



On the thermal diffusion in polymer solutions: Case study on bicomponent film drying



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ABSTRACT

This paper aims to theoretically explain experimental observations regarding the thermal diffusion of polymers in polymer solutions. 3D governing equations for mass and heat diffusion in polymer solutions were derived in the framework of classical irreversible thermodynamics using local equilibrium hypothesis, Onsager reciprocal relations and Prigogine's theory in systems in mechanical equilibrium. The mutual diffusion coefficient, thermal diffusion coefficient and thermal conductivity enter the governing equations as functions of thermodynamic variables and phenomenological coefficients that are bounded to some theoretical constraints. It was shown that the derivative of the linear combination of chemical potentials of polymer and solvent with respect to temperature plays an important role in thermal diffusion in polymer solutions. Thermal diffusion coefficient derived in the model can qualitatively explain the experimental observations in the literature regarding the dependence of thermal diffusion of polymers to molecular weight, polymer chain rigidity and viscosity of the solvent. Numerical simulation of the governing equations for a 1D drying process of polymer solutions indicates that the model is able to capture the effect of thermal diffusion. This effect manifests itself as an increase in local concentration of the solvent on the warm side of a temperature gradient during a solution casting process.

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1. Introduction

Thermal diffusion or Ludwig–Soret effect is the mass diffusion driven by applying a temperature gradient on multi-component systems [1]. Although during the past decade this effect in polymer solutions has been studied [2–8], the physics underlying this phenomenon is not fully understood [9]. Moreover, there is no expression for thermal diffusion of polymers derived on a first-principles basis to relate thermal diffusion to thermodynamic variables.

According to recent experiments, thermal diffusion coefficient in polymer solutions is found to be an increasing function of molecular weight for short chains while reaching a plateau at high molecular weights [4–7]. It also has inverse dependence on the solvent viscosity [6]. Moreover, rigid polymer chains have higher thermal diffusion coefficients than more flexible ones [5,6,8].

The objective of this paper was to derive an equation for thermal

diffusion coefficient in polymer solutions from the fundamental laws of thermodynamics and explain experimental observations related to the thermal diffusion coefficient of polymers in polymer solutions. The thermal diffusion coefficient will be derived by developing a model to describe the evolution of mass and heat diffusion in polymer solutions. The governing equations derived for evolution of concentration and temperature, were used to simulate drying process of polymer solutions as an important example of a nonequilibrium process. Evaporation of solvent from a polymer solution has importance in technologies related to painting, coating, inkjet printing, manufacturing polymer films and production of electronic devices. Apart from the vast technological importance, it is one of the important problems of soft matter physics. In order to have a control on this process, one should have a good understanding of the physics underlying the problem. In most of the studies, the process of drying of polymer solutions is assumed to be an isothermal process which is not a reliable assumption. As Feynman [10] mentioned in his celebrated lectures on physics, once a liquid evaporates it gradually cools. If the molecules of vapor return to the liquid it can result in generation of heat but if by blowing the return of vapor molecules is prevented

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then the liquid is cooled. An immediate drawback of neglecting temperature gradient in a polymer solution undergoing evaporation of solvent is that the effect of thermal diffusion is eliminated. This can affect the concentration profiles because the contribution of thermal diffusion to the mass flux is missed. Therefore, neglecting the variation of temperature cannot provide us with an accurate picture of kinetics of drying process.

The paper is organized as follows: In the second part a model is developed in the framework of classical irreversible thermodynamics and 3D governing equations are derived for evolution of concentration and temperature in polymer solutions. In the third part the initial and boundary conditions for a simple 1D drying process are formulated. The results of simulation and the model are discussed in the last part.

2. Model

We consider a non-reacting multi-component mixture in which non-convective mass diffusion and heat conduction occur. The system is considered to be in one phase, far from the critical region of phase separation. We also assume the system is in mechanical equilibrium.

The hypothesis of local equilibrium allows the fundamental equation of classical thermodynamics to be valid for every volume element in the system, although the whole system is not in equilibrium [1]. Using this hypothesis and Prigogine's theorem for systems in mechanical equilibrium, the rate of change of entropy per unit volume for a two-component system (polymer solution) is given by (See Appendix A)

$$\frac{ds}{dt} = -\nabla \cdot \left(\frac{J_q - \mu J_1}{T} \right) - \frac{1}{T^2} \nabla T \cdot (J_q - \mu J_1) - \frac{1}{T} J_1 \cdot \nabla \mu, \quad (2.1)$$

where s, J_q, J_1, T and μ are entropy per unit volume, heat flux, solvent mass flux, absolute temperature and linear combination of chemical potential of components, respectively. It should be noticed that time derivative in Eq. (2.1) is substantial time derivative (See Appendix A).

We can write Eq. (2.1) in the following form

$$\frac{ds}{dt} = -\nabla \cdot J_s + \sigma, \quad (2.2)$$

where J_s is the entropy flux and σ is the rate of entropy production per unit volume of the system

$$J_s = \frac{1}{T} (J_q - \mu J_1), \quad (2.3)$$

$$\sigma = -\frac{1}{T} J_1 \cdot \nabla \mu - \frac{1}{T^2} \nabla T \cdot (J_q - \mu J_1). \quad (2.4)$$

One can see that σ is a bilinear form of fluxes J_1 and $(J_q - \mu J_1)$ and thermodynamic forces $-1/T(\nabla \mu)$ and $-1/T^2(\nabla T)$.

In the linear region of nonequilibrium thermodynamics, the fluxes can be written in terms of the forces as shown in Eqs. (2.5) and (2.6) which in matrix presentation would yield Eq. (2.7)

$$J_1 = l_{11} \left(-\frac{1}{T} \nabla \mu \right) + l_{12} \left(-\frac{1}{T^2} \nabla T \right), \quad (2.5)$$

$$J_q - \mu J_1 = l_{21} \left(-\frac{1}{T} \nabla \mu \right) + l_{22} \left(-\frac{1}{T^2} \nabla T \right), \quad (2.6)$$

$$\begin{pmatrix} J_1 \\ J_q - \mu J_1 \end{pmatrix} = \begin{pmatrix} l_{11} & l_{12} \\ l_{21} & l_{22} \end{pmatrix} \begin{pmatrix} -\frac{1}{T} \nabla \mu \\ -\frac{1}{T^2} \nabla T \end{pmatrix}. \quad (2.7)$$

Entries of matrix $L = (l_{ij})_{2 \times 2}$ are Onsager's coefficients and based on Onsager's reciprocity relations, off-diagonal entries of matrix L are identical [11].

In conditions for which linear flux-force relations are valid, rate of entropy production takes the quadratic form [11].

$$\begin{aligned} \sigma = & l_{11} \left(-\frac{1}{T} \nabla \mu \right)^2 + (l_{12} + l_{21}) \left(-\frac{1}{T} \nabla \mu \right) \left(-\frac{1}{T^2} \nabla T \right) \\ & + l_{22} \left(-\frac{1}{T^2} \nabla T \right)^2 > 0. \end{aligned} \quad (2.8)$$

Matrix $L = (l_{ij})_{2 \times 2}$ which satisfies Eq. (2.8) should be positive definite and to be so, its entries should satisfy the conditions

$$l_{11} > 0, \quad l_{22} > 0, \quad l_{11} l_{22} > (l_{12})^2. \quad (2.9)$$

It is interesting to note that, if we let $l_{11}/T = \alpha$, $l_{12}/T^2 = \beta$, $l_{21}/T = \delta$ and $l_{22}/T^2 = \gamma$, we can recast Eqs. (2.5) and (2.6) in the same way presented by Landau [12]. Doing so, keeping in mind that δ can be replaced with βT because of equality of l_{12} and l_{21} , and replacing $\nabla \mu$ with the right hand side of Eq. (2.10), knowing the fact that chemical potential is a function of concentration (volume fraction of solvent φ) and temperature, we find

$$\nabla \mu = \left(\frac{\partial \mu}{\partial \varphi} \right)_T \nabla \varphi + \left(\frac{\partial \mu}{\partial T} \right)_\varphi \nabla T, \quad (2.10)$$

$$J_1 = -\alpha \left(\frac{\partial \mu}{\partial \varphi} \right)_T \nabla \varphi - \left[\alpha \left(\frac{\partial \mu}{\partial T} \right)_\varphi + \beta \right] \nabla T, \quad (2.11)$$

$$J_q = \left(\mu + \frac{\beta}{\alpha} T \right) J_1 - \left(\gamma - \frac{\beta^2}{\alpha} T \right) \nabla T. \quad (2.12)$$

In order to preserve the positive definiteness of matrix L , the following conditions should be satisfied:

$$\alpha > 0, \quad \gamma > 0, \quad \beta < \sqrt{\alpha \gamma T^{-1}}. \quad (2.13)$$

After deriving the heat and mass fluxes, we obtain (see Appendix A) the governing equations

$$\rho_1 \frac{d\varphi}{dt} = \nabla \cdot \left\{ \alpha \left(\frac{\partial \mu}{\partial \varphi} \right)_T \nabla \varphi + \left[\alpha \left(\frac{\partial \mu}{\partial T} \right)_\varphi + \beta \right] \nabla T \right\}, \quad (2.14)$$

$$\rho c_P \frac{dT}{dt} = -\nabla \cdot \left\{ \left(\mu + \frac{\beta}{\alpha} T \right) J_1 - \left(\gamma - \frac{\beta^2}{\alpha} T \right) \nabla T \right\}, \quad (2.15)$$

where ρ and c_P are the mass density and isobaric specific heat capacity of the solution respectively and are assumed to be constant.

It should be noted that $\alpha(\partial \mu / \partial \varphi)_T$, $[\alpha(\partial \mu / \partial T)_\varphi + \beta]$ and $(\gamma - (\beta^2/\alpha)T)$ are the mutual diffusion coefficient D_M , thermal diffusion coefficient D_T and thermal conductivity, respectively. The expression derived for thermal diffusion coefficient shows two different contributions. In addition to the original contribution of temperature gradient which is reflected by the phenomenological coefficient β , the derivative of linear combination of chemical potentials of the components with respect to temperature also

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