Thermodiffusion and coupled phenomena / Thermodiffusion et phénomènes couplés

Thermophoresis of linear polymer chains

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A R T I C L E   I N F O

A B S T R A C T

The thermophoresis of a linear polymer chain in a solvent is examined theoretically and is shown to be due to the action of two forces. The first one is Waldmann's thermophoretic force (stemming from the departure of the molecular-velocity distribution from Maxwell's equilibrium distribution), which here is extrapolated to a dense medium by using scaling considerations. The second force is due to the fact that the viscous friction varies with position owing to the temperature gradient, which brings a zeroth-order correction to the Stokes law of friction. The present scaling theory is compared with recent experiments and is found to account for: (i) the existence of both signs of the thermodiffusion coefficient; (ii) the absolute magnitude of the coefficient; (iii) the fact that it is independent of the chain length in the high-polymer limit; and (iv) the dependence on solvent viscosity. The variation of the coefficient for short chains is also examined.

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1. Introduction

There is a large body of experimental evidences [1–5] showing that the thermodiffusion coefficient D_T of a polymer chain in a good solvent in the dilute concentration range becomes independent of the polymerization index N in the limit $N \gg 1$. An early theoretical treatment, by Brochard and de Gennes [6], justified that finding on the basis of Onsager's reciprocity theorem between heat and matter transports. Information on matter transport under a temperature gradient was derived from examination of isothermal heat transport. The authors considered the single-particle level which they described in terms of particle and energy *generalized velocities* (in $m\,s^{-1}$ and $J\,m\,s^{-1}$, respectively, in SI units) instead of considering an ensemble of particles usually described in terms of particle and energy *current densities* in non-equilibrium thermodynamical approaches (in $m^{-2}\,s^{-1}$ and $J\,m^{-2}\,s^{-1}$, respectively). However, as shown by Coleman and Truesdell [7], the reciprocity theorem may not retain its usual form when expressed with such unusual variables. We also showed that there is no proportionality between D_T and the particle velocity [8]. Moreover, in [6] the reciprocity theorem provides neither a pictorial view of thermodiffusion nor the dependence on physical parameters other than N.

In this communication, the treatment is revisited at the particle level without the reciprocity theorem, by using de Gennes's scaling methods for a long polymer chain [9] and a specific mechanism for the drift due to the temperature gradient [10]. Sections 2 and 3 are devoted to the velocity response to a deterministic force and to a temperature gradient, respectively. In Section 4, we switch from the picture of motion (thermophoresis) to that of transport (thermodiffusion) in order to confront the theoretical formula to the experimental thermodiffusion findings. Section 5 briefly looks at short chains.

2. The velocity response of a single polymer chain to a deterministic force

In the treatment of [6], the drift velocity $\mathbf{v}_d$ of a single polymer chain through a solvent is written as a linear combination of an external force $\mathbf{f}$ and of the temperature gradient ∇T,
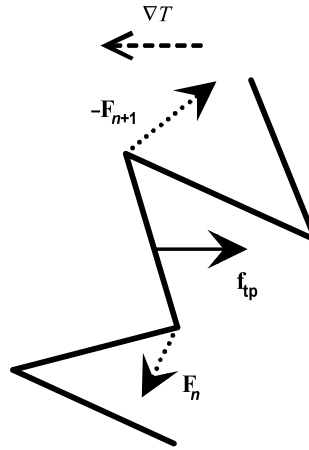
Fig. 1. The polymer chain is a sequence of N rigid rods of length l each. The rods are pictured as slender, i.e. $l \gg a$. The nth rod is subjected to forces $\mathbf{F}_n$ and $-\mathbf{F}_{n+1}$ from the two neighboring rods and to a thermophoretic force $\mathbf{f}_{\mathrm{tp}}$ directed against ∇T.

$$\mathbf{v}_d = \mu \mathbf{f} + L''_{12}(-\nabla T/T) \tag{1}$$

In (1), μ has the meaning of the mechanical mobility of the chain and L''_{12} is a thermophoretic coefficient. In this article, the chain is viewed as a sequence of rigid rods [9,11], of length l (persistence length) and diameter a. The rods are indexed by n ranging from 1 to N, so that N henceforth denotes an effective polymerization index (Fig. 1). Over scales shorter than l the chain is a rigid rod and above l it is a flexible coil. We take the rod as slender, i.e. $l \gg a$, and our formulae are asymptotic, in keeping with the spirit of scaling [9]. The end-to-end distance is determined by the quality of the solvent: in a good solvent the root-mean-square value L scales as $N^{0.6}l$. A scaling relation involving a purely numerical factor of order unity is denoted by $\cong$ instead of $=$. As an example, we write $L \cong N^{0.6}l$. Thereby we do not make a distinction between the persistence length, the Kuhn length and the effective-bond length [5,11,12].

We briefly review the calculation of μ, i.e. the velocity response to a deterministic force $\mathbf{f}$, before considering the response to a thermophoretic force caused by ∇T in Section 3. At a low Reynolds number, the dynamics of each rod is governed by the Stokes law of force balance,

$$\mathbf{f}_n - \mathbf{v}_n/\mu_n = 0 \tag{2}$$

where $\mathbf{f}_n = \mathbf{f}/N$ is the external force acting upon the nth rod, μ_n is the mechanical mobility of the rod and $\mathbf{v}_n$ is the vector drift velocity of the rod relative to the surrounding solvent. Averaging over orientations and dropping a numerical factor $\ln(l/a)$ [13], $\mu_n \cong 1/\eta l$, where η is the solvent viscosity. The inverse mobility $1/\mu_n$ is what Ahlrichs and Dünweg [14] call the *bare friction coefficient*. The Reynolds number is $\rho v_n l/\eta$, where ρ is the mass density of the solvent. Just as $\mathbf{v}_d$, the drift velocity $\mathbf{v}_n$ is a coarse-grained quantity pertinent over time scales much longer than the Zimm time τ of the rod, such that $D_n \tau \cong l^2$ ($D_n \cong kT/\eta l$ is the rod's diffusivity and k is the Boltzmann constant). Taking $\eta \approx 10^{-3}$ Pa s (cyclohexane) and $l = 1.4$ nm, we find $\tau \approx 10^{-9}$ s.

Each rod, when moving through the solvent under the force $\mathbf{f}/N$, creates a back-flow velocity field. Summing up the contributions from all rods, it is found [15] that the velocity field $\mathbf{u}(\mathbf{r}, t)$ of the solvent *inside the coil* does not vanish with respect to the remainder of the solvent outside the coil, which is taken to be at rest in the laboratory frame. The relative velocity $\mathbf{v}_n$ is thus $\mathbf{V}_n - \mathbf{u}(\mathbf{r}_n, t)$, where $\mathbf{V}_n$ is the velocity of the nth rod relative to the laboratory frame and $\mathbf{r}_n$ is the location of that rod. It is found [14,15] that $\mathbf{u}(\mathbf{r}_n, t)$ is nearly equal to the drift velocity of the chain, thereby reducing the friction force $-\mathbf{v}_n/\mu_n$ undergone by the rod. The drift velocity of the chain is that of the center of mass in the laboratory frame,

$$\mathbf{v}_d = (1/N) \sum_{1 \leqslant n \leqslant N} \mathbf{V}_n \tag{3}$$

Summing up the equations of motion (2) of all rods yields that of the chain,

$$\mathbf{v}_d = \mu_n(\mathbf{f}/N) + (1/N) \sum_{1 \leqslant n \leqslant N} \mathbf{u}(\mathbf{r}_n, t) \tag{4}$$

The coefficient of $\mathbf{f}$ in (4) is $\mu_n/N \cong 1/N\eta l$ but the actual equation of motion is [6,15]

$$\mathbf{v}_d = \mu \mathbf{f}, \quad \text{with } \mu \cong 1/\eta L \cong 1/N^{0.6}\eta l \tag{5}$$

Thereby the effect of the back-flow term in (4) is to renormalize the mobility μ by a factor $N^{0.4} \gg 1$ compared to its bare value $1/N\eta l$. That physical picture has been checked in detail in numerical simulations [14,16].

3. The velocity response of a single polymer chain to a temperature gradient

We now come to the response to a temperature gradient in (1). It differs from the response to a deterministic force in two ways. First, the back-flow effects are absent, as noticed by Brochard and de Gennes [6] («les effets de rétrocourant qui contrôlent μ n'ont pas d'influence sur l'effet Soret»). The deterministic force $\mathbf{f}/N$ applied to each rod gave rise to a *directed* flow of solvent $\mathbf{u}$ inside the coil because $\mathbf{f}$ is *static and uniform* (actually, $\mathbf{f}$ may vary over times much longer than the Zimm time of the whole chain and over lengths much larger than L). In contrast, a stochastic force field such as that generated by thermal fluctuations has a very wide spectrum of temporal and spatial frequencies. The standard representation of a stochastic force [17] is a white noise containing the full spectrum of temporal frequencies. This is an idealization, for the force has a finite (albeit very short) correlation time. In the same way, the spatial correlation *length* of a position-dependent stochastic force is finite but extremely short. Virtually all wavevectors are present, so that the back-flow contributions to $\mathbf{v}_d$ add up destructively. A stochastic force field cannot build up a directed contribution to $\mathbf{v}_d$ as appears in (4). The upshot is that mobility is not renormalized by the back-flow ($\mathbf{V}_n = \mathbf{v}_n$).

Secondly, besides the thermophoretic force acting upon each rod as a result of the thermal disequilibrium of the solvent (see below), there exists an effective force $kT\nabla(\ln\mu_n)$ dragging the rod toward locations of larger mobility or smaller friction [10,18]. It is a correction to the drag force, which changes the Stokes law (2) for the nth rod into

$$\mathbf{f}_n - \mathbf{v}_n/\mu_n + kT\nabla(\ln\mu_n) = 0 \tag{6}$$

The effective force arises because the random kicks of the thermal bath do not average out to zero but are biased towards larger values of μ_n. Expression $kT\nabla(\ln\mu_n)$ of the differential friction force was derived for a Brownian particle (i.e. much heavier than the molecules of the medium), using the theory of Brownian motion [10,18]. In keeping with the ladder of scales $a \ll l \ll L$ underlying the present work, we shall therefore use expression $kT\nabla(\ln\mu_n)$ valid for Brownian particles. In the experimental examples [5], the rod is heavier than the solvent molecules as the Kuhn length is made up of 6–12 monomers.

We now have to specify the force $\mathbf{f}_n$ undergone by the nth rigid rod. First, the rod undergoes forces from its two neighbors: if we denote by $\mathbf{F}_n$ the force exerted by the $(n-1)$th rod on the nth rod, the latter will exert a force $\mathbf{F}_{n+1}$ on the $(n+1)$th rod (Fig. 1). Those forces were tacitly disregarded in [6,15] for reasons which will become clear shortly. Secondly, because of the temperature gradient the medium is not in equilibrium around the rod. When the medium is a rarefied gas, the disequilibrium gives rise to a net force upon the rod due to the non-canceling impacts of fast and slow molecules. The impacts should not be calculated as Einstein did [19]. When performed properly, such a calculation delivers zero in the absence of a pressure gradient [20]. Waldmann showed [21] that, because the gas is not in equilibrium, the mechanical action of the molecules does not reduce to the sum of the pressure forces. There is an extra force, called the thermophoretic force and henceforth denoted as $\mathbf{f}_{tp}$, due to the anisotropy in the molecular-velocity distribution function. Fast and slow molecules depart from Maxwell's local-equilibrium distribution in different ways. Their departure from equilibrium is beyond reach of thermodynamics and involves the product of ∇T and of the molecular mean free path λ of the rarefied gas. Denoting by n_2 the number density of gas molecules and by σ_t the momentum-transfer cross section of the rod, we have [10]

$$\mathbf{f}_{tp} \cong -n_2\sigma_t\lambda\nabla(kT) \tag{7}$$

The minus sign is the one pertinent for scattering of monatomic molecules with a hard sphere [21]. The general expression of $\mathbf{f}_{tp}$ [10] suggests that both signs are possible, depending on the energy dependences of both the molecule-particle cross section and the non-equilibrium energy distribution. Polyatomicity affects the shape of the latter distribution so as to alter the numerical prefactor in (7). However, because of the presence of a density-of-states factor favoring faster molecules [10] in the scattering integral defining $\mathbf{f}_{tp}$, it is likely that the numerical prefactor retains its negative sign.

For a hard rod, instead of the hard sphere envisaged by Waldmann, $\sigma_t \cong al$, where a is a molecular dimension typifying the rod's diameter (we are using a geometrical, energy-independent cross section). In a liquid medium, (i) molecules are polyatomic instead of monatomic and (ii) the simple picture of two-body collision events is not accurate. Yet, in keeping with the scaling approach taken in this communication, we shall extrapolate Waldmann's result in the crudest way, letting $n_2 \cong 1/a^3$ and $\lambda \cong a$. We thus get $\mathbf{f}_{tp} = -\alpha_{tp}\nabla(kT)$ with a thermophoretic force coefficient

$$\alpha_{tp} \cong l/a \tag{8}$$

Note that $\mathbf{f}_{tp}$ is the same on all rods because we are considering a coarse-grained description over a time scale enabling random disorientation of each rod with respect to the vector ∇T. Disorientation modifies $\sigma_t \cong al$ so as to introduce a geometrical factor of the order of unity, not considered here.

The upshot of all this is that the force undergone by the nth rod is

$$\mathbf{f}_n = \mathbf{F}_n - \mathbf{F}_{n+1} + \mathbf{f}_{tp} \tag{9}$$

where the minus sign stems from Newton's third law. From expressions (6) and (9), we get the velocity of the center of mass (3):

$$\mathbf{v}_d = \mu_n\big[((\mathbf{F}_1 - \mathbf{F}_{N+1})/N) + \mathbf{f}_{tp} + kT\nabla(\ln\mu_n)\big] \tag{10}$$

The forces $\mathbf{F}_1$ and $\mathbf{F}_{N+1}$ are loose end effects: the beginning of the first rod and the end of the last rod do not undergo a force from another rod, but from the solvent. In the limit $N \gg 1$ of a long chain, (i) end effects are negligible, which is why they were disregarded a priori in [6] and [15], and (ii) the drift velocity

$$\mathbf{v}_d \approx \mu_n \big[\mathbf{f}_{\mathrm{tp}} + kT\nabla(\ln \mu_n) \big] \tag{11}$$

does not depend on N. However, the measured quantity is not the drift (or thermophoretic) velocity, but the thermodiffusion coefficient D_T which is defined together with the diffusivity D by means of a particle-current equation, and this is dealt with in the next section.

4. From thermophoresis to thermodiffusion

There is no simple proportionality between the particle drift velocity and the particle current density, as the former is a vector whereas the latter is a vector *field*. The transport of a chain through the solvent consists of drift and diffusion. Drift refers to the rate of change of the vector displacement $\langle \mathbf{r} \rangle$, with $\langle \cdot \rangle$ denoting an ensemble average, while diffusion refers to the rate of change of variance in $\mathbf{r}$. This picture holds when the chain is very dilute among the solvent molecules which make up the reference frame. Otherwise diffusion should be understood as *mutual diffusion* in a binary mixture, and the simple kinematic picture of diffusion used here would not hold [22]. Specifically, the diffusivity can be defined here as

$$D = (1/6)\big(\mathrm{d}\langle(\mathbf{r} - \langle\mathbf{r}\rangle)^2\rangle/\mathrm{d}t\big) \tag{12}$$

starting from an ensemble of particles sharply localized at $\mathbf{r}_0$. In an inhomogeneous medium, D is a function of position $\mathbf{r}_0$. Here, inhomogeneity is due to the $T(\mathbf{r})$ field.

The rate of change of the chain's number density n (not to be confused with the rod index used in Sections 2 and 3) is the negative divergence of the particle-current density $\mathbf{j}$. In the theory of stochastic processes [17,23], $\mathbf{j}$ is given by

$$\mathbf{j} = \mathbf{v}_d n - \nabla(Dn) \tag{13}$$

The first contribution to $\mathbf{j}$ stems from the motion of the centroid $\langle \mathbf{r} \rangle$ whereas the second one is associated with the spreading about $\langle \mathbf{r} \rangle$. The contributions are sometimes known as orthokinetic and perikinetic, respectively [24]. It is straightforward to rewrite $\mathbf{j}$ as

$$\mathbf{j} = (\mathbf{v}_d - \nabla D)n - D\nabla n \tag{14}$$

Identifying $\mathbf{j}$ with its phenomenological expression $-D\nabla n - nD_T\nabla T$ relates the thermodiffusion coefficient D_T to the thermophoretic velocity,

$$D_T(-\nabla T) = \mathbf{v}_d - \nabla D \tag{15}$$

An alternative demonstration of (15) can be found elsewhere [8].

For a long polymer chain, it is well established [6,15] that $D = kT\mu \cong N^{-0.6}kT/\eta l$. It vanishes as $N \to +\infty$. From relations (11) and (15), we have in that limit

$$D_T(-\nabla T) = \mu_n \big[\mathbf{f}_{\mathrm{tp}} + kT\nabla(\ln \mu_n) \big] \tag{16}$$

Using the thermophoretic force coefficient α_{tp} and mobility μ_n of a rod, we obtain

$$D_T \cong k/(\eta l)\big[\alpha_{tp} + \big(\mathrm{d}\ln(\eta l)/\mathrm{d}\ln T\big) \big] \tag{17}$$

That formula shows that D_T is independent of N, in agreement with experiments [1–5]. D_T is the sum of two contributions: one is due to the thermophoretic force acting upon each rod, with a coefficient $\alpha_{\mathrm{tp}} \cong l/a$ roughly ranging from 6 to 12, and the other is due to the temperature dependence of ηl. The first contribution is positive whereas the second one is negative: both viscosity and the persistence length drop as T increases. Table 1, after [25], lists values of $(\mathrm{d}\ln\eta/\mathrm{d}\ln T)$ under standard conditions in some solvents; they lie about -4. An estimate [11,12] of $(\mathrm{d}\ln l/\mathrm{d}\ln T)$ is -1, but it can be more negative in molecular models [26] where the flexural rigidity may depend on T. Therefore the two contributions in (17) have the same order of magnitude (a few times unity) *but* different signs. Depending on the polymer/solvent system studied, D_T may be positive or negative, but a positive D_T is more likely. This accounts for the opposite signs of D_T observed in polystyrene and n-alcane solutions. A stiffer chain has a larger $\alpha_{\mathrm{tp}} \cong l/a$ but a lower k/l so that D_T is not strongly sensitive to stiffness. The typical magnitude of $\eta|D_T|$ expected from (17) is k/l, which is hardly dependent on the solvent viscosity η. Taking $l = 1.4$ nm yields $\eta|D_T| \cong 10^{-14}$ J K^{-1} m^{-1}, in line with the values actually measured for long chains, namely 0.6×10^{-14} J K^{-1} m^{-1} for polystyrene in various solvents and -0.5×10^{-14} J K^{-1} m^{-1} for n-alcane in cyclooctane [5].

Because our approach rests upon scaling considerations, it cannot predict numerical factors of order unity, which are sensitive to the very chemical microstructure, reminiscent of two-body scattering cross sections which are molecule-dependent, and practically speaking lie outside the realm of analytical theories of the liquid state. However, our approach does predict

Table 1
Temperature dependence of dynamical viscosity η under standard conditions in various solvents, after [25].

Solvent	$(d \ln \eta / d \ln T)$
Chloroform $CHCl_3$	−3.1
Tetrahydrofuran C_4H_8O	−3.2
Ethylacetate $C_4H_8O_2$	−3.6
Ethylbenzene C_8H_{10}	−3.7
Toluene C_7H_8	−3.8
Cyclooctane C_8H_{16}	−4.2
Cyclohexane C_6H_{12}	−4.5

universal trends such as (i) the absolute magnitude of D_T, (ii) the existence of two signs reflecting the existence of two forces (thermophoretic force and differential friction) and (iii) the fact that $\eta|D_T| \approx k/l$ does not significantly depend on the solvent. While the latter feature is conspicuous for polystyrene [4,5], the fact that a long chain of n-alcane exhibits $\eta D_T = +0.087 \times 10^{-14}$ JK^{-1} m^{-1} in toluene, instead of -0.5×10^{-14} JK^{-1} m^{-1} in cyclooctane, is consistent with (17) since both α_{tp} and $[d \ln(\eta l)/d \ln T]$ change with the solvent used. The replacement of cyclooctane by toluene increases $(d \ln \eta / d \ln T)$ (see Table 1) and therefore D_T, in line with the observation. It is not expected to change $(d \ln l/d \ln T)$ significantly, but the change in α_{tp} is hard to guess.

5. Short chains

Scaling considerations have proved their efficiency in the case of long chains but sometimes yield a fair result near the limit of validity [9], i.e. $N = 1$. A chain of length l has a drift velocity given by (10) instead of (11). Let us temporarily ignore the force $\mathbf{F}_1 - \mathbf{F}_{N+1} = \mathbf{F}_1 - \mathbf{F}_2$ in (10). Then the variation of D_T with N is only due to the non-proportionality (15) between D_T and $\mathbf{v}_d$. Denoting by $D_{T,N}$ the D_T of a chain of N persistence lengths, we obtain

$$D_{T,1} = k\mu_n [\alpha_{tp} + d \ln(\eta l)/d \ln T] + d(kT\mu_n)/dT = k\mu_n(\alpha_{tp} + 1) \tag{18}$$

We have recovered the usual relation between D_T and the force coefficient α_{tp} pertinent to a particle sufficiently dilute in a medium for the mixture to be thermodynamically ideal [10,20]. The fact that $[d \ln(\eta l)/d \ln T] \approx -4$ (for $N \gg 1$) in (17) is replaced by 1 (for $N = 1$) in (18) means an algebraic decrease in $D_{T,N}$ as N increases. The expected relative variation is

$$(D_{T,\infty} - D_{T,1})/D_{T,\infty} = -[1 - (d \ln(\eta l)/d \ln T)]/[\alpha_{tp} + (d \ln(\eta l)/d \ln T)] \tag{19}$$

Numerically, this is roughly −100% if $\alpha_{tp} = 10$. The opposite behavior is actually observed, with $D_{T,N}$ algebraically *increasing* as N increases [5]. This means that we may not ignore end effects. It should be remarked that, in using the same α_{tp} in (17) and (18), we have also ignored end effects in the expression of Waldmann's thermophoretic force for $N = 1$. Likewise, using the same μ_n for long and short chains is open to criticism. However, the calculation (19) shows that the non-proportionality between thermodiffusion and thermophoresis has the same order of magnitude (albeit with a different sign) as the observed difference between the D_T of a short and a long chain. Therefore the non-proportionality between $\mathbf{v}_d$ and D_T cannot be ignored in interpreting the behavior of short chains.

6. Conclusions

In this communication, we have theoretically investigated the velocity response of a flexible polymer chain in a good solvent to a temperature gradient, by breaking up the flexible chain into rigid rods, each of which is treated as a Brownian particle. The response has been pictured as the upshot of two forces. One is due to the anisotropy in the molecular-velocity distribution function when the solvent is subjected to a temperature gradient; it is Waldmann's thermophoretic force in a rarefied gas, here scaled down to the molecular mean free path. The other force is the differential friction, which is the correction to the Stokes friction force caused by the temperature gradient. The first force is thermophobic whereas the second is thermophilic but frequently weaker. Whereas a deterministic force is uniform and static, the force field due to thermal fluctuations is spatiotemporally uncorrelated and unable to generate back-flow effects. The main features observed in experiments (e.g. $\eta|D_T| \approx 10^{-14}$ JK^{-1} m^{-1} is little dependent on η and independent of $N \gg 1$) are reproduced qualitatively without adjusting parameters. The treatment has used scaling relations omitting numerical prefactors but keeping all dimensional factors. The prefactors are system-dependent and their values are unlikely to be calculable analytically. The same was already true of thermodynamic quantities in polymer physics [9] and we have found no argument suggesting that kinetic quantities could be easier to calculate than thermodynamic ones. Finally, for a short chain the difference between thermophoresis and thermodiffusion is of the same order of magnitude as the experimental variation in D_T and thus cannot be ignored in interpreting the observations.

Acknowledgements

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