令和４年度 修士学位論文

形態自由度に着目した高分子溶液における
ソーレ効果の理論解析

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Abstract

In dilute polymer solutions under temperature gradients, mass fluxes are induced by the Soret effect. This phenomenon is called the Soret effect. In this study, I discuss the influence of the conformational degrees of freedom of polymer. I construct a molecular theory with the conformational degrees of freedom. For the sake of simplicity, I model a polymer as a dumbbell, where two particles are connected by a spring. I derive the Fokker-Planck equation for center of mass to obtain the Soret coefficients S_T^*. The molecular theory reveal that this quantity is independent of the spring constant. Further, I conduct molecular simulations. The simulations revealed that S_T^* takes almost the same value independent of the spring constant when the mass ratio is large. This result means that conformational degrees of freedom does not affect the mass flux. In contrast, when the mass ratio is small, depending on the spring constant, the Soret coefficient alters its sign due to the modification in the distribution of conformational degrees of freedom and motion of the dumbbell.

Contents

Chapter 1

Introduction

1.1 Transport phenomena

Let us consider a macroscopic non-equilibrium three-dimensional system where several fluxes are induced by thermodynamic forces. For instance, I can observe several fluxes such as the mass flux, energy flux and so on under temperature gradient. In such an environment, mass and heat move from warmer to colder places. These phenomena are so called the transport phenomena.

1.2 Soret effect

In this study, I focus on the mass flux under temperature gradient. A concentration gradient is induced by a temperature gradient for some binary mixtures of fluids due to the mass transfer[1]. This phenomenon is the so-called thermodiffusion or the Ludwig-Soret effect being characterized by the Soret coefficient S_T defined as follows.

$$S_T = \frac{1}{c(1-c)} \frac{\partial T(x)}{\partial x} \bigg/ \frac{\partial c(x)}{\partial x}.. \tag{1.1}$$

Here, $T(x)$ at x is the temperature field, $c(x)$ at x is the volume fraction of one component and c is the spatial average of $c(x)$. One of the fluids moves to the cold side when S_T is positive, whereas it moves to the hot side when S_T is negative. I sometimes encounter the another definitions of Soret coefficient α_T and S_T^* as follows.

$$\alpha_T = \bar{T} S_T, \tag{1.2}$$

$$S_T^* = c S_T, \tag{1.3}$$

where $\bar{T}$ is the spatial average in entire system of $T(x)$. I call α_T as dimensionless Soret coefficient. I employ α_T because the Soret coefficient is proportional to the $1/\bar{T}$. In another systems, I sometimes encounter the S_T^*. In particular, the S_T^* is employed in the colloid systems. In the colloid systems, I make coarse-grained and consider the solvent motion as noise. In this way, when I focus only on the motion of one component, the S_T^* is useful.

1.3   Previous studies about the Soret effect

In binary gases, Chapman and Enskog[2] theoretically derived S_T. When they derive the S_T, they assume the rigid body collisions. The theory has been experimentally found out by Chapman and Dootson[3], Blüh et al.[4], and Ibbs et al.[5].

Historically, many experiments have been conducted in liquids mixtures[6, 7, 8, 9, 10, 11]. For example, Tanner[7, 8], Prigogine et al.[9, 10] and Saxton et al.[11] studied in organic liquids. Korsching et al.[12] studied a sequence of experiments on isotope separation.

Various theoretical and numerical studies have been reported to explain the experimental data of Soret coefficients. For example, molecular dynamics (MD) simulations are effective to study the Soret coefficients of liquids[13, 14]. In MD simulations, there are two different methods to calculate the Soret coefficient. One is the non-equilibrium MD (NEMD) simulation method, in which a temperature gradient is applied to the system. The Soret coefficient can be calculated without phenomenological assumptions. Reith and Müller-Plathe [15], and Galliero et al [16, 17] utilized the RNEMD method to realize the temperature gradient RNEMD method reverses the usual cause-and-effect picture of nonequilibrium simulations. Heat flow is artificially maintained by exchanging velocities of selected particles to realize the temperature gradient. From this method, they can directly calculate the Soret coefficient. With such a RNEMD simulation, they report the particles with a larger mass move toward the colder region on the binary mixtures of Lennard-Jones(LJ) liquids. Apart from these NEMD simulations, an equilibrium molecular dynamics (EMD) simulation has been used. The Soret coefficient is calculated from the linear response theory in equilibrium[18]. Hoheisel and Vogelsang[19] conducted a systematic study of the Soret coefficient and they indicate what kind of particles move to the low-temperature side.

Another way, thermodynamic and phenomenological models have been developed. In such phenomenological models[20, 21, 22, 23, 24, 25, 26, 27, 28, 29], the Soret coefficient is expressed by the macroscopic thermodynamic quantities such as the heat of transport and the molar enthalpy. However, its physical mechanisms are still not understood completely due to the strong correlation between molecular collisions.

1.4   Previous studies about the Soret effect in polymer solution

I usually treat the molecules as rigid with no conformational degrees of freedom. However, polymers are examples of molecules that have large conformational degrees of freedom. It was experimentally reported[30] that the Soret coefficient S_T of the dilute polymer solutions changes with the molecular weight. The Soret coefficient is positive and satisfy the power low of molecular weight when the molecular weight is large. In this way, the Soret coefficient of polymer with large conformational degrees of freedom is positive. However, Giglio and Vendramini[31]

reported that a negative Soret coefficient for a polymer dissolved in water. Kita[32] reported that the Soret coefficient of polymer in various aqueous solutions changes its sign depending on the water fraction due to the influence of hydrogen bonds. Thus, the Soret coefficient of polymers is generally positive, but is is negative in systems with strong interactions.

To understand this phenomenon, several workers have developed a hydrodynamic/Brownian motion thermodiffusion models[27, 33, 34, 35]. For instance, Würger[27] derived the Soret coefficient in the framework of non-equilibrium thermodynamics and reported that is proportional to the difference in partial enthalpy per volume. Brenner[34] derived the Soret coefficient considering the thermal expansion coefficient. These models are successful in predicting the experimental data, but usually contain fitting parameters that are not easily determined or even well understood. In contrast, another approach is based on linear nonequilibrium thermodynamics and the concept of the net heat of transport. This model[36] predicts experimental data qualitatively if the net heat of transport is properly simulated.

Although some theoretical studies on the Soret effect of the polymer systems have been reported, the microscopic mechanism remains unclear even the system without the strong interaction. This is due to the large conformational degrees of freedom of polymer. To understand the effect of conformational degrees of freedom on the Soret coefficient, Araki and Chikakiyo[37] numerically studied the Soret effect in the dimer-monomer mixtures. They reported that the conformational degrees of freedom of the molecules can contribute significantly to the Soret effect. Although their system does not directly apply to the polymer solutions, I can expect that the Soret coefficient of polymer is sensitive to the conformational degrees of freedom.

1.5 Purpose and constitution

As I explained above, the effect of the conformational degrees of freedom on the Soret effect is not fully understood. In this work, I simply model a polymer as a dumbbell which consist of two particles connected by a bond potential. I assume that the bond potential is a harmonic potential for simplicity. I consider the dynamics of a single dumbbell molecule under a small and linear temperature gradient. I calculate the alternative definition of Soret coefficient $S_T^* = S_T/\phi$[38]. Here, ϕ is a volume fraction of one of the components. To see the effects of the conformational degrees of freedom on the Soret coefficient, I work on theoretical analysis and molecular dynamics simulation.

In chapter 2, I construct a molecular theory. I consider the underdamped Langevin equation for a dumbbell. Here, I express the temperature as the function of position in an inhomogeneous temperature environment. I derive the approximate Fokker-Planck equation for the center of mass position of dumbbell by using three assumptions. Firstly, I assume that the momentum relax so quickly. Secondary, I assume that the distribution of bond vector rapidly approaches to the

local equilibrium distribution. Finally, I assume the bond potential is a harmonic potential. I derive the Soret coefficient from approximate Fokker-Planck equation for the center of mass position of dumbbell at the steady state.

In chapter 3, I explain the methods of the nonequilibrium molecular dynamics simulation (NEMD) and perform NEMD simulations in dumbbell-monomer mixture. I calculate the temperature field and the probability distribution for the center of mass position of dumbbell. I observe the Soret coefficient from the ratio of gradients of these quantities.

Chapter 2

Dumbbell obeying Langevin equation

In this chapter, I derive the Soret coefficient theoretically. Firstly, I explain the coarse-grained level before the introduction of model. In general, the particles obey the Hamiltonian dynamics if I do not make coarse-grained. However, it is difficult to consider the dynamics of polymer without coarse-grained due to the difference of time scale of motion between polymer and solvent. Thus, I make coarse-grained the Hamiltonian dynamics and employ the Langevin dynamics. In this dynamics, the solvent is expressed as noise and the polymer are subjected to force induced by chemical potential $\Phi(\boldsymbol{R})$. In this work, I simply model a polymer as a dumbbell.
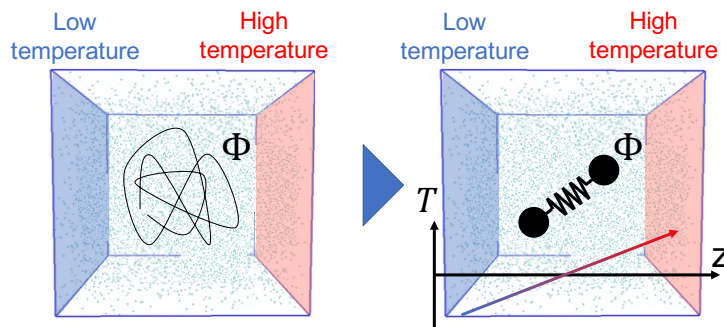

Figure 2.1: The system in this study

2.1 Model

I consider dynamic equations for a dumbbell model in an ihnomogeneous temperature environment. I model a dumbbell as a two particles connected by a bond potential. I assume the dumbbell are subjected to force induced by chemical potential gradient. The temperature is not spatially homogeneous, and I express the inhomogeneous temperature field as $T(\boldsymbol{R})$. Here, $\boldsymbol{R}$ is the position. If I assume that the particles obey the Langevin dynamics, I have two equations. One is the overdamped Langevin equation, the other is the underdamped Langevin equation. Overdampted Langevin equation is the equation which ignore the inertial term. If I employ the overdampted Langevin equation in this study, the equation is ill-termed due to the $T(\boldsymbol{R})$. Thus, I employ the underdamped Langevin dynamics. The dynamic equations are

$$\frac{d\boldsymbol{P}_i(t)}{dt} = -\frac{1}{2}\frac{\partial \Phi(\boldsymbol{R}_i(t))}{\partial \boldsymbol{R}_i(t)} - \frac{\partial U(\boldsymbol{R}_1(t) - \boldsymbol{R}_2(t))}{\partial \boldsymbol{R}_i(t)} - \gamma\frac{\boldsymbol{P}_i(t)}{m} + \sqrt{2\gamma k_B T(\boldsymbol{R}_i)}\boldsymbol{w}_i(t),$$

$$\tag{2.1}$$

$$\frac{d\boldsymbol{R}_i(t)}{dt} = \frac{\boldsymbol{P}_i(t)}{m}. \tag{2.2}$$

Here $\boldsymbol{R}_i$ and $\boldsymbol{P}_i$ are the position and momentum of the i-th particle ($i = 1, 2$), γ is the friction coefficient, m is the mass, $U(\boldsymbol{R}_1(t) - \boldsymbol{R}_2(t))$ is the bond potential, $\Phi(\boldsymbol{R}_i(t))$ is the chemical potential and k_B the Boltzmann constant. $\boldsymbol{w}_i(t)$ is the Gaussian white noise which satisfy the fluctuation-dissipation relation:

$$\langle \boldsymbol{w}_i(t) \rangle = 0 \tag{2.3}$$

$$\langle \boldsymbol{w}_i(t)\boldsymbol{w}_j(t') \rangle = \mathbf{1}\delta_{ij}\delta(t - t') \tag{2.4}$$

where $\langle ... \rangle$ represents the statistical average and $\mathbf{1}$ is the unit tensor.

2.2 Theory

2.2.1 Derivation for $\Psi(r, q, p, \pi, t)$

It would be convenient to use the center of mass position and the bond vector instead of particle positions. I introduce the center of mass position $\boldsymbol{R} \equiv (\boldsymbol{R}_1 + \boldsymbol{R}_2)/2$ and the bond vector $\boldsymbol{Q} \equiv \boldsymbol{R}_2 - \boldsymbol{R}_1$. I also introduce the momenta for the center of mass and the bond vector, $\boldsymbol{P} \equiv \boldsymbol{P}_1 + \boldsymbol{P}_2$ and $\boldsymbol{\Pi} \equiv (\boldsymbol{P}_2 - \boldsymbol{P}_1)/2$.

I derive the Soret coefficient from the approximate Fokker-Planck equation for $\boldsymbol{R}$. Firstly, I consider the Fokker-Planck equation for the probability distribution $\Psi(r, q, p, \pi, t)$:

$$\Psi(r, q, p, \pi, t) = \langle \delta(r - \boldsymbol{R}(t))\delta(q - \boldsymbol{Q}(t))\delta(p - \boldsymbol{P}(t))\delta(\pi - \boldsymbol{\Pi}(t)) \rangle. \tag{2.5}$$

The Fokker-Planck equation becomes as follows by using Ito formula.

$$
\begin{aligned}
\frac{\partial \Psi(r,q,p,\pi,t)}{\partial t} = & -\frac{\partial}{\partial r} \cdot \left[\frac{p\Psi(r,q,p,\pi,t)}{2m} \right] - \frac{\partial}{\partial q} \cdot \left[\frac{2\pi\Psi(r,q,p,\pi,t)}{m} \right] \\
& + \frac{\partial}{\partial p} \cdot \left[\left(\frac{\partial \Phi(r)}{\partial r} + \frac{\gamma p}{m} + \frac{1}{2}\gamma k_B q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial}{\partial \pi} \right) \Psi(r,q,p,\pi,t) \right] \\
& + \frac{\partial^2}{\partial p^2} \cdot [2\gamma k_B T(r)\Psi(r,q,p,\pi,t)] \\
& + \frac{\partial}{\partial \pi} \cdot \left[\left(\frac{\partial U(q)}{\partial q} + \gamma\frac{\pi}{m} + \frac{1}{2}\gamma k_B q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial}{\partial p} \right) \Psi(r,q,p,\pi,t) \right] \\
& + \frac{\partial^2}{\partial \pi^2} \cdot \left[\frac{1}{2}\gamma k_B T(r)\Psi(r,q,p,\pi,t) \right].
\end{aligned}
\tag{2.6}
$$

Here I expand the temperature and chemical potential as follows because the temperature gradient is small:

$$
T(r \pm q/2) \approx T(r) \pm \frac{q}{2} \cdot \frac{\partial T(r)}{\partial r}, \tag{2.7}
$$

$$
\Phi(r \pm q/2) \approx \Phi(r) \pm \frac{q}{2} \cdot \frac{\partial \Phi(r)}{\partial r}. \tag{2.8}
$$

2.2.2 Derivation for $\Psi'(r,q,t)$

In this section, I derive the Fokker-Planck equation for the probability distribution for r and q $\Psi'(r,q,t)$ from the $\Psi(r,q,p,\pi,t)$. Because the behavior on a very short time scale is not of interest, I utilize the adiabatic elimination method[39] to eliminate the variables which relax so quickly. Here, I can rewrite the Fokker-Planck equation by introducing the Fokker-Planck operator $\mathscr{L}_1$:

$$
\frac{\partial \Psi(r,q,p,\pi,t)}{\partial t} = \mathscr{L}_1 \Psi(r,q,p,\pi,t), \tag{2.9}
$$

$$
\mathscr{L}_1 = \gamma\bar{\mathscr{L}} + \Delta\mathscr{L}, \tag{2.10}
$$

$$
\begin{aligned}
\bar{\mathscr{L}} f(r,q,p,\pi) = & \frac{\partial}{\partial p} \cdot \left[\frac{p}{m}f(r,q,p,\pi) + \frac{1}{2}k_B q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial f(r,q,p,\pi)}{\partial \pi} \right] \\
& + \frac{\partial}{\partial \pi} \cdot \left[\frac{\pi}{m}f(r,q,p,\pi) + \frac{1}{2}k_B q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial f(r,q,p,\pi)}{\partial p} \right] \\
& + \frac{\partial^2}{\partial p^2} \cdot [2k_B T(r)f(r,q,p,\pi)] \\
& + \frac{\partial^2}{\partial \pi^2} \cdot \left[\frac{1}{2}k_B T(r)f(r,q,p,\pi) \right], \tag{2.11}
\end{aligned}
$$

$$
\begin{aligned}
\Delta\mathscr{L} f(r,q,p,\pi) = & -\frac{\partial}{\partial r} \cdot \left[\frac{pf(r,q,p,\pi)}{2m} \right] - \frac{\partial}{\partial q} \cdot \left[\frac{2\pi f(r,q,p,\pi)}{m} \right] \\
& + \frac{\partial}{\partial p} \cdot \left[\frac{\partial \Phi(r)}{\partial r}f(r,q,p,\pi) \right] + \frac{\partial}{\partial \pi} \cdot \left[\frac{\partial U}{\partial q}f(r,q,p,\pi) \right],
\end{aligned}
\tag{2.12}
$$

where $f(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi})$ is an arbitrary function of $\boldsymbol{r},\boldsymbol{q},\boldsymbol{p}$, and $\boldsymbol{\pi}$. $(\boldsymbol{p},\boldsymbol{\pi})$ obeys the Gaussian distribution in equilibrium when $\boldsymbol{r},\boldsymbol{q}$ is fixed. I express the local equilibrium distribution as

$$P_{leq}(\boldsymbol{p},\boldsymbol{\pi}|\boldsymbol{r},\boldsymbol{q}) = \left[2mk_B\pi\sqrt{T^2(\boldsymbol{r}) - \left(\frac{\boldsymbol{q}}{2}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}}\right)^2}\right]^{-3}$$

$$\exp\left[-\frac{\left(T(\boldsymbol{r})p^2/4 + T(\boldsymbol{r})\pi^2 - (\boldsymbol{q}/2)\cdot(\partial T(\boldsymbol{r})/\partial \boldsymbol{r})\,\boldsymbol{p}\cdot\boldsymbol{\pi}\right)}{\left[mk_B\left[T^2(\boldsymbol{r}) - [(\boldsymbol{q}/2)\cdot(\partial T(\boldsymbol{r})/\partial \boldsymbol{r})\,\boldsymbol{p}\cdot\boldsymbol{\pi}]^2\right]\right]}\right]. \quad (2.13)$$

This local equilibrium distribution satisfy for large γ because I can neglect $\Delta\mathscr{L}$ compared to $\bar{\mathscr{L}}$. Here I expand on γ^{-1} and neglect the secondary or higher order terms of γ^{-1} I can derive the Fokker-Planck equation for distribution $\Psi'(\boldsymbol{r},\boldsymbol{q},t)$ by using the projection operator $\mathscr{P}$ as follows[39]:

$$\frac{\partial \Psi'(\boldsymbol{r},\boldsymbol{q},t)}{\partial t} = -\gamma^{-1}\mathscr{P}\Delta\mathscr{L}\bar{\mathscr{L}}^{-1}\Delta\mathscr{L}\Psi'(\boldsymbol{r},\boldsymbol{q},t), \quad (2.14)$$

with

$$\Psi'(\boldsymbol{r},\boldsymbol{q},t) = \int d\boldsymbol{p}d\boldsymbol{\pi}\Psi(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi},t), \quad (2.15)$$

$$\mathscr{P}\Psi(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi},t) = P_{leq}(\boldsymbol{p},\boldsymbol{\pi}|\boldsymbol{r},\boldsymbol{q})\int \Psi(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi},t)d\boldsymbol{p}d\boldsymbol{\pi}. \quad (2.16)$$

Finally, the Fokker-Planck equation becomes as follows:

$$\frac{\partial \Psi'(\boldsymbol{r},\boldsymbol{q},t)}{\partial t} = \gamma^{-1}\left(\frac{\partial}{\partial \boldsymbol{r}}\cdot\left[\frac{1}{2}k_B\frac{\partial}{\partial \boldsymbol{r}}\left(T(\boldsymbol{r})\Psi'(\boldsymbol{r},\boldsymbol{q},t)\right) + \frac{k_B}{2}\boldsymbol{q}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}}\frac{\partial \Psi'(\boldsymbol{r},\boldsymbol{q},t)}{\partial \boldsymbol{q}}\right]\right.$$

$$+ \frac{\partial}{\partial \boldsymbol{r}}\cdot\left[\frac{1}{2}\frac{\partial\Phi(\boldsymbol{r})}{\partial \boldsymbol{r}}\Psi'(\boldsymbol{r},\boldsymbol{q},t)\right] \quad (2.17)$$

$$\left.+ \frac{\partial}{\partial \boldsymbol{q}}\cdot\left[2k_BT(\boldsymbol{r})\frac{\partial \Psi'(\boldsymbol{r},\boldsymbol{q},t)}{\partial \boldsymbol{q}} + 2\frac{\partial U(\boldsymbol{q})}{\partial \boldsymbol{q}}\Psi'(\boldsymbol{r},\boldsymbol{q},t)\right]\right). \quad (2.18)$$

2.2.3 Derivation for $\Psi''(r,t)$

In this section, I derive the Fokker-Planck equation for the probability distribution for r $\Psi'''(r,t)$ from the $\Psi'(r,q,t)$. Here, I rewrite the Fokker-Planck equation by the operator $\mathscr{L}_2$:

$$\frac{\partial \Psi'(r,q,t)}{\partial t} = \mathscr{L}_2 \Psi'(r,q,t), \tag{2.19}$$

$$\mathscr{L}_2 = \mathscr{L}' + \mathscr{L}'', \tag{2.20}$$

$$\mathscr{L}'g(r,q) = \frac{\partial}{\partial q} \cdot \left[2k_B T(r) \frac{\partial g(r,q)}{\partial q} + 2\frac{\partial U(q)}{\partial q} g(r,q) \right], \tag{2.21}$$

$$\mathscr{L}''g(r,q) = \frac{\partial}{\partial r} \cdot \left[\frac{1}{2} k_B \frac{\partial}{\partial r} (T(r)g(r,q)) + \frac{k_B}{2} q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial g(r,q)}{\partial q} \right]$$

$$+ \frac{\partial}{\partial r} \cdot \left[\frac{1}{2} \frac{\partial \Phi(r)}{\partial r} g(r,q) \right], \tag{2.22}$$

where $g(r,q)$ is the arbitrary function of r and q. I express the local equilibrium distribution as

$$P_{leq}(q|r) = \frac{1}{\int \exp\left(-\frac{U(q)}{k_B T(r)}\right) dq} \exp\left(-\frac{U(q)}{k_B T(r)}\right). \tag{2.23}$$

If I assume that the distribution of q rapidly approaches to the local equilibrium distribution compared to the time scale of r, I only consider the the local equilibrium distribution of q (the ground state dominance approximation). Then I can rewrite the Fokker-Planck equation as

$$\frac{\partial \Psi''(r,t)}{\partial t} \approx \int dq' \mathscr{L}'' P_{leq}(q' \mid r). \tag{2.24}$$

In general, if the polymer is ideal chain, the elasticity of polymer obeys the Hooke's law[40]. Thus, I consider the case where the bond potential is harmonic potential:

$$U(q) = Kq^2. \tag{2.25}$$

Here, $q = |q|$ is the bond length, K is the spring constant. From eq. (2.24), I have the Fokker-Planck equation for r (mass flux):

$$\frac{\partial \Psi''(r,t)}{\partial t} = \gamma^{-1} \left(\frac{\partial}{\partial r} \cdot \left[\frac{1}{2} k_B \frac{\partial T(r)}{\partial r} \Psi''(r,t) + \frac{1}{2} k_B T(r) \frac{\partial \Psi''(r,t)}{\partial r} \right] \right.$$

$$\left. + \frac{\partial}{\partial r} \cdot \left[\frac{1}{2} \frac{\partial \Phi(r)}{\partial r} \Psi''(r,t) \right] \right). \tag{2.26}$$

I derive the Soret coefficient from the mass flux. I consider the situation where a constant temperature gradient is applied in the z-direction. The system

is isotropic in the x and y direction. At the steady state, $\frac{\partial \Psi''(\mathbf{r},t)}{\partial t} = 0$. I get the Soret coefficient S_T^*:

$$S_T^* = \frac{1}{T_c} + \frac{1}{k_B T_c} \frac{\partial \Phi(z)}{\partial z} \bigg/ \frac{\partial T(z)}{\partial z}, \qquad (2.27)$$

with

$$T_c = \frac{1}{2L} \int_{-L}^{L} T(z)dz, \qquad (2.28)$$

where L is the system size. The Soret coefficient is independent of the spring constant and is equal to that for a colloidal particle with no conformational degrees of freedom[38]. This result means that conformational degrees of freedom does not affect the Soret coefficient of the examined system.

2.3   Model system

In this section, I consider the model system. I consider the dynamics of a single dumbbell molecule under a small and liner temperature gradient. In this system, I can expand the temperature field and chemical potential field as follows:

$$T(z) = T_c + az, \qquad (2.29)$$
$$\Phi(z) = \Phi_c + bk_B z, \qquad (2.30)$$

where T_c and Φ_c are the temperature and chemical potential at center. a and b are the constant value which is independent at z. By introducing eqs. (2.29) and (2.29), I rewrite the S_T^*:

$$S_T^* = \frac{1}{T_c} + \frac{b}{aT_c} \qquad (2.31)$$

Appendix

2.A The properties of Langevin equation for (R, Q, P, Π)

In this section, I evaluate the Langevin equation for (R, Q, P, Π). If the temperature gradient is small, it would be convenient to expand the chemical potential before calculation as follows

$$\Phi(r \pm q/2) \approx \Phi(r) \pm \frac{q}{2} \cdot \frac{\partial \Phi(r)}{\partial r} \tag{2.32}$$

I rewrite the the dynamic equations eqs. (2.1)-(??) by (R, Q, P, Π)

$$\frac{dP(t)}{dt} = -\frac{\partial \Phi(R(t))}{\partial R(t)} - \gamma \frac{P(t)}{m} + \zeta(R(t), Q(t), t), \tag{2.33}$$

$$\frac{d\Pi(t)}{dt} = -\frac{\partial U(Q(t))}{\partial Q(t)} - \gamma \frac{\Pi(t)}{m} + \xi(R(t), Q(t), t), \tag{2.34}$$

$$\frac{dR(t)}{dt} = \frac{P(t)}{2m}, \tag{2.35}$$

$$\frac{dQ(t)}{dt} = \frac{2\Pi(t)}{m}, \tag{2.36}$$

with

$$\zeta(R, Q, t) \equiv \sqrt{2\gamma k_B T \left(R - \frac{Q}{2} \right)} w_1(t) + \sqrt{2\gamma k_B T \left(R + \frac{Q}{2} \right)} w_2(t), \tag{2.37}$$

$$\xi(R, Q, t) \equiv \frac{1}{2} \left(-\sqrt{2\gamma k_B T \left(R - \frac{Q}{2} \right)} w_1(t) + \sqrt{2\gamma k_B T \left(R + \frac{Q}{2} \right)} w_2(t) \right). \tag{2.38}$$

Now I consider the fluctuation-dissipation relation for the noises $\zeta(R, Q, t)$ and $\xi(R, Q, t)$. The first order statistical moments are trivially zero:

$$\langle \zeta(R(t), Q(t), t) \rangle = 0. \qquad \langle \xi(R(t), Q(t), t) \rangle = 0. \tag{2.39}$$

The second order moments are not that simple.

$$\langle \boldsymbol{\zeta}_i(\boldsymbol{R}(t),\boldsymbol{Q}(t),t)\boldsymbol{\zeta}_i(\boldsymbol{R}(t'),\boldsymbol{Q}(t'),t') \rangle$$

$$= 4\gamma k_B \left(\frac{T\left(\boldsymbol{R}+\frac{\boldsymbol{Q}}{2}\right) + T\left(\boldsymbol{R}-\frac{\boldsymbol{Q}}{2}\right)}{2} \right) \mathbf{1}\delta(t-t'), \qquad (2.40)$$

$$\langle \boldsymbol{\xi}_i(\boldsymbol{R}(t),\boldsymbol{Q}(t),t)\boldsymbol{\xi}_i(\boldsymbol{R}(t'),\boldsymbol{Q}(t'),t') \rangle$$

$$= \gamma k_B \left(\frac{T\left(\boldsymbol{R}+\frac{\boldsymbol{Q}}{2}\right) + T\left(\boldsymbol{R}-\frac{\boldsymbol{Q}}{2}\right)}{2} \right) \mathbf{1}\delta(t-t'), \qquad (2.41)$$

$$\langle \boldsymbol{\zeta}_i(\boldsymbol{R}(t),\boldsymbol{Q}(t),t)\boldsymbol{\xi}_i(\boldsymbol{R}(t'),\boldsymbol{Q}(t'),t') \rangle$$

$$= \gamma k_B \left(T\left(\boldsymbol{R}+\frac{\boldsymbol{Q}}{2}\right) - T\left(\boldsymbol{R}-\frac{\boldsymbol{Q}}{2}\right) \right) \mathbf{1}\delta(t-t'). \qquad (2.42)$$

2.B Derivation for the Fokker-Planck equation

Now I consider the Fokker-Planck equation for the probability distribution

$$\Psi(r,q,p,\pi) = \langle \delta(r - R(t))\delta(q - Q(t))\delta(p - P(t))\delta(\pi - \Pi(t)) \rangle. \quad (2.43)$$

I derive the Fokker-Planck equation by Ito formula.

$$d\delta(r - R)\delta(q - Q)\delta(p - P)\delta(\pi - \Pi)$$

$$= \frac{\partial}{\partial r}\delta(r - R)\delta(q - Q)\delta(p - P)\delta(\pi - \Pi)\left(-\frac{P}{2m}\right)dt$$

$$+ \delta(r - R)\frac{\partial}{\partial q}\delta(q - Q)\delta(p - P)\delta(\pi - \Pi)\left(-2\frac{\Pi}{m}\right)dt$$

$$+ \delta(r - R)\delta(q - Q)\frac{\partial}{\partial p}\delta(p - P)\delta(\pi - \Pi)$$

$$\left[\left(\frac{\partial\Phi(R)}{\partial R} + \gamma\frac{P}{m}\right)dt + \left(\sqrt{2\gamma k_B\left(T\left(R - \frac{Q}{2}\right) + T\left(R + \frac{Q}{2}\right)\right)}\right)\cdot dB_t\right]$$

$$+ \delta(r - R)\delta(q - Q)\delta(p - P)\frac{\partial}{\partial\pi}\delta(\pi - \Pi)$$

$$\left[\left(\frac{\partial U(Q)}{\partial Q} + \gamma\frac{\Pi}{m}\right)dt + \left(\sqrt{\frac{\gamma k_B\left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)}{2}}\right)\cdot dB_t\right]$$

$$+ \delta(r - R)\delta(q - Q)\frac{\partial}{\partial p}\delta(p - P)\frac{\partial}{\partial\pi}\delta(\pi - \Pi)$$

$$\left[\gamma k_B\left(T\left(R + \frac{Q}{2}\right) - T\left(R - \frac{Q}{2}\right)\right)dt\right]$$

$$+ \frac{1}{2}\delta(r - R)\delta(q - Q)\frac{\partial^2}{\partial p^2}\delta(p - P)\delta(\pi - \Pi)$$

$$\left[2\gamma k_B\left(T\left(R - \frac{Q}{2}\right) + T\left(R + \frac{Q}{2}\right)\right)dt\right]$$

$$+ \frac{1}{2}\delta(r - R)\delta(q - Q)\delta(p - P)\frac{\partial^2}{\partial\pi^2}\delta(\pi - \Pi)$$

$$\left[\frac{\gamma k_B\left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)}{2}dt\right] \quad (2.44)$$

I take the average in each term, and I obtain the Fokker-Plank equation as follows

$$
\begin{aligned}
\frac{\partial \Psi(r,q,p,\pi)}{\partial t} = &- \frac{\partial}{\partial r} \cdot \left[\frac{p\Psi(r,q,p,\pi)}{2m} \right] - \frac{\partial}{\partial q} \cdot \left[\frac{2\pi\Psi(r,q,p,\pi)}{m} \right] \\
&+ \frac{\partial}{\partial p} \cdot \left[\left(\frac{\partial \Phi(r)}{\partial r} + \frac{\gamma p}{m} \right) \Psi(r,q,p,\pi) \right] \\
&+ \frac{\partial^2}{\partial p^2} \cdot \left[2\gamma k_B \left(\frac{T\left(r+\frac{q}{2}\right) + T\left(r-\frac{q}{2}\right)}{2} \right) \Psi(r,q,p,\pi) \right] \\
&+ \frac{\partial}{\partial \pi} \cdot \left[\left(\frac{\partial U(q)}{\partial q} + \gamma \frac{\pi}{m} \right) \Psi(r,q,p,\pi) \right] \\
&+ \frac{\partial^2}{\partial \pi^2} \cdot \left[\frac{1}{2}\gamma k_B \left(\frac{T\left(r+\frac{q}{2}\right) + T\left(r-\frac{q}{2}\right)}{2} \right) \Psi(r,q,p,\pi) \right] \\
&+ \frac{\partial}{\partial \pi} \cdot \frac{\partial}{\partial p} \left[\gamma k_B \left(T\left(r+\frac{q}{2}\right) - T\left(r-\frac{q}{2}\right) \right) \Psi(r,q,p,\pi) \right].
\end{aligned}
$$

(2.45)

2.C Interpretation of stochastic integral

2.C.1 Ito and Stratonovich integral

In this section, I discuss the interpretation of stochastic integral. The stochastic integral can be classified into two interpretation. One is Ito integral, the other is Stratonovich integral. The Ito is mathematically and technically the most satisfactory, but it is not always the most natural choice physically. On the other hand, the Stratonovich integral is the natural choice physically, but the calculation is not straightforward. The Ito integral and Stratonovich integral can be defined as follows:

$$
f(s)\left[B_{s+\Delta s} - B_s\right] \quad (Ito), \tag{2.46}
$$

$$
\frac{f(s+\Delta s) + f(s)}{2}\left[B_{s+\Delta s} - B_s\right] \quad (Stratonovich), \tag{2.47}
$$

where B_t is the Wiener process, $f(x)$ is the arbitrary function.

In general, I need not consider the interpretation of stochastic integral. I mean that no matter which interpretation is used, the result remains the same. However, I need to calculate carefully when I consider multiplicative noises. I show an example of multiplicative noise and problem of stochastic integral. I consider the ordinary differential equation as follows:

$$
\frac{dx(t)}{dt} = x(t)\delta(t-1), \tag{2.48}
$$

where $x(t)$ is the function of time t. $x(0) = 1$, $x(1+\Delta t) = x_{i+1}$ and $x(1) = x_i = 1$. I consider the time evolution function of time t. I calculate the time evolution

function using the Ito and Stratonovich interpretation.

$$\frac{x_{i+1} - x_i}{\Delta t} = x_i \frac{1}{\Delta t} \rightarrow x(1+0) = 2 \quad (Ito) \tag{2.49}$$

$$\frac{x_{i+1} - x_i}{\Delta t} = \frac{x_{i+1} + x_i}{2} \frac{1}{\Delta t} \rightarrow x(1+0) = 3 \quad (Stratonovich) \tag{2.50}$$

These two results show that Ito and Stratonovich integral show the different results. Thus, I need to discuss the interpretation of stochastic integral in your cases and write which stochastic integral is employed.

2.C.2 In my cases

In this section, I calculate the stochastic differential equation by using Ito and Stratonovich integral and discuss the difference between Ito and Stratonovich results. I consider Langevin equation as follows:

$$\frac{d}{dt} \begin{bmatrix} R(t) \\ Q(t) \\ P(t) \\ \Pi(t) \end{bmatrix} = \begin{bmatrix} \frac{P(t)}{2m} \\ \frac{2\Pi(t)}{m} \\ -\gamma\frac{P(t)}{m} \\ -\gamma\frac{\Pi(t)}{m} \end{bmatrix} + \sqrt{2\gamma k_B} B \begin{bmatrix} w_1(t) \\ w_2(t) \\ w_3(t) \\ w_4(t) \end{bmatrix}, \tag{2.51}$$

where

$$B = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{\left(T\left(R+\frac{Q}{2}\right)+T\left(R-\frac{Q}{2}\right)\right)} & 0 \\ 0 & 0 & 0 & \frac{1}{2}\sqrt{\left(T\left(R+\frac{Q}{2}\right)-T\left(R-\frac{Q}{2}\right)\right)} \end{bmatrix} \tag{2.52}$$

I derive the stochastic differential equation using Ito and Stratonovich integral as follows.

$$dx = a dt + b dW(t) \quad (Ito), \tag{2.53}$$

$$dx = \left[a - \left(\frac{\partial}{\partial R}, \frac{\partial}{\partial Q}, \frac{\partial}{\partial P}, \frac{\partial}{\partial \Pi}\right) B\right] dt + b dW(t) \quad (Stratonovich), \tag{2.54}$$

Thus, I can calculate the stochastic differential equation by Ito formula.

$$
dR = \frac{P(t)}{2m} dt
$$

$$
dQ = \frac{2\Pi(t)}{m} dt
$$

$$
dP = -\gamma \frac{P(t)}{m} dt + \sqrt{2\gamma k_B \left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$
d\Pi = -\gamma \frac{\Pi(t)}{m} dt + \sqrt{\frac{\gamma k_B}{2} \left(T\left(R + \frac{Q}{2}\right) - T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$(2.55)$$

I also calculate the stochastic differential equation by Stratonovich interpretation.

$$
dR = \frac{P(t)}{2m} dt
$$

$$
dQ = \frac{2\Pi(t)}{m} dt
$$

$$
dP = \left[-\gamma \frac{P(t)}{m} - \frac{\partial}{\partial P} \sqrt{2\gamma k_B \left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)} \right] dt
$$

$$
+ \sqrt{2\gamma k_B \left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$
= -\gamma \frac{P(t)}{m} dt + \sqrt{2\gamma k_B \left(T\left(R + \frac{Q}{2}\right) + T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$
d\Pi = \left[-\gamma \frac{\Pi(t)}{m} - \frac{\partial}{\partial \Pi} \sqrt{\frac{\gamma k_B}{2} \left(T\left(R + \frac{Q}{2}\right) - T\left(R - \frac{Q}{2}\right)\right)} \right] dt
$$

$$
+ \sqrt{\frac{\gamma k_B}{2} \left(T\left(R + \frac{Q}{2}\right) - T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$
= -\gamma \frac{\Pi(t)}{m} dt + \sqrt{\frac{\gamma k_B}{2} \left(T\left(R + \frac{Q}{2}\right) - T\left(R - \frac{Q}{2}\right)\right)} dW(t)
$$

$$(2.56)$$

2.D   Derivation for the Fokker-Planck equation for (r,q)

In this section, I derive the Fokker-Planck equation for (r,q). I can rewrite the Fokker-Planck equation by using the projection operator $\mathscr{P}$, so I get the equation as

$$\frac{\partial v}{\partial t} = -\gamma^{-1}\,\mathscr{P}\Delta\mathscr{L}\,\bar{\mathscr{L}}^{-1}\Delta\mathscr{L}v, \tag{2.57}$$

with

$$v = \mathscr{P}\Psi(r,q,p,\pi,t). \tag{2.58}$$

Firstly, I calculate the L_2v as follows

$$
\begin{aligned}
L_2v = &\left(\left[-\frac{p}{2m}\frac{\partial}{\partial r}-\frac{2\pi}{m}\frac{\partial}{\partial q}+\frac{\partial U}{\partial q}\frac{\partial}{\partial \pi}+\frac{\partial\Phi(r)}{\partial r}\frac{\partial}{\partial p}\right]\right.\\
&\left(\frac{1}{2\pi mk_BT(r)}\right)^3\exp\left[-\frac{1}{mk_BT^2(r)}\left(\frac{T(r)}{4}p^2+T(r)\pi^2-\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}p\pi\right)\right]\right)\\
&\int\int f(r,q,p,\pi)dpd\pi\\
= &\left(\left(-\left[\frac{\partial}{\partial r}\frac{1}{2m}-\frac{1}{mk_BT^2(r,q)}\left[\left(\frac{\partial U}{\partial q}\right)\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}-\frac{\partial\Phi(r)}{\partial r}\frac{T(r)}{2}\right]\right]p\right.\right.\\
&\left.-\left[\frac{\partial}{\partial q}\frac{2}{m}+\frac{1}{mk_BT^2(r,q)}\left[\left(\frac{\partial U}{\partial q}\right)2T(r)-\frac{\partial\Phi(r)}{\partial r}\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}\right]\right]\pi\right)\\
&\left(\frac{1}{2\pi mk_BT(r)}\right)^3\exp\left[-\frac{1}{mk_BT^2(r,q)}\left(\frac{T(r)}{4}p^2+T(r)\pi^2-\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}p\pi\right)\right]\right)\\
&\int\int f(r,q,p,\pi)dpd\pi \tag{2.59}
\end{aligned}
$$

I introduce the Hermite-polynomial for $\boldsymbol{p}, \boldsymbol{\pi}$ as shown below

$$
\begin{aligned}
H_0(\boldsymbol{p}') &= \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{p}'^2}{2mk_B T(\boldsymbol{r})}\right] \\
H_1(\boldsymbol{p}') &= \boldsymbol{p}' \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{p}'^2}{2mk_B T(\boldsymbol{r})}\right] \\
H_2(\boldsymbol{p}') &= \frac{1}{\sqrt{2}}(\boldsymbol{p}'^2 - 1) \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{p}'^2}{2mk_B T(\boldsymbol{r})}\right] \\
H_3(\boldsymbol{p}') &= \frac{1}{\sqrt{6}}(\boldsymbol{p}'^3 - 3mpk_B T(\boldsymbol{r})) \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{p}'^2}{2mk_B T(\boldsymbol{r})}\right] \\
H_0(\boldsymbol{\pi}) &= \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{\pi}'^2}{mk_B T(\boldsymbol{r})}\right] \\
H_1(\boldsymbol{\pi}) &= \boldsymbol{\pi}' \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{\pi}'^2}{mk_B T(\boldsymbol{r})}\right] \\
H_2(\boldsymbol{\pi}) &= \frac{1}{\sqrt{2}}(\boldsymbol{\pi}^2 - 1) \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{\pi}'^2}{mk_B T(\boldsymbol{r})}\right] \\
H_3(\boldsymbol{\pi}) &= \frac{1}{\sqrt{6}}(\boldsymbol{\pi}^3 - 3m\pi k_B T(\boldsymbol{r})) \left(\frac{1}{2m\pi k_B T(\boldsymbol{r})}\right)^{3/2} \exp\left[-\frac{\boldsymbol{\pi}'^2}{mk_B T(\boldsymbol{r})}\right]
\end{aligned}
\tag{2.60}
$$

It would be convenient to calculate the momentum term and potential term. Thus I decompose as follows

$$
L_2 = L_{21} + L_{22} \tag{2.61}
$$

$$
L_{21} = -\frac{\partial}{\partial r}\frac{\boldsymbol{p}}{2m} - \frac{\partial}{\partial q}\frac{2\boldsymbol{\pi}}{m} \tag{2.62}
$$

$$
\begin{aligned}
L_{22} = &-\frac{1}{mk_B T^2(\boldsymbol{r}, \boldsymbol{q})}\left[\left(\frac{\partial U}{\partial q}\right)\frac{\boldsymbol{q}}{2} \cdot \frac{\partial T(\boldsymbol{r})}{\partial r} - \frac{\partial \Phi(\boldsymbol{r})}{\partial r}\frac{T(\boldsymbol{r})}{2}\right]\boldsymbol{p} \\
&+\frac{1}{mk_B T^2(\boldsymbol{r}, \boldsymbol{q})}\left[\left(\frac{\partial U}{\partial q}\right)2T(\boldsymbol{r}) - \frac{\partial \Phi(\boldsymbol{r})}{\partial r}\frac{\boldsymbol{q}}{2} \cdot \frac{\partial T(\boldsymbol{r})}{\partial r}\right]\boldsymbol{\pi}
\end{aligned}
\tag{2.63}
$$

I perform the transformation of variables by using $p' = \frac{1}{\sqrt{2}}\left(p - \frac{q}{T(r)} \cdot \frac{\partial T(r)}{\partial r}\pi\right)$、
$\pi' = \sqrt{2}\pi$.

$$
\begin{aligned}
L_{21}v_1 =& \left(-\left[\frac{\partial}{\partial r}\frac{1}{2m}\right]\left[\sqrt{2}p' + \frac{q}{T(r)} \cdot \frac{\partial T(r)}{\partial r}\pi'\right] - \left[\frac{\partial}{\partial q}\frac{2}{m}\right]\frac{\pi'}{\sqrt{2}}\right) \\
& \left(\frac{1}{2\pi m k_B T(r)}\right)^3 \exp\left[-\frac{p'^2}{2m k_B T(r)}\right]\exp\left[-\frac{\pi'^2}{2m k_B T(r)}\right] \\
& \int\int f(r,q,p,\pi)dpd\pi \\
=& -\frac{1}{m}\left(\left[\frac{\partial}{\partial r}\frac{1}{2} + \frac{1}{2T(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_1(p') + \left[\frac{\partial}{\partial q}2\right]\frac{1}{\sqrt{2}}P_1(\pi)\right. \\
& + \left[\frac{q}{2T(r)} \cdot \frac{\partial T(r)}{\partial r}\frac{\partial}{\partial r}\right]P_1(\pi) + \left[\frac{\sqrt{6}}{4m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_3(p') \\
& + \left[\frac{\sqrt{2}}{m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_2(p')P_1(p') \\
& \left.+ \left[\frac{\sqrt{2}}{4m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_1(p')P_2(\pi)\right) \\
& \int\int f(r,q,p,\pi)dpd\pi
\end{aligned}
$$

(2.64)

Secondly, I calculate the $L_1^{-1}L_{21}v$ as follows

$$
\begin{aligned}
L_1^{-1}L_{21}v =& \left(\left[\frac{\partial}{\partial r}\frac{1}{2} + \frac{1}{2T(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_1(p') + \left[\frac{\partial}{\partial q}2\right]\frac{1}{\sqrt{2}}P_1(\pi)\right. \\
& + \left[\frac{q}{2T(r)} \cdot \frac{\partial T(r)}{\partial r}\frac{\partial}{\partial r}\right]P_1(\pi) + \left[\frac{\sqrt{6}}{4m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}\frac{1}{3}P_3(p') \\
& + \left[\frac{\sqrt{2}}{m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\frac{1}{2}\sqrt{2}P_2(p')P_1(p') \\
& \left.+ \left[\frac{\sqrt{2}}{4m k_B T^2(r)}\frac{\partial T(r)}{\partial r}\right]\frac{1}{2}\sqrt{2}P_1(p')P_2(\pi)\right)
\end{aligned}
$$

(2.65)

Finally, I calculate the $PL_{21}L_1^{-1}L_{21}v$ as follows

$$PL_2L_1^{-1}L_{21}v = -\frac{1}{m}P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\int d\boldsymbol{p}d\boldsymbol{\pi}\left[-\frac{\partial}{\partial\boldsymbol{r}}\cdot\frac{1}{2}\left[\boldsymbol{p}' + \frac{\boldsymbol{q}}{T(r)}\frac{\partial T(r)}{\partial\boldsymbol{r}}\boldsymbol{\pi}\right] - \frac{\partial}{\partial\boldsymbol{q}}[2\boldsymbol{\pi}]\right]$$

$$\left(\left[\frac{\partial}{\partial\boldsymbol{r}}\frac{1}{2} + \frac{1}{2T(r)}\frac{\partial T(r)}{\partial\boldsymbol{r}}\right]\sqrt{2}P_1(\boldsymbol{p}') + \left[\frac{\partial}{\partial\boldsymbol{q}}2\right]\frac{1}{\sqrt{2}}P_1(\boldsymbol{\pi})\right.$$

$$+ \left[\frac{\boldsymbol{q}}{2T(r)}\cdot\frac{\partial T(r)}{\partial\boldsymbol{r}}\frac{\partial}{\partial\boldsymbol{r}}\right]P_1(\boldsymbol{\pi}) + \left[\frac{\sqrt{6}}{4mk_BT^2(r)}\frac{\partial T(r)}{\partial\boldsymbol{r}}\right]\sqrt{2}\frac{1}{3}P_3(\boldsymbol{p}')$$

$$+ \left[\frac{\sqrt{2}}{mk_BT^2(r)}\frac{\partial T(r)}{\partial\boldsymbol{r}}\right]\frac{1}{2}\sqrt{2}P_2(\boldsymbol{p}')P_1(\boldsymbol{p}')$$

$$\left.+ \left[\frac{\sqrt{2}}{4mk_BT^2(r)}\frac{\partial T(r)}{\partial\boldsymbol{r}}\right]\frac{1}{2}\sqrt{2}P_1(\boldsymbol{p}')P_2(\boldsymbol{\pi})\right)$$

$$\int\int f(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi})d\boldsymbol{p}d\boldsymbol{\pi}$$

$$= -P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\left(\frac{\partial}{\partial\boldsymbol{r}}\cdot\left[\frac{k_B}{2}\frac{\partial}{\partial\boldsymbol{r}}(T(r))f(\boldsymbol{r},\boldsymbol{q}) + \frac{k_B\boldsymbol{q}}{2}\cdot\frac{\partial T(r)}{\partial\boldsymbol{r}}\frac{\partial f(\boldsymbol{r},\boldsymbol{q})}{\partial\boldsymbol{q}}\right]\right.$$

$$+ \frac{\partial}{\partial\boldsymbol{r}}\cdot\left[\frac{k_B}{2}\frac{\partial T(r)}{\partial\boldsymbol{r}}f(\boldsymbol{r},\boldsymbol{q})\right]$$

$$\left.+ \frac{\partial}{\partial\boldsymbol{q}}\cdot\left[2k_BT(r)\frac{\partial f(\boldsymbol{r},\boldsymbol{q})}{\partial\boldsymbol{q}}\right]\right)$$

$$(2.66)$$

I calculate the $PL_{22}L_1^{-1}L_{21}v$ as follows

$$
\begin{aligned}
PL_{22}L_1^{-1}L_{21}v = {}& -\frac{1}{m}P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\int d\boldsymbol{p}d\boldsymbol{\pi} \\
& \left(-\frac{1}{mk_BT^2(r)}\left[\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\frac{\boldsymbol{q}}{2}\cdot\frac{\partial T(r)}{\partial r}-\frac{\partial\Phi(r)}{\partial r}\frac{T(r)}{2}\right]\sqrt{2}\boldsymbol{p}'\right]\right. \\
& \left.+\frac{1}{mk_BT^2(r)}\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)2T(r)\right]\frac{\boldsymbol{\pi}'}{\sqrt{2}}\right) \\
& \left(\left[\frac{\partial}{\partial r}\frac{1}{2}+\frac{1}{2T(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}P_1(\boldsymbol{p}')+\left[\frac{\partial}{\partial \boldsymbol{q}}2\right]\frac{1}{\sqrt{2}}P_1(\boldsymbol{\pi})\right. \\
& +\left[\frac{\boldsymbol{q}}{2T(r)}\cdot\frac{\partial T(r)}{\partial r}\frac{\partial}{\partial r}\right]P_1(\boldsymbol{\pi})+\left[\frac{\sqrt{6}}{4mk_BT^2(r)}\frac{\partial T(r)}{\partial r}\right]\sqrt{2}\frac{1}{3}P_3(\boldsymbol{p}') \\
& +\left[\frac{\sqrt{2}}{mk_BT^2(r)}\frac{\partial T(r)}{\partial r}\right]\frac{1}{2}\sqrt{2}P_2(\boldsymbol{p}')P_1(\boldsymbol{p}') \\
& \left.+\left[\frac{\sqrt{2}}{4mk_BT^2(r)}\frac{\partial T(r)}{\partial r}\right]\frac{1}{2}\sqrt{2}P_1(\boldsymbol{p}')P_2(\boldsymbol{\pi})\right) \\
& \int\int f(r,\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi})d\boldsymbol{p}d\boldsymbol{\pi} \\
= {}& P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\left(\frac{2}{k_BT(r)}\left(\frac{\partial U(\boldsymbol{q})}{\partial \boldsymbol{q}}\right)^2 f(r,\boldsymbol{q})\right)
\end{aligned}
$$

$$(2.67)$$

I also calculate the potential term as follows

$$
\begin{aligned}
L_{22}v_1 =& \left(-\frac{1}{mk_BT^2(r)}\left[\left(\frac{\partial U}{\partial q}\right)\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}-\frac{\partial\Phi(r)}{\partial r}\frac{T(r)}{2}\right]\right.\\
&\times\left[\sqrt{2}p'+\frac{q}{T(r)}\cdot\frac{\partial T(r)}{\partial r}\pi'\right]\\
&+\left.\left[\frac{1}{mk_BT^2(r)}\left[\left(\frac{\partial U}{\partial q}\right)2T(r)-\frac{\partial\Phi(r)}{\partial r}\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}\right]\right]\frac{\pi'}{\sqrt{2}}\right)\\
&\left(\frac{1}{2\pi mk_BT(r)}\right)^3\exp\left[-\frac{p'^2}{2mk_BT(r)}\right]\exp\left[-\frac{\pi'^2}{2mk_BT(r)}\right]\\
&\int\int f(r,q,p,\pi)dpd\pi\\
=&-\frac{1}{m}\left(\left[\frac{1}{k_BT^2(r)}\left[\left(\frac{\partial U}{\partial q}\right)\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}-\frac{\partial\Phi(r)}{\partial r}\frac{T(r)}{2}\right]\right]\sqrt{2}H_1(p')\right.\\
&-\left.\left[\frac{\sqrt{2}}{k_BT(r)}\left(\frac{\partial U}{\partial q}\right)\right]H_1(\pi')\right)\int\int f(r,q,p,\pi)dpd\pi
\end{aligned}
$$

$$(2.68)$$

Secondly, I calculate the $L_1^{-1}L_{21}v$ as follows

$$
\begin{aligned}
L_1^{-1}L_{22}v =& \left(\left[\frac{1}{k_BT^2(r)}\left[\left(\frac{\partial U}{\partial q}\right)\frac{q}{2}\cdot\frac{\partial T(r)}{\partial r}-\frac{\partial\Phi(r)}{\partial r}\frac{T(r)}{2}\right]\right]\sqrt{2}H_1(p')\right.\\
&-\left.\left[\frac{\sqrt{2}}{k_BT(r)}\left(\frac{\partial U}{\partial q}\right)\right]H_1(\pi')\right)\int\int f(r,q,p,\pi)dpd\pi
\end{aligned}
$$

$$(2.69)$$

Finally, I calculate the $PL_{22}L_1^{-1}L_{21}v$ as follows

$$PL_{22}L_1^{-1}L_{22}v = -P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\int d\boldsymbol{p}d\boldsymbol{\pi}$$

$$\left(-\frac{1}{mk_BT^2(\boldsymbol{r})}\left[\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\frac{\boldsymbol{q}}{2}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}} - \frac{\partial \Phi(\boldsymbol{r})}{\partial \boldsymbol{r}}\frac{T(\boldsymbol{r})}{2}\right]\sqrt{2}\boldsymbol{p}'\right]\right.$$

$$\left.+\frac{1}{mk_BT^2(\boldsymbol{r})}\left[\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)2T(\boldsymbol{r})\right]\frac{\boldsymbol{\pi}'}{\sqrt{2}}\right]\right)$$

$$\left(\left[\frac{1}{k_BT^2(\boldsymbol{r})}\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\frac{\boldsymbol{q}}{2}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}} - \frac{\partial \Phi(\boldsymbol{r})}{\partial \boldsymbol{r}}\frac{T(\boldsymbol{r})}{2}\right]\right]\sqrt{2}H_1(\boldsymbol{p}')\right.$$

$$\left.-\left[\frac{\sqrt{2}}{k_BT(\boldsymbol{r})}\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\right]H_1(\boldsymbol{\pi}')\right)$$

$$\int\int f(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi})d\boldsymbol{p}d\boldsymbol{\pi}$$

$$= -P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\left(\frac{2}{k_BT(\boldsymbol{r})}\left(\frac{\partial U(\boldsymbol{q})}{\partial \boldsymbol{q}}\right)^2 f(\boldsymbol{r},\boldsymbol{q})\right)$$

$$(2.70)$$

I calculate the $PL_{21}L_1^{-1}L_{22}v$ as follows

$$PL_{21}L_1^{-1}L_{22}v = -mP_0(\boldsymbol{p})P_0(\boldsymbol{\pi})\int d\boldsymbol{p}d\boldsymbol{\pi}$$

$$\left[-\frac{\partial}{\partial \boldsymbol{r}}\frac{\boldsymbol{p}}{2m} - \frac{\partial}{\partial \boldsymbol{q}}\frac{2\boldsymbol{\pi}}{m}\right]$$

$$\left(\left[\frac{1}{k_BT^2(\boldsymbol{r})}\left[\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\frac{\boldsymbol{q}}{2}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}} - \frac{\partial \Phi(\boldsymbol{r})}{\partial \boldsymbol{r}}\frac{T(\boldsymbol{r})}{2}\right]\right]\sqrt{2}H_1(\boldsymbol{p}')\right.$$

$$\left.-\left[\frac{\sqrt{2}}{k_BT(\boldsymbol{r})}\left(\frac{\partial U}{\partial \boldsymbol{q}}\right)\right]H_1(\boldsymbol{\pi}')\right)$$

$$\int\int f(\boldsymbol{r},\boldsymbol{q},\boldsymbol{p},\boldsymbol{\pi})d\boldsymbol{p}d\boldsymbol{\pi}$$

$$= -P_0(\boldsymbol{p})P_0(\boldsymbol{\pi})$$

$$\left(\frac{\partial}{\partial \boldsymbol{r}}\cdot\left[\frac{1}{2}\left(\frac{\partial \Phi(\boldsymbol{r})}{\partial \boldsymbol{r}}\right)f(\boldsymbol{r},\boldsymbol{q})\right] + \frac{\partial}{\partial \boldsymbol{q}}\cdot\left[2\frac{\partial U(\boldsymbol{q})}{\partial \boldsymbol{q}}f(\boldsymbol{r},\boldsymbol{q})\right]\right)$$

$$(2.71)$$

To summarize the equations in previous page, I can obtain the Fokker-Planck equation for (r, q)

$$\frac{\partial \Psi(r,q,t)}{\partial t} = \gamma^{-1} \left(\frac{\partial}{\partial r} \cdot \left[\frac{1}{2} k_B \frac{\partial}{\partial r} T(r) \Psi(r,q,t) + \frac{k_B}{2} q \cdot \frac{\partial T(r)}{\partial r} \frac{\partial}{\partial q} \Psi(r,q,t) \right] \right.$$

$$+ \frac{\partial}{\partial r} \cdot \left[\frac{1}{2} \frac{\partial \Phi(r)}{\partial r} \Psi(r,q,t) \right] \qquad (2.72)$$

$$\left. + \frac{\partial}{\partial q} \cdot \left[2k_B T(r) \frac{\partial}{\partial q} \Psi(r,q,t) + 2 \frac{\partial U(q)}{\partial q} \Psi(r,q,t) \right] \right). \quad (2.73)$$

2.E Relaxation time of momenta

In this section, I evaluate the relaxation time of momenta. I consider the Fokker-Planck equation of momentum $\psi((p,\pi,r,q,t))$

$$\frac{\partial \psi((p,\pi,r,q,t))}{\partial t} = \hat{\mathscr{L}} \psi((p,\pi,r,q,t)), \qquad (2.74)$$

with the Fokker-Planck operator defined as

$$\hat{\mathscr{L}} \psi(p,\pi,r,q,t) = \frac{\partial}{\partial p} \cdot \left[\left[\frac{p}{m} + 2k_B \bar{T}(r,q) \frac{\partial}{\partial p} + k_B \Delta T'(r,q) \frac{\partial}{\partial \pi} \right] \psi(p,\pi,r,q,t) \right]$$

$$+ \frac{\partial}{\partial \pi} \cdot \left[\left[\frac{\pi}{m} + \frac{1}{2} k_B \bar{T}(r,q) \frac{\partial}{\partial p} + k_B \Delta T'(r,q) \frac{\partial}{\partial p} \right] \psi(p,\pi,r,q,t) \right]$$

$$(2.75)$$

To derive the relaxation time of momentum, I need the equilibrium distribution $\psi(p,\pi|r,q)$. I can write the equilibrium distribution as follows

$$\psi(p,\pi|r,q) =$$
$$\exp \left[-\frac{1}{mk_B \bar{T}^2(r,q)} \left(\frac{\bar{T}(r,q)}{4} p^2 + \bar{T}(r,q)\pi^2 - \frac{1}{2}\Delta T'(r,q) p \cdot \pi \right) \right] \qquad (2.76)$$

The eigenvalue λ and eigenfunction $\psi(p,\pi|r,q)$ satisfy the eigenvalue equation

$$\hat{\mathscr{L}} \psi(p,\pi|r,q) = \lambda \psi(p,\pi|r,q) \qquad (2.77)$$

Here I introduce the variable transform to make the transfer operator self-adjoint:

$$\tilde{\psi}(p,\pi|r,q) \equiv$$
$$\exp \left[\frac{1}{2mk_B \bar{T}^2(r,q)} \left(\frac{\bar{T}(r,q)}{4} p^2 + \bar{T}(r,q)\pi^2 - \frac{1}{2}\Delta T'(r,q) p \cdot \pi \right) \right] \psi(p,\pi|r,q)$$

$$(2.78)$$

I derive the eigenvalue from Eqs. 2.77 and 2.78.

$$-\lambda\,\tilde\psi\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]$$

$$=\frac{\partial}{\partial p}\cdot\left(\left[\frac{p}{m}+2k_B\bar{T}(r,q)\frac{\partial}{\partial p}+k_B\Delta T'(r,q)\frac{\partial}{\partial\pi}\right]\tilde\psi\right.$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]\right)$$

$$+\frac{\partial}{\partial\pi}\cdot\left(\left[\frac{\pi}{m}+\frac{1}{2}k_B\bar{T}(r,q)\frac{\partial}{\partial p}+k_B\Delta T'(r,q)\frac{\partial}{\partial p}\right]\tilde\psi\right.$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]\right)$$

$$=\frac{\partial}{\partial p}\cdot\left(\left[\frac{p}{2m}\tilde\psi-\frac{\Delta T'(r,q)\pi}{2m\bar{T}(r,q)}\tilde\psi+2k_B\bar{T}(r,q)\frac{\partial\tilde\psi}{\partial p}\right]\right.$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]\right)$$

$$\frac{\partial}{\partial\pi}\cdot\left(\left[\frac{\pi}{2m}\tilde\psi-\frac{\Delta T'(r,q)p}{8m\bar{T}(r,q)}\tilde\psi+\frac{1}{2}k_B\bar{T}(r,q)\frac{\partial\tilde\psi}{\partial\pi}\right]\right.$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]\right)$$

$$=\left(\frac{1}{m}-\frac{p^2}{8m^2\bar{T}(r,q)}-\frac{\pi^2}{2m^2\bar{T}(r,q)}\right)\tilde\psi$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\,\pi\right)\right]$$

$$+2k_B\bar{T}(r,q)\frac{\partial^2\tilde\psi}{\partial p^2}$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]$$

$$+\frac{1}{2}k_B\bar{T}(r,q)\frac{\partial^2\tilde\psi}{\partial\pi^2}$$

$$\exp\left[-\frac{1}{2mk_B\bar{T}^2(r,q)}\left(\frac{\bar{T}(r,q)}{4}p^2+\bar{T}(r,q)\pi^2-\frac{1}{2}\Delta T'(r,q)p\cdot\pi\right)\right]$$

$$(2.79)$$

Then I have the eigenvalue equation

$$\gamma\left(\frac{p^2}{8m^2k_B\bar{T}(r,q)}\tilde{\psi} - 2k_B\bar{T}(r,q)\frac{\partial^2\tilde{\psi}}{\partial p^2} + \frac{\pi^2}{2m^2k_B\bar{T}(r,q)}\tilde{\psi} - \frac{1}{2}k_B\bar{T}(r,q)\frac{\partial^2\tilde{\psi}}{\partial\pi^2}\right)$$
$$= \left(\lambda + \frac{\gamma}{m}\right)\tilde{\psi} \tag{2.80}$$

This eigenvalue equation has the same form of the Schrödinger equation for a six-dimensional harmonic potential and thus I can calculate eigenfunctions and eigenvalues straightforwardly. The $(n_1,n_2,n_3,l_1,l_2,l_3)$th eigenvalues and eigendunction are given as

$$\lambda^{(n_i,l_i)} = \gamma\left(\frac{n_1+n_2+n_3+l_1+l_2+l_3}{m}\right) \tag{2.81}$$

$$\tilde{\psi}^{(n_i,l_i)} = \sum_{n_1,n_2,n_3,l_1,l_2,l_3}^{\infty}\left(\frac{1}{m\pi}\right)^3 2^{-(n_1+n_2+n_3+l_1+l_2+l_3)/2}(n_1!n_2!n_3!l_1!l_2!l_3!)^{-1/2}$$

$$H_{n_1}\left(\frac{p_x}{\sqrt{4mk_B\bar{T}(r,q)}}\right)H_{n_2}\left(\frac{p_y}{\sqrt{4mk_B\bar{T}(r,q)}}\right)H_{n_3}\left(\frac{p_z}{\sqrt{4mk_B\bar{T}(r,q)}}\right)$$

$$H_{l_1}\left(\frac{\pi_x}{\sqrt{mk_B\bar{T}(r,q)}}\right)H_{l_2}\left(\frac{\pi_y}{\sqrt{mk_B\bar{T}(r,q)}}\right)H_{l_3}\left(\frac{\pi_z}{\sqrt{mk_B\bar{T}(r,q)}}\right)$$

$$\exp\left(-\frac{p_x^2+p_y^2+p_z^2}{8mk_B\bar{T}(r,q)}\right)\exp\left(-\frac{\pi_x^2+\pi_y^2+\pi_z^2}{2mk_B\bar{T}(r,q)}\right), \tag{2.82}$$

where $H_n(x)$ is the nth-order Hermite polynomial. From the Eq. 2.81, I can derive the relaxation time of momentum.

$$\tau = \frac{m}{\gamma(n_1+n_2+n_3+l_1+l_2+l_3)} \tag{2.83}$$

if the γ is large enough, the relaxation time is small.

2.F Relaxation time of bond vector

In this section, I evaluate the relaxation time of bond vector. I consider the Fokker-Planck equation of momentum $\psi(r,q,t)$

$$\frac{\partial\psi(r,q,t)}{\partial t} = \hat{\mathscr{L}}\psi(r,q,t), \tag{2.84}$$

with the Fokker-Planck operator defined as

$$\mathscr{L}\psi(r,q,t) = \frac{1}{\gamma}\left(\frac{\partial}{\partial r}\cdot\left[\frac{k_B}{2}\frac{\partial}{\partial r}(T(r)\psi(r,q,t)) + \frac{k_Bq}{2}\cdot\frac{\partial T(r)}{\partial r}\frac{\partial\psi(r,q,t)}{\partial q}\right]\right.$$
$$+\frac{\partial}{\partial r}\cdot\left[\frac{k_B}{2}\frac{\partial T(r)}{\partial r}\psi(r,q,t)\right]$$
$$\left.+\frac{\partial}{\partial q}\cdot\left[2Kq\psi(r,q,t) + 2k_BT(r)\frac{\partial\psi(r,q,t)}{\partial q}\right]\right)$$

To derive the relaxation time of bond vector, I need the equilibrium distribution $\psi(\boldsymbol{q}|\boldsymbol{r})$. I can write the equilibrium distribution as follows

$$\psi(\boldsymbol{q}|\boldsymbol{r}) = \exp\left(-\frac{Kq^2}{2k_B T(\boldsymbol{r})}\right) \tag{2.85}$$

The eigenvalue λ and eigenfunction $\psi(\boldsymbol{q}|\boldsymbol{r})$ satisfy the eigenvalue equation

$$\hat{\mathscr{L}}\psi(\boldsymbol{q}|\boldsymbol{r}) = \lambda\,\psi(\boldsymbol{q}|\boldsymbol{r}) \tag{2.86}$$

Here I introduce the variable transform to make the transfer operator self-adjoint:

$$\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r}) \equiv \exp\left(-\frac{Kq^2}{4k_B T(\boldsymbol{r})}\right)\psi(\boldsymbol{q}|\boldsymbol{r}) \tag{2.87}$$

I derive the eigenvalue from Eqs. 2.86 and 2.87.

$$-\gamma\lambda \exp\left(-\frac{Kq^2}{4k_B T(\boldsymbol{r})}\right)\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r})$$

$$= \left(\frac{\partial}{\partial \boldsymbol{r}} \cdot \left[\frac{k_B}{2}\frac{\partial}{\partial \boldsymbol{r}}(T(\boldsymbol{r})\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r})) + \frac{k_B \boldsymbol{q}}{2} \cdot \frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}}\frac{\partial \tilde{\psi}(\boldsymbol{q}|\boldsymbol{r})}{\partial \boldsymbol{q}} + \frac{k_B}{2}\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}}\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r})\right]\right.$$

$$\left. + \frac{\partial}{\partial \boldsymbol{q}} \cdot \left[2K\boldsymbol{q}\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r}) + 2k_B T(\boldsymbol{r})\frac{\partial \tilde{\psi}(\boldsymbol{q}|\boldsymbol{r})}{\partial \boldsymbol{q}}\right]\right)$$

$$-\gamma\lambda \exp\left(-\frac{Kq^2}{4k_B T(\boldsymbol{r})}\right)\tilde{\psi}(\boldsymbol{q}|\boldsymbol{r}) = K\Psi - \frac{K^2 \boldsymbol{q}\cdot\boldsymbol{q}}{2k_B T(\boldsymbol{r})}\Psi + 2k_B T(\boldsymbol{r})\frac{\partial^2 \Psi}{\partial \boldsymbol{q}^2} \tag{2.88}$$

Then I have the eigenvalue equation

$$\frac{K^2 \boldsymbol{q}\cdot\boldsymbol{q}}{2k_B T(\boldsymbol{r})}\psi - 2k_B T(\boldsymbol{r})\frac{\partial^2 \psi}{\partial \boldsymbol{q}^2} = (K + \gamma\lambda)\psi \tag{2.89}$$

This eigenvalue equation has the same form of the Schrödinger equation for a three-dimensional harmonic potential and thus I can calculate eigenfunctions and eigenvalues straightforwardly. The (n_1, n_2, n_3)th eigenvalues and eigendunction are given as

$$\lambda^{(n_i)} = \frac{2K(n_1 + n_2 + n_3)}{\gamma} \tag{2.90}$$

$$\Psi^{(n)} = \sum_{n_1,n_2,n_3}^{\infty} \left(\frac{1}{m\pi}\right)^{3/2} 2^{-(n_1+n_2+n_3)/2}(n_1! n_2! n_3!)^{-1/2}$$

$$H_{n_1}\left(\frac{q_x}{\sqrt{2mk_B \bar{T}(\boldsymbol{r},\boldsymbol{q})}}\right) H_{n_2}\left(\frac{q_y}{\sqrt{2mk_B \bar{T}(\boldsymbol{r},\boldsymbol{q})}}\right) H_{n_3}\left(\frac{q_z}{\sqrt{2mk_B \bar{T}(\boldsymbol{r},\boldsymbol{q})}}\right)$$

$$\exp\left(-\frac{K(q_x^2 + q_y^2 + q_z^2)}{4k_B \bar{T}(\boldsymbol{r},\boldsymbol{q})}\right) \tag{2.91}$$

where $H_n(x)$ is the nth-order Hermite polynomial. From the Eq. 2.90, I can derive the relaxation time of bond vector.

$$\tau = \frac{\gamma}{2K(n_1 + n_2 + n_3)} \tag{2.92}$$

Chapter 3

Simulations

In this chapter, I perform a NEMD simulations to see the effect of conformational degrees of freedom on the Soret coefficient. In NEMD simulations, I can calculate the Soret coefficient directly without phenomenological assumptions. I can calculate the Soret coefficient in EMD method, but it is difficult to deal with the heat flux in MD simulation. I discuss the interpretation of heat flux in the previous research[41]. Thus, I employ the NEMD simulation to see the effect of the conformational degrees of freedom on the Soret coefficient.

In this chapter, I model a polymer as a dumbbell, where two particles are connected by a spring. If the mass and size of dumbbell are large compared to the solvent, the dumbbell obeys the Langevin dynamics. In contrast, if the mass and size of dumbbell are almost same with solvent, the dumbbell obeys the Hamiltonian dynamics. To see the difference affect on the Soret coefficient, I introduce the two models of dumbbell. Details below.
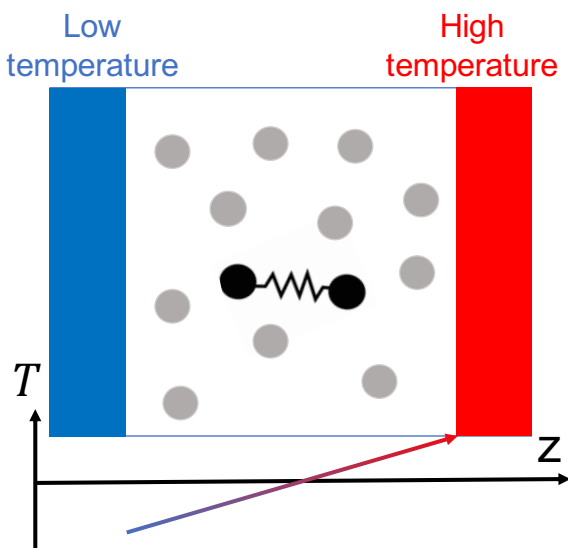

Figure 3.0.1: Simulation system.

3.1 Simulation setting

I consider dumbbell-monomer binary mixtures under a small and linear tempera-
ture gradient. Particle 1 is the dumbbell, where two particles are connected by a
spring and particle 2 are the monomer. The inter-particle interaction $U_{ij}(r)$ between
i component and j component is written as follows.

$$U_{ij}(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right] + U_{c,ij} & (r \le r_c) \\ 0 & (r > r_c) \end{cases} \tag{3.1}$$

Here, r is the distance between two particles, $\sigma_{i}j = (\sigma_1 + \sigma_2)/2$ is the particle size
between i component and j component σ_i is the particle size of i component and ε
is the intensity parameter. $U_{c,ij}$ is the potential shift to attain $U(r_c) = 0$ at $r = r_c$.
The two particles in each dumbbell are bounded by a harmonic potential.

$$U_{bond}(r) = K(r - r_0)^2 \tag{3.2}$$

where k is the spring constant, while r_0 is the natural length of the bond, and I
set $r_0 = 2^{1/6}\sigma_1$. The inter-particle potential between particles in each dumbbell
is not included. The mass of the particles is given by m_1 and m_2. I chose units
of length, energy and mass as σ_2, ε, and m_2. I set the number of monomers and
dumbbells are N_m and N_d (total particle number N_t). I consider the situation where
a constant temperature gradient is applied in the z-direction. I set the system size
in the z-direction by referring to [37]. A temperature gradient is imposed by using
a boundary NEMD simulations. The temperatures in these thermostatting regions
are imposed by Langevin thermostat. The difference between T_h and T_c is set within
the range in which the probability distribution of the center of mass of a dumbbell
linearly changes in the z direction. In the other regions, the equations of motion
were integrated with the velocity Verlet algorithm[42] in LAMMPS[43], in which
the time step is $\delta t = 0.005$.

In case $\frac{m_1}{m_2} \gg 1$:

I performed the NEMD simulations with 16000 particles with the density at 0.7 and the mixing ratio $(2N_d/N_t)$ at 0.00003. The mass and size of the dumbbell are $m_1/m_2 = 125$ and $\sigma_1/\sigma_2 = 5$. The thermostatting regions are set up at the both edges of the rectangular cell. The temperatures in these thermostatting regions are imposed to T_h in the range of $3.6 < z < 7.2$ and $T = T_c$ in the range of $60.8 < z < 64.4$ ($T_h > T_c$) by Langevin thermostat.
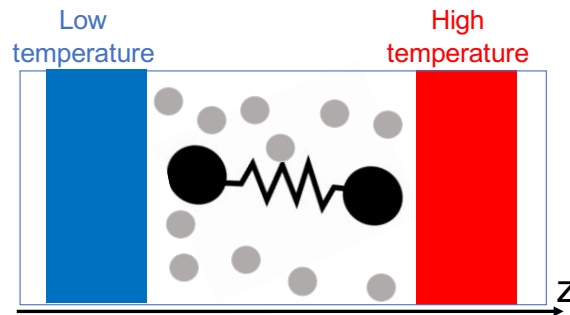

Figure 3.1.1: Simulation system.

In case $\frac{m_1}{m_2} \approx 1$:

I performed the NEMD simulations with 64000 particles with the density at 0.7 and the mixing ratio $(2N_d/N_t)$ at 0.1. The mass and size of the dumbbell are $m_1/m_2 = 1$ and $\sigma_1/\sigma_2 = 1$. The thermostatting regions are set up at the both edges and at the center of the rectangular cell. The temperatures in these thermostatting regions are imposed to $T = T_h$ at the both edges and $T = T_c$ at the center ($T_h > T_c$) by Langevin thermostat.
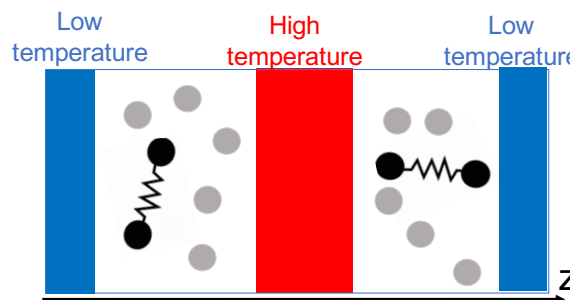

Figure 3.1.2: Simulation system.

In these simulations, I calculate the temperature field $T(z)$ and the probability distribution function for z $P(z)$. In case $\frac{m_1}{m_2} \gg 1$, I can see the monomer as concentration field. Thus, I calculate the Soret coefficient S_T^*:

$$S_T^* = -\frac{\partial P(z)}{dz} \Big/ \frac{\partial T}{\partial z} \qquad (3.3)$$

In contrast, in case $\frac{m_1}{m_2} \approx 1$, I can not ignore the dynamics of monomer. Thus, I calculate the dimensionless Soret coefficient α_T:

$$\alpha_T = -\frac{T_c}{\bar{c}_d(1-\bar{c}_d)} \frac{\partial c_d(z)/\partial z}{\partial T(z)/\partial z}. \qquad (3.4)$$

Here $c_d(z)$ is the fraction at x defined by $c_d(z) = \frac{\rho_d(z)}{\rho_d(z)+\rho_m(z)}$, $\rho_d(z)$ is the density of dumbbell at x, $\rho_m(z)$ is the density of monomer at z and T is the temperature at z. T_c and $\bar{c}_d$ is the spatial average in entire system of $T(z)$ and $c_d(z)$.

3.2   Large mass ratio

In this section, I perform the NEMD simulations. To obey the Langevin equation for dumbbell, I set the mass and size of the dumbbell are $m_1/m_2 = 125$ and $\sigma_1/\sigma_2 = 5$. I confirm this dumbbell model obeys the Langevin equation (see APPENDIX).

3.2.1   Temperature field

Figure 3.2.1 shows the temperature field in the z-direction.

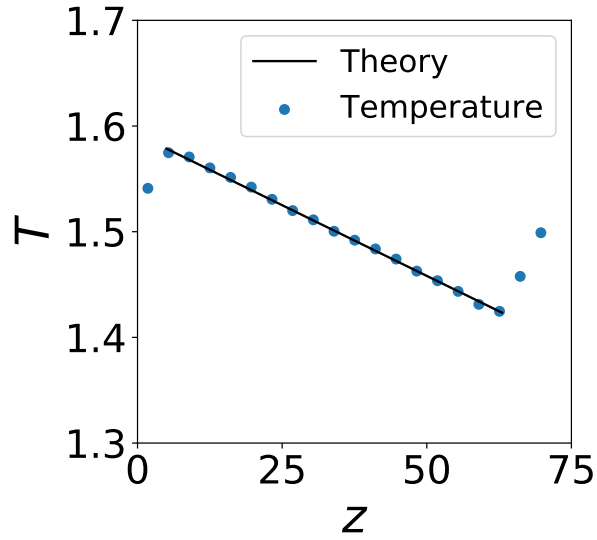Figure 3.2.1: Temperature field in the z-direction.

Figure 3.2.1 demonstrates that temperature field agrees with the theoretical expectation. Here, I calculate the theoretical expectation as follows:

$$T(z) \propto -\frac{T_h - T_c}{L} = -0.0028z, \qquad (3.5)$$

where L is the length from the center of thermostat region of T_h to the center of thermostat region of T_c in the z-direction. The results demonstrate the periodic temperature gradient is applied in the system.

3.2.2 Probability distribution function $P(z)$

Figure 3.2.2 shows the probability distribution function for z. Figure 3.2.2 demonstrates that $P(z)$ has a maximum value at $z \approx 60$. That means the dumbbells move to the cold side under temperature gradient. I also note that $P(z)$ in the thermostat regions behave nonlinear profile. This is due to the energy stability, diffusion and conformation of dumbbell. Because the Soret coefficient is defined in the liner region, I focus on the $20 < z < 50$.
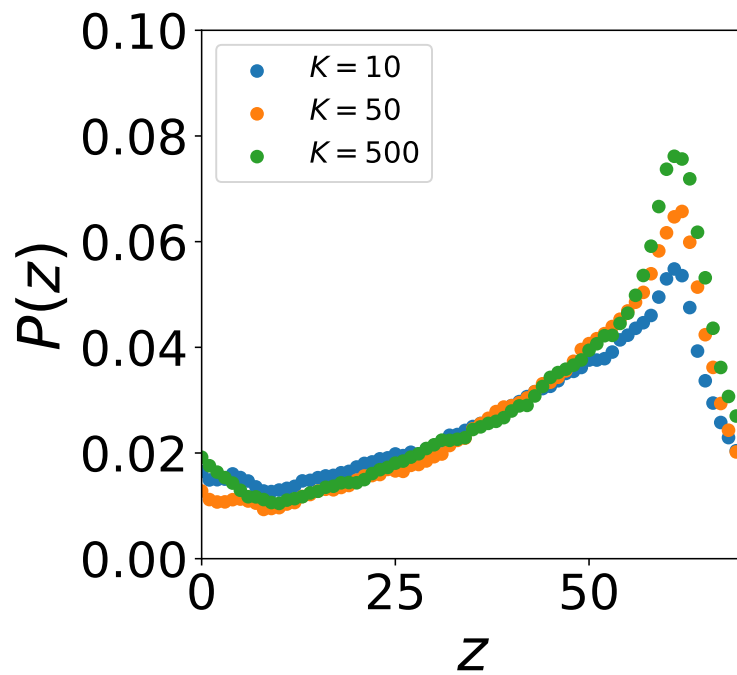

Figure 3.2.2: Probability distribution function of z.

Figure 3.2.3 shows the probability distribution function for z in the range $20 < z < 50$. Figure 3.2.3 demonstrates that $P(z)$ has no dependence on the K. This result means that conformational degrees of freedom does not affect the mass flux.

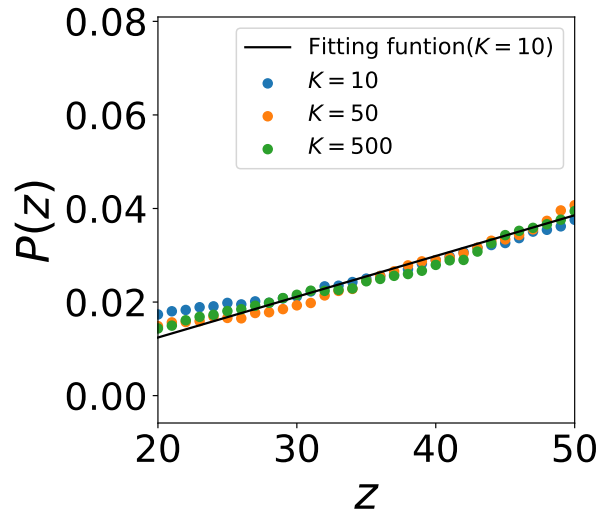Figure 3.2.3: Probability distribution function of z in the range $20 < z < 50$.

3.2.3 Soret coefficient S_T^*

To compare with theoretical results, I calculate the Soret coefficient S_T^*. Figure 3.2.4 shows the S_T^* for various K. This result means that conformational degrees of freedom does not affect the Soret coefficient like the theoretical results.
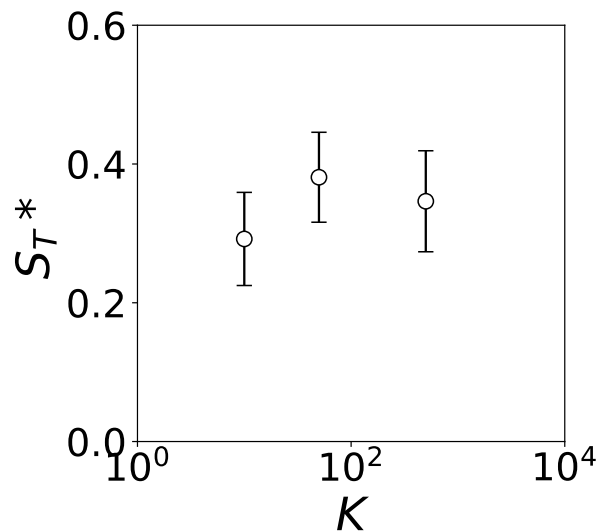

Figure 3.2.4: S_T^* as a function of K.

3.3 Small mass ratio

In this section, I discuss the dependence on the model of dumbbell. I set the mass and size of the dumbbell are $m_1/m_2 = 1$ and $\sigma_1/\sigma_2 = 1$. This dumbbell does not obey the Langevin equation and it is like a dimer molecule.

3.3.1 Temperature field

Before the data acquisition, I confirm that the temperature gradient can be imposed. Figure 3.3.1 shows the temperature gradient in the z-direction.
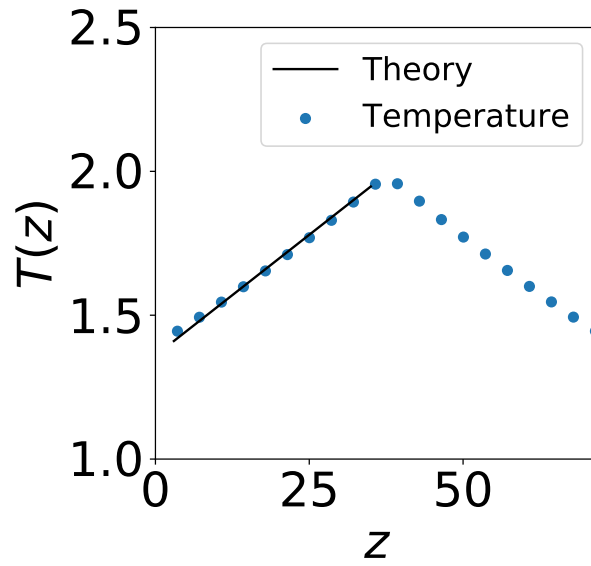
Figure 3.3.1: Temperature field in the z-direction.

Figure 3.3.1 demonstrates that temperature field agrees with the theoretical expectation. Here, I calculate the theoretical expectation as follows:

$$T(z) \propto -\frac{T_h - T_c}{L} = 0.017z \quad (0 < z < 35), \tag{3.6}$$

where L is the length from the center of thermostat region of T_h to the center of thermostat region of T_c in the z-direction. The results demonstrate the periodic temperature gradient is applied in the system.

3.3.2 Probability distribution function $P(z)$

Figure 3.3.2 shows the probability distribution function for z.
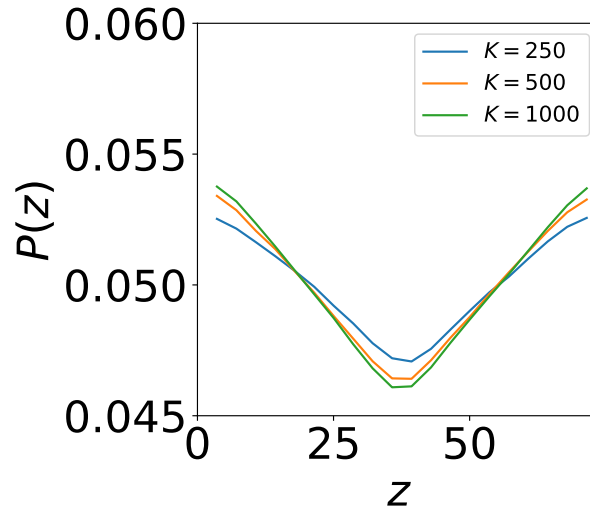
Figure 3.3.2: Probability distribution function of z.

Figure 3.3.2 demonstrates that $P(z)$ has a maximum value at both edges. That means the dumbbells move to the cold side under temperature gradient. I also found that $P(z)$ depends on K value. As the K increase, the gradient of $P(z)$ is larger. This result means that the dumbbell whose conformation easily changes tends to move to the cold side. Thus, conformational degrees of freedom affects the mass flux unlike the theoretical results.

3.3.3 Soret coefficient α_T

I discuss the dependence on K value of dimensionless Soret coefficient α_T. Figure 3.3.3 shows the dependence of the dimensionless Soret coefficient α_T of dumbbells on the spring constant K.

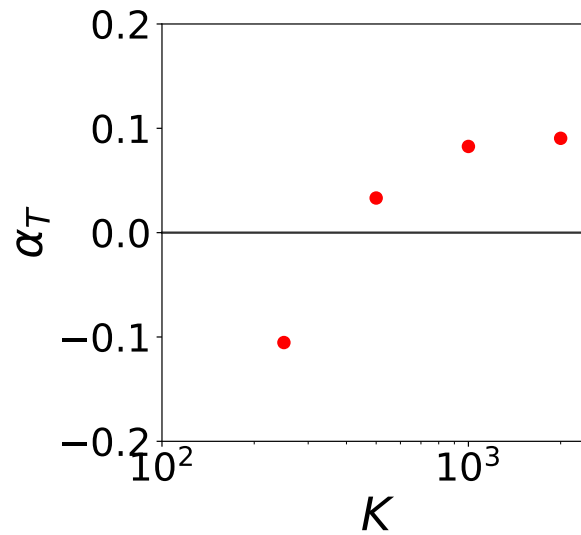Figure 3.3.3: α_T as a function of K.

When the spring stiffness is hard, α_T is positive. As the spring stiffness is Iakened, α_T change from positive to negative. From this result, I found that even if the interaction between components 1 and 2 is identical, the Soret coefficient can change its sign just by changing the distribution of internal degrees of freedom and motion of the dumbbell.

3.3.4 Probability distribution function of bond length

In this subsection, I focus on the probability distribution function of bond length $P(r)$ because the Soret coefficient depend on the size of particle. Figure 3.3.4 show the $P(r)$ with different K and T.
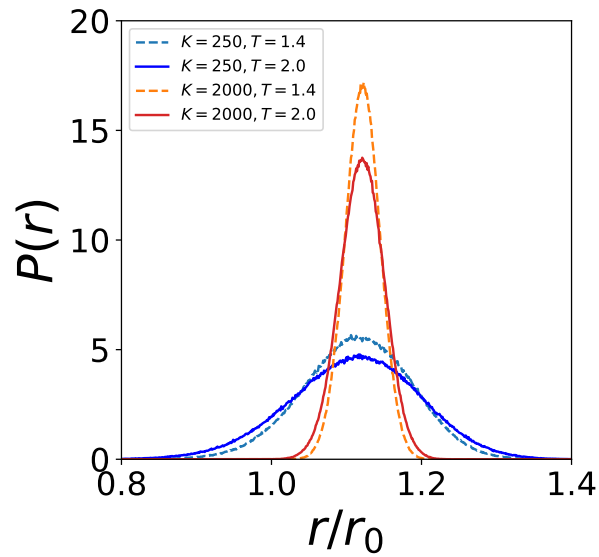

Figure 3.3.4: Probability distribution function of bond length.

The mean value of bond length is independent of K. The width of the bond length distribution becomes sharper as K increases. I concluded that α_T may change to reflect changes in the bond length distribution.

Appendix

3.A Dumbbells obey Langevin equation

In this section, I confirm whether dumbbells obey Langevin equation or not. To confirm this fact, I calculate the mean square displacement(MSD) and correlation function of bond vector.

3.A.1 MSD

In this subsection, I calculate the MSD to confirm that the dumbbells exhibit normal diffusion. Figure 3.A.1 shows the MSD of dumbbells.
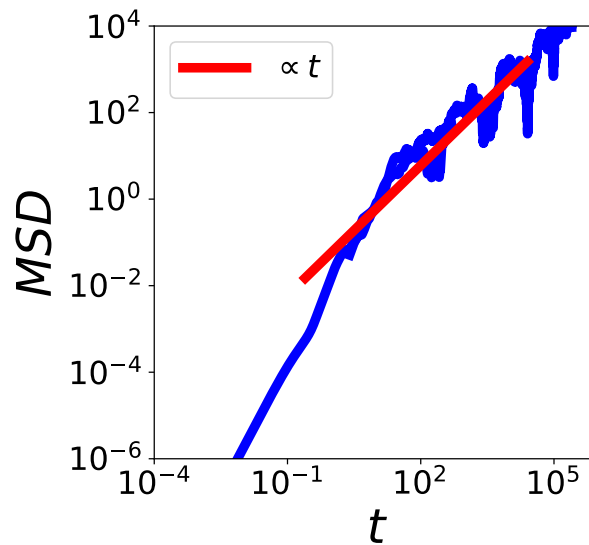

Figure 3.A.1: MSD of dumbbell.

Figure 3.A.1 demonstrates that MSD is proportional to time t at $t > 10^{-1}$. This result means dumbbells show the normal diffusion.

3.A.2 Correlation function of bond vector

In this subsection, I calculate the correlation function of bond vector and compare the results from molecular dynamics and Langevin dynamics. To calculate the correlation function of bond vector in Langevin dynamics, I calculate the effective spring constant and cut off length. Figure 3.A.2 shows the probability distribution function of bond vector in MD simulation.
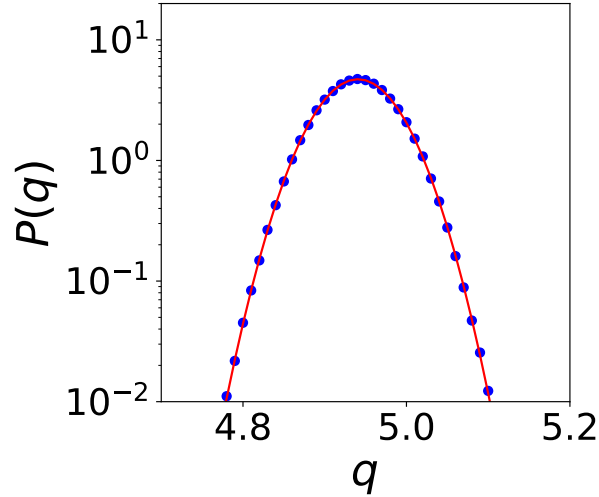

Figure 3.A.2: Profiles of probability distribution of bond vector.

Here, the fitting function can be written as follows:

$$P(q) = \exp\left(-\frac{1}{k_B T}\left[236q^2 - 2333q + 5762\right]\right)$$
$$P(q) = A * \exp\left(-236\left[q - 4.94\right]^2\right)$$

(3.7)

From this fitting function, I can get the effective spring constant and cut off length.

$$K = 236$$
$$r_c = 4.95$$

By using these results, I calculate the correlation function of bond vector by Langevin dynamics. Figure 3.A.2 shows the correlation function of bond vector calculated by molecular dynamics (MD) and Langevin dynamics (LE).
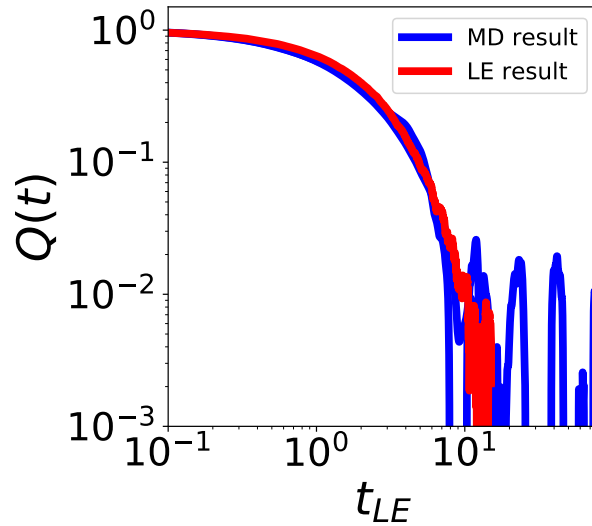

Figure 3.A.3: Correlation function of bond vector calculated by molecular dynamics and Langevin dynamics.

Figure 3.A.2 demonstrates that the correlation functions of bond vector calculated from molecular dynamics and Langevin dynamics are same. This result means the dumbbells obey Langevin equation.

Chapter 4

Discussions

I note the relation between theoretical results and simulation. I perform the NEMD simulations with two dumbbell models. One model has a large mass and size compared to the solvent. The other model has a small mass and size compared to the solvent. The constructed dumbbell model in my theory has a large mass and size, so the simulation results of section 3.2 agree with the theoretical results. In contrast, the simulation results of section 3.3 are different from the theoretical results. This inconsistency is due to the difference in the relaxation time of variables. The constructed dumbbell model in my theory has a large mass and size, so I can discuss the center of mass as the variable which has a different time scale with the momentum and bond vector. However, the dumbbell model of section 3.3 can not assume the time separation because the dumbbell obeys not Langevin dynamics but Hamiltonian dynamics. Thus, these results are natural. Here, I introduce the previous research[37]. Araki and Chicakiyo studied the Soret effect in dimer-monomer mixtures. This system has a small mass and size contrast. They reported the conformational degrees of freedom of the molecules can contribute significantly to the Soret effect. Their results agree with the simulation results of section 3.3.

I also note that my results do not directly apply the experimental data of molecular weight dependence of the Soret coefficient. In order to correctly describe the experimental data, the contribution of conformational degrees of freedom to chemical potential must also be taken into account. In future studies, I study the relation between chemical potential and conformational degrees of freedom. By setting the chemical potential as a function of the center of mass and bond vector, I will be able to construct a theory to reproduce the experimental data.

Chapter 5

Conclusions

To see the contributions of conformational degrees of freedom to the Soret coefficient S_T^*, I construct a molecular theory with the conformational degrees of freedom. The theory reveal that S_T^* is independent of the spring constant and is equal to that for a colloidal particle with no conformational degrees of freedom. This result means that conformational degrees of freedom does not affect the Soret coefficient of the examined system.

In another method, I conduct a molecular simulation. When the mass ratio is large, the simulation revealed that S_T^* has almost same values for each spring constant. This result means that conformational degrees of freedom does not affect the mass flux like the theoretical results. In contrast, when the mass ratio is small, the simulation reveal that the Soret coefficient can change significantly enough to change sign just by changing the distribution of internal degrees of freedom and motion of the dumbbell.

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