ can be truncated at second order in ψ ,

$$n_i \simeq \frac{\epsilon \psi^2}{2\lambda^2 k_B T}, \quad \rho \simeq -\frac{\epsilon \psi}{\lambda^2}, \quad (7)$$

where $\lambda^2 = 1/8\pi n_0 l_B$ denotes the Debye length and $l_B = e^2/4\pi\epsilon k_B T$ the Bjerrum length. Inserting Eq. (6) and Eq. (7) in Eq. (5), the force exerted by the bead j can be written as

$$\mathbf{f}_j = \left(\frac{\tau \epsilon E_j^2}{2k_B T} - \frac{\delta \alpha \epsilon \psi_j}{e \lambda^2} \right) k_B \nabla T. \quad (8)$$

In linear-response approximation with respect to the applied temperature gradient, the configurational average is done with the isotropic equilibrium distribution function. Then the only finite component of the mean drag velocity is along electric field axis, and the tensor equation (3) simplifies to a scalar one, where the Oseen tensor is replaced by its diagonal part $G(r) = 1/6\pi\eta r$. Inserting the density force in Eq. (3) and averaging over the position i on the polymer chain, we find the thermophoretic mobility

$$D_T = D_T^{(1)} + \frac{1}{n} \sum_{i,j \neq i} (I(r_{ij}) - J(r_{ij})), \quad (9)$$

with

$$I(r_{ij}) = G(r_{ij}) \int dV f_j(\mathbf{r}), \quad (10)$$

and

$$J(r_{ij}) = \int dV G(|\mathbf{r}_{ij} - \mathbf{r}|) f_j(\mathbf{r}). \quad (11)$$

The second term in parenthesis depends on the details of the counterion distribution; for later use we expand the pre-average Oseen tensor in term of Legendre Polynomials $P_k(\cos \theta)$, with $\cos \theta = \widehat{\mathbf{r}}_{ij} \cdot \widehat{\mathbf{r}}$,

$$G(|\mathbf{r}_{ij} - \mathbf{r}|) = \frac{1}{6\pi\eta} \sum_{k=0}^{\infty} P_k(\cos \theta) \frac{h_{ij}^k}{H_{ij}^{k+1}}, \quad (12)$$

where $h_{ij} = \min(r, r_{ij})$ denotes the smaller of the distances r and r_{ij} , and $H_{ij} = \max(r, r_{ij})$ the larger one.

II. THERMOPHORETIC MOBILITY

We still have to compute the volume integrals in Eqs. (10) and (11). In the Debye-Hückel limit, the screened potential ψ_j and the corresponding electric field $E_j = -\nabla \psi_j$ are given by

$$\psi_j = \zeta \frac{a}{r} e^{-r/\lambda}. \quad (13)$$

Inserting this relation into Eq. (3) one finds that the only finite contribution stems from the term $k = 0$ in Eq. (9); the remainder vanishes because of the isotropic screening cloud of a single monomer. Assuming that the particle's radius a is much smaller than the Debye length λ ($a \ll \lambda$), the volume integral $I(r_{ij}) - J(r_{ij})$ is readily performed by doing a first order development in term of a/λ ,

$$\langle I(r_{ij}) - J(r_{ij}) \rangle = \tau \frac{\epsilon a^2 \zeta^2}{6\eta T} \left\langle \frac{e^{-2r_{ij}/\lambda}}{r_{ij}^2} \right\rangle - 2S \frac{\epsilon a \zeta}{3\eta} \left\langle \frac{e^{-r_{ij}/\lambda}}{r_{ij}} \right\rangle, \quad (14)$$

where $S = \delta\alpha k_B/e$ is the electrolyte Seebeck coefficient. Eq. (14) characterizes the hydrodynamic interactions between monomers and shows that the latter are exponentially screened. To find the complete expression of the mobility, we start by simplifying the configurational average by treating the molecules as rigid rods, $r_{ij} = |i - j|d$, where d is the monomer spacing along the contour length. Since the force field is exponentially screened, the main contribution to Eq. (9) stems from within the screened length where the distance is that of a rigid molecule.

Replacing the double sum by the double integral over i and j , then Eq. (9) becomes

$$D_T = D_T^{(1)} + \frac{1}{n} \left\{ \tau \frac{\epsilon a^2 \zeta^2}{6\eta T} \int_1^n didj \left(\frac{e^{-2|i-j|d/\lambda}}{|i-j|^2 d^2} \right) - 2S \frac{\epsilon a \zeta}{3\eta} \int_1^n didj \left(\frac{e^{-|i-j|d/\lambda}}{|i-j|d} \right) \right\}. \quad (15)$$

Eliminating the absolute value and computing the double integral over i and j , we finally obtain the thermophoretic mobility in the form:

$$D_T = D_T^{(1)} + \frac{2a}{d} \left[\tau \frac{\epsilon a \zeta^2}{6\eta d T} \left\{ (1 + 2n\hat{d}) \frac{E_{-2\hat{d}} - E_{-2n\hat{d}}}{n} + e^{-2\hat{d}} - \frac{e^{-2n\hat{d}}}{n} \right\} - 2S \frac{\epsilon \zeta}{3\eta} \left\{ E_{-n\hat{d}} - E_{-\hat{d}} + \frac{e^{-n\hat{d}} - e^{-\hat{d}}}{n\hat{d}} \right\} \right], \quad (16)$$

with the single-monomer expression

$$D_T^{(1)} = \frac{\epsilon}{3\eta} \left(\tau \frac{\zeta^2}{T} - 2S\zeta \right),$$

the potential $\zeta = \hat{z}e/4\pi\epsilon a$, and the effective valency \hat{z} . We have also defined the reduced monomer distance $\hat{d} = d/\lambda$ in units of the Debye length, and use the shorthand notation for the exponential integral

$$E_x = \text{Ei}(x) = \int_{-\infty}^x \frac{e^{-u}}{u} du.$$

We introduce moreover the dimensionless quantities

$$\chi_\epsilon = \frac{a^2}{d^2} \left\{ (1 + 2n\hat{d}) \frac{E_{-2\hat{d}} - E_{-2n\hat{d}}}{n} + e^{-2\hat{d}} - \frac{e^{-2n\hat{d}}}{n} \right\},$$

$$\chi_S = \frac{2a}{d} \left(E_{-n\hat{d}} - E_{-\hat{d}} + \frac{e^{-n\hat{d}} - e^{-\hat{d}}}{n\hat{d}} \right),$$

and thus obtain the thermophoretic mobility in the form

$$D_T = \frac{\epsilon \zeta^2}{3\eta T} (1 + \chi_\epsilon) \tau - \frac{2\epsilon \zeta}{3\eta} (1 + \chi_S) S. \quad (17)$$

So far we have not specified the effective valency \hat{z} which is a measure for the fraction of uncondensed counterions. For very short chains all counterions remain mobile, and we have $\hat{z} = 1$, whereas for long chains the effective valency takes the value $\hat{z} = \xi^{-1}$, with the Manning parameter $\xi = l_B/d$. In other words, if the linear charge density e/d of a polymer is higher than e/l_B , counterion condensation reduces the effective valency from $1/d$ to the value $1/l_B$. This effect occurs only if $l_B > d$; in the case of weakly charged polymers $d > l_B$, there is no counterion condensation.

Yet this value occurs only for sufficiently long chains. As the number n of molecular units increases there is a crossover of the valency from unity to ξ^{-1} , which is described by

$$\hat{z} = \xi^{-1} + \frac{1 - \xi^{-1}}{1 + \beta_n}, \quad (18)$$

where the quantity β_n is zero for short chains and tends for infinity for long polymers. This crossover constitutes an intricate problem of polyelectrolytes, which is beyond the scope of the present work. Here we use the simple form $\beta_n = (n^2 - 1) n_0^{-2}$, which increases with the square of the molecular length and where the parameter n_0 determines the cross-over length. In principle, n_0 depends on the Debye length. We find that the data shown in Fig. 2) are well described by $n_0 = 80$. A more complex dependency of β_n on n and on the Debye length would slightly modify the decrease of the mobility at high molecular weight, yet would not affect the initial increase.

Debye length λ (nm)	Soret coefficient S_T ($10^{-2}/\text{K}$) at $T = 15^\circ \text{C}$					
	2 mer	5 mer	10 mer	22 mer	50 mer	80 mer
2.2	0.78	1.19	1.86		2.11	3
3	1.03	1.49	2.12	2.86	3.10	3.27
4.2	1.15	1.9	2.7		3.69	4.6
5.2	1.29	1.89	2.89	3.8	5.19	4.8
6.2	1.45	1.89	2.59	4.2	5.79	6.21
7	1.5	1.89	3.2	4.41	5.8	6.31
8	1.43	2.25	3.07	4.44	6.58	6.29
9.7	1.48	2.09	3.4	4	7.1	6.09
11.3	1.45	2.2	3.29		8.81	5.21

TABLE I: Experimental value of ssDNA Soret coefficient in function of the Debye length at the corresponding chain length: 5 monomers, 10 monomers, 22 monomers, and 80 monomers.

Introducing the effective charge \hat{z} and the Bjerrum length l_B in the Eq. (16), one obtains the simple expression for the thermophoretic mobility

$$D_T = \frac{k_B}{12\pi\eta a} \left\{ \hat{z}^2 \frac{l_B}{a} (1 + \chi_\epsilon) \tau + 2\hat{z} (1 + \chi_S) \hat{S} \right\}. \quad (19)$$

Consequently, the overall velocity of the DNA- chain can be written as

$$\mathbf{u} = \frac{\zeta^2}{3\eta} (1 + \chi_\epsilon) \nabla\epsilon + \frac{2\epsilon\zeta}{3\eta} (1 + \chi_S) \mathbf{E}_T. \quad (20)$$

The velocity \mathbf{u} comprises two terms, which are proportional to the permittivity gradient of the solvent and to the electrolyte Seebeck field. These contributions carry different hydrodynamic correction factors χ_ϵ and χ_S . Both vanish in the monomer limit $n = 1$ and increase with the molecular length. In the limit $n \rightarrow \infty$ the coefficients χ_ϵ and χ_S tend towards the values $2\hat{d}E_{-2\hat{d}} + e^{-2\hat{d}}$ and $-E_{-\hat{d}} \approx \ln(\lambda/d)$, respectively.

Due to hydrodynamic interactions, the thermophoretic mobility D_T increases with the chain length, whereas at higher molecular weight, counterion condensation results in a decrease of D_T with n . As a consequence, D_T shows a maximum at some intermediate value n_{\max} , as shown in Fig. 2a.

III. COMPARISON WITH EXPERIMENT

The above theory gives the thermophoretic mobility D_T , whereas experiments often probe the Soret coefficient $S_T = D_T/D$, where the diffusion coefficient $D = k_B T / 6\pi\eta R_h$ is determined by the hydrodynamic radius R_h of the molecule. Fig. 1 shows the measured values of R_h [6]. The values for $n = 10$ and 22 slightly increase with the Debye length, as expected from the increased stiffness in weak electrolytes. The data for $n = 5$ and 50 show a slight decrease and significant scatter. Unfortunately, for such short molecules, there is no simple and generally formula for the hydrodynamic radius.

In order to obtain a rational bases for comparing our D_T to the measured S_T , we have fitted the data to the simple law

$$R_h = R(n) [1 + (\lambda - \lambda_0) / L],$$

where $R(n)$ is taken as an adjustable parameter. We have adjusted this form mainly to the data at $n = 10$ and 22, since they seem to be most reliable in view of what is expected. The theory curves of Fig. 3 are calculated according to $S_T = D_T/D$, with the theoretica expression for D_T and the above fit curve for D . Accordingly, the experimental values in Fig. 2 are obtained from $D_T = DS_T$.

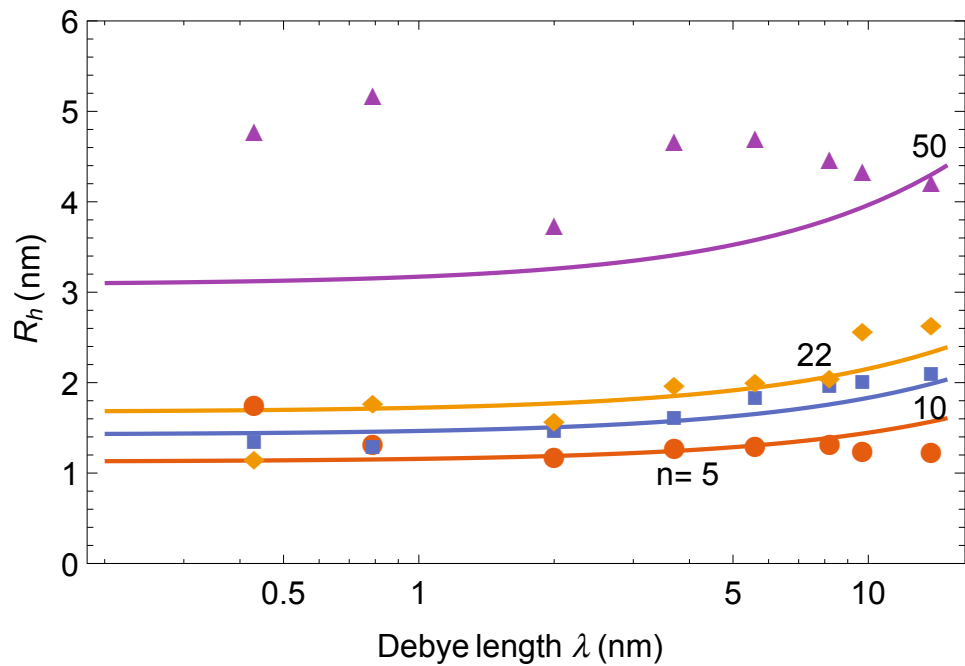


FIG. 1: Variation of the hydrodynamic radius with Debye length and molecular weight. The data points are taken from Ref. [6]. The curves are given by the expression $R_h = R(n)[1 + (\lambda - \lambda_0)/\lambda_1]$. The parameters $\lambda_0 = 7$ nm and $\lambda_0 = 42$ nm are chosen in order to provide a good fit to the measured data. The prefactors are: $R(5) = 1.35$ nm, $R(10) = 1.71$ nm, $R(22) = 2.01$ nm, $R(50) = 3.7$ nm, $R(80) = 4.74$ nm.

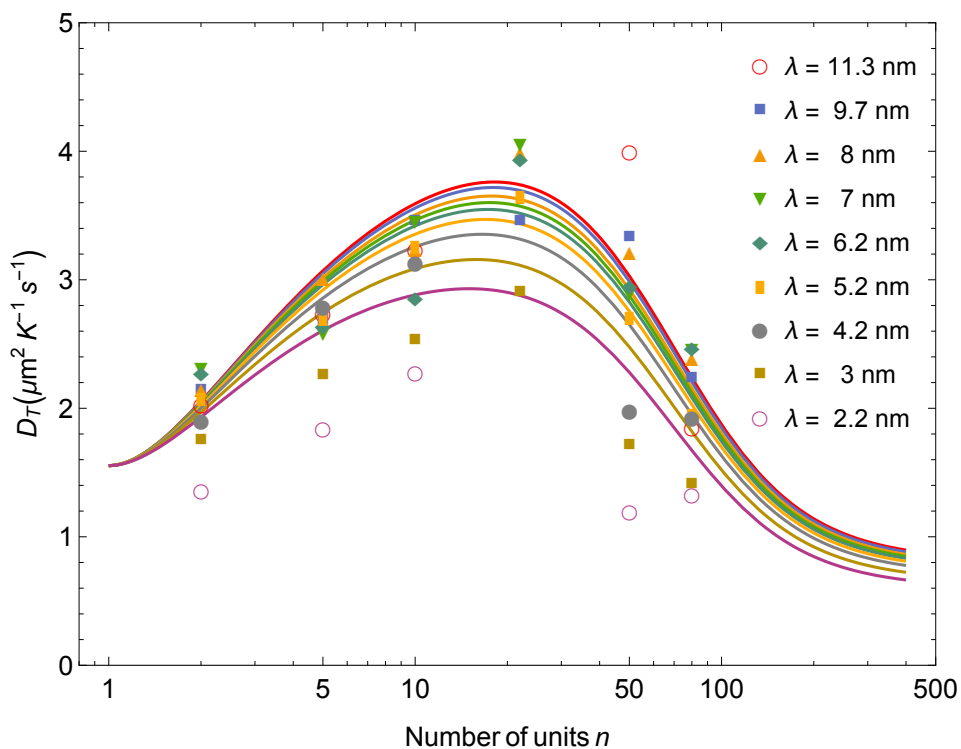
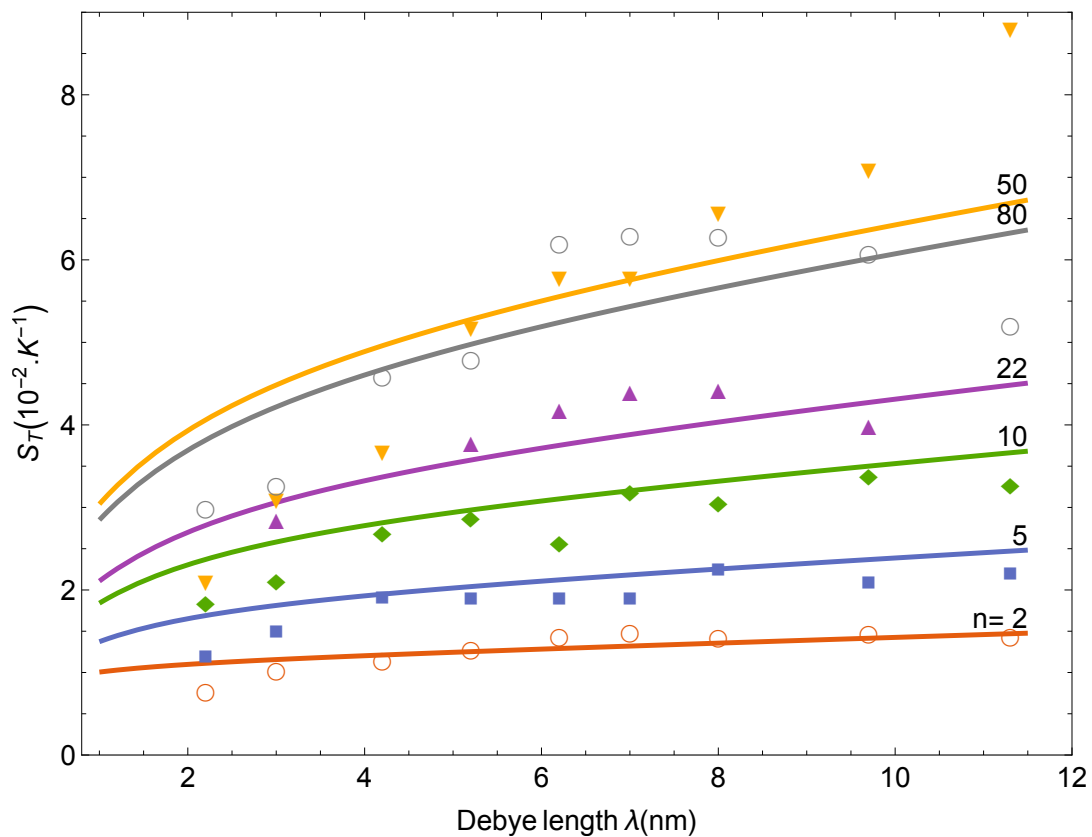
(a) Thermophoretic mobility D_T (b) Soret coefficient S_T

FIG. 2: Variation of experimental and analytical: a) thermophoretic mobility D_T in function of the chain length n . b) Soret coefficient S_T in function of the Debye length λ . The parameters used here for the two graphs are: the monomer's size $a = 4.25\text{\AA}$ and distance between monomer $d = 3\text{\AA}$, the reduced Seebeck coefficient $\hat{S} = 0$.

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