Thermophoresis of polymers by non-isothermal dissipative particle dynamics

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1 Introduction

In presence of a temperature gradient, a concentration gradient of particles can be built up. This phenomenon is called thermodiffusion, thermophoresis or Ludwig-Soret effect [6, 5]. A encompass theory for thermophoresis still lacks so system-specified simulations are widely used to explore the filed. Multi-scale computer simulations, such as molecular dynamics simulation and hydrodynamics simulation, were used to study system exhibt thremophoresis[2]. However, MD simulation is computational expensive while hydrodynamic simulation coarse-grained microscopic details of the molecules. Dissipative particle dynamics (DPD) simulation, as an mesoscopic method, can achieve satisfactory compromise between speed and retaining molecular structural details . Therefore, non-isothermal DPD is a powerful tool to tackle thermophoresis when the molecular-level dynamics need to be taken into account[3].

Thermophoresis can be characterized by a phenological thermophoretic flux, J_{tp}, in addition to the Fick's diffuse flux J_{diff}. The total mass flux in a temperature gradient driven system is

$$J_{\text{tot}} = J_{\text{tp}} + J_{\text{diff}} = -D_T c \nabla T - D \nabla c, \qquad (1)$$

where D_T is called thermodiffusion constant and D is the diffusion constant. A wildly used quantity to characterize thermophoresis is the Soret coefficient, which is defined as $S_T \equiv \frac{D_T}{D}$. When the system reaches a steady state, the total flux is zero and we find

$$S_T = -\frac{\nabla c^{\text{ss}}}{c^{\text{ss}} \nabla T} = -\frac{\nabla \ln c^{\text{ss}}}{\nabla T}. \qquad (2)$$

where c^{ss} is the steady-state concentration distribution. Positive S_T indicates that the particle is thermophobic, while negative S_T is for thermophilic particles.

1.1 Models of thermophoresis

Thermophoresis of ideal gas One simple example of thermophoresis is the ideal gas. Ideal gas is governed by the state equation, $PV = nRT$. When a temperature gradient is applied to a box of ideal gas, the pressure of the system should be constant in the steady state, which gives a temperature-dependent of concentration.

$$c(x) \equiv \frac{n}{V} = \frac{P}{RT} \qquad (3)$$

From this concentration distribution, one can find the Soret coefficient, by definition, as $S_T = \frac{1}{T}$ and see that gas particles tends to accumulate in the cold region.

Internal state induced thermophoresis Recently, Liang et. al. showed internal degrees of freedom of a molecule can contribute to thermophoresis[3]. Let us suppose we have a molecule with multiple internal states and an internal state has its own energy and transport property. A multi-state particle under a certain temperature has an effective diffusion coefficient $D_{\text{eff}} = \langle D_i \rangle$ where $\langle \cdot \rangle = \sum_{\text{all states}} D_i e^{-E_i/k_B T}$. The temperature can

shape the probability distribution in the internal space by the Boltzmann factor e^{-E_i/k_BT} and gives a temperature-dependent effective diffusion constant. The total flux of the system is thus

$$J = -\nabla(cD_{\text{eff}}) = -\nabla D_{\text{eff}} c - D_{\text{eff}} \nabla c \tag{4}$$

The first term tends to bring the particles to the slow-diffusion region, and the second term tends to flatten the concentration distribution. In comparison with Eq. 4 one can find the thermodiffusion coefficient as $D_T = \nabla_T D_{\text{eff}}$. And the Soret coefficient is thus

$$S_T \equiv \frac{D_T}{D} = \nabla_T \ln D_{\text{eff}} \tag{5}$$

1.2 Dissipative particle dynamics

Dissipative particle dynamics (DPD) is a mesoscopic scale simulation method, which provides a much faster implementation than molecular dynamics. DPD is described by the following equations of motion[4]

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v_i}, \quad \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i = \mathbf{f}_i^{\text{int}} + \mathbf{f_i}^{\text{ext}} \tag{6}$$

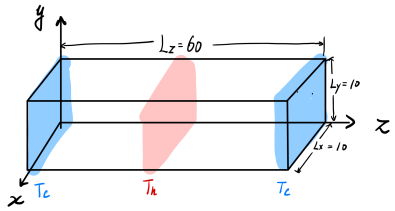
where the force can be split into the internal part and external part. The inter-particle interaction can be further divided into a conservative force F_{ij}^C, a dissipative forceF_{ij}^D and a random force F_{ij}^R. The conservative force is often given as a soft repulsive force.

$$\begin{aligned} \mathbf{F}_{ij}^C &= a_{ij} w^C(r) \hat{\mathbf{r}}_{ij}, \\ w^C(r) &= \begin{cases} (1-r) & r < 1.0 \\ 0 & r \geq 1.0, \end{cases} \end{aligned} \tag{7}$$

where the conservative parameter a_{ij} identify the strength of the conservative force. Larger a_{ij} means larger repulsive interaction between particle j and particle i. A temperature gradient can be introduced into a DPD simulated system by modifying the random force to the corresponding local temperature. Hence, we get a non-isothermal DPD simulation method.

2 Simulation

In the simulation, we used the same conservative parameter a_{ij} for all beads, which means all beads have the same chemical properties. The difference between polymers and water beads is the shape. A polymer is made of multiple beads connected in a row, while a water molecule is a single bead.



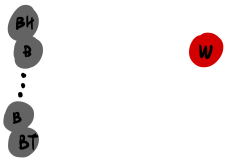


Figure 1: Simulation setup.

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Polymer Water    0.8 " (W) "
Polymer Spring   0.1  " (BH (n B) BT) "
Polymer MWater   0.1  " (B) "
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The above code box shows how the molecules are created. Water molecule is defined as a single bead polymer (W), a polymer is a chain (BH (n B) BT) of length $n + 2$ and the MWater is used to track the distribution of water.

The simulation box is of size $10 \times 10 \times 60$ ($x \times y \times z$). A temperature gradient is set up along z axis symmetrically: high temperature T_h in the middle and low temperature T_c at two ends of the box. The transition of temperature from hot to cold regions is linear. Using the simulation, we studied how does the non-uniform distribution affected by the controlled physical quantities, such as forces applied on two ends of a polymer, length of the polymer, and the strength of the temperature gradient.

The tricky part of the simulation is the relaxation time. In the initial state, the polymers are not uni-

formly distributed but more concentrated in the center of the simulation box. What are we interested is the steady-state and thus we need to wait enough time before measuring the system. To identify the relaxation time, we took equilibrium DOP simulation and find after t 10^5, the distribution of polymers is uniform. Therefore, for non-isothermal DPD, the measurement is taken after $t = 1.5 \times 10^5$.

3 Results

3.1 Temperature dependence of Soret coefficient

For the first case, we put a polymer of length $L = 3$ in different temperature gradients. Which can show how does the T-gradient strength change the thermophoretic properties.

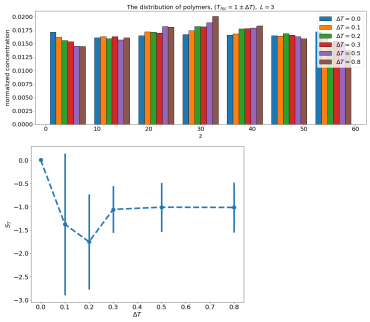


Figure 2: Thermophoresis of polymers under various temperature gradients.

In Fig. 2, we can see more significant non-uniform distribution in larger gradient cases. This is apparent since we have the concentration gradient proportional to the temperature gradient, given by the phenomenological relation $\nabla c^{\mathrm{ss}} = -c^{\mathrm{ss}} S_T \nabla T$. But does the Soret coefficient depend on the T-gradient? According to Fig. 2, we see the Soret coefficient is almost constant with respect to non-zero ΔT, from which we can state that the Soret coefficient is independent of the T-gradient for polymers.

3.2 Size dependence of Soret coefficient

How does the size of a particle affect its thermophoretic properties is always a hot topic in the field of thermophoresis[1]. Using non-isothermal DPD, we can check the thermophoretic behaviors of polymers of different lengths.

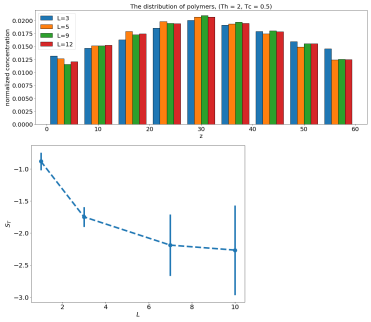


Figure 3: Thermophoresis of polymers of different lengths.

In Fig. 3, we see the concentration distributions of shorter polymers ($L = 3$ or 5) are flatter than others. The length-dependence of thermophoretic behavior can be more clearly shown by calculating the Soret coefficient. As shown in Fig. 3, longer polymers have larger Soret coefficients, and it shows an asymptotic trend: the Soret coefficient of polymer tends to a constant value with increasing of its length. This result agrees with what has been observed in real systems, that the Soret coefficient of long polymers chain does not depend on the length[7].

3.3 Stretched polymers

In all the above results, we see a free polymer chain can exhibit thermophoresis. Using the internal-state theory to explain, we can say that the configuration space of the polymer can be regarded as the internal space, and different configurations have different transport properties. One simple way to shows this is by checking the end-to-end distance of a polymer under different temperatures.

In Fig. 4, we see the end-to-end length of a polymer has temperature dependence. At low tempera-

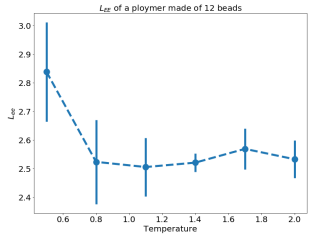


Figure 4: End-to-end length of polymers under different temperatures.

ture, a polymer has larger end-to-end distance which makes it diffuse slower according to Stokes-Einstein law. This temperature-dependent diffusivity can give raise to thermophoresis. Note that this estimation is oversimplified since we only take into account a statistical quantity, L_{ee}, and drop out the microscopic details of the configuration of polymer. But this analysis can give us some insights on how does the internal state of a particle change its transport property.

To further explore the role of the internal states of a polymer on thermophoresis, we applied forces on the two ends of polymer to stretch it. A stretched polymer should respond to the temperature and shows a more significant temperature-dependent shape. Two cases are studied: applied force perpendicular to the temperature gradient and parallel to the temperature gradient.

In Fig. 5, we can see stretching forces perpendicular to the gradient do not change the polymer's thermophoretic property much. However, the parallel force on the polymer significantly increases the Soret coefficient. One possible explanation is that parallel force can change the diffusion constant of the polymer more significant and thus results in a larger Soret coefficient, while a perpendicular force won't change the particles cross-section in x-y plane (the temperature is along z axis). In the center of the box, high temperature leads to a larger entropic spring constant so that polymers in the middle is less stretched along z-direction than the polymers in the two cold ends. A less stretched polymer has a larger cross-section in x-y plane and thus diffuses slower. Therefore, with parallel forces applied, polymers diffuse slower when they are in the hot center and faster at the cold ends,

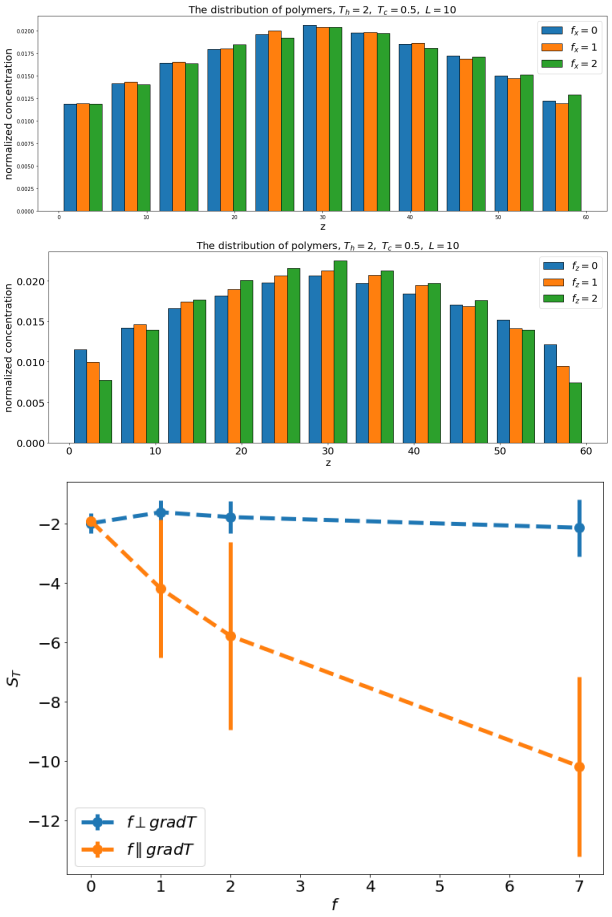


Figure 5: Thermophoresis of stretched polymers.

which will lead to a larger Soret coefficient.

4 Conclusions

In this report, we used non-isothermal DPD to study the thermophoresis of polymers. The non-isothermal DPD results agree with the experiment results. Therefore, we can state that DPD it is a powerful tool to study thermophoresis of molecular with internal structures. The stretched polymer simulation qualitatively matches with what is predicted by the internal-state thermophoresis model. Further study can be done to check if the internal-state

thermophoresis model can quantitatively predict the stretched polymers' thermophoresis.

References

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