

Lattice model for thermodiffusion in polymer solutions

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When a temperature gradient is applied to a polymer solution, the polymer typically migrates to the colder regions of the fluid as a result of thermal diffusion (Soret effect). However, in recent thermodiffusion experiments on poly(ethylene-oxide) (PEO) in a mixed ethanol/water solvent it is observed that for some solvent compositions the polymer migrates to the cold side, while for other compositions it migrates to the warm side. In order to understand this behavior, we have developed a two-chamber lattice model for thermodiffusion in liquid mixtures and dilute polymer solutions. For mixtures of PEO, ethanol, and water we take compressibility and hydrogen bonding between PEO and water molecules into account and calculate Soret coefficients for given temperature, pressure, and solvent composition. The sign of the Soret coefficient of PEO is found to change from negative (polymer enriched in warmer region) to positive (polymer enriched in cooler region) as the water content of the solution is increased, in agreement with experimental data. We note a close relationship between the solvent quality and the partitioning of the polymer between the two chambers, which may explain why negative Soret coefficients for polymers are so rarely observed. We also investigate the Soret effect in ethanol water mixtures and find a change in sign of the Soret coefficient of water at high water concentrations in qualitative agreement with experimental data.

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I. INTRODUCTION

A temperature gradient applied to a fluid mixture generally induces a net mass flow, which results in the formation of a concentration gradient. This effect is known as thermodiffusion or the Ludwig-Soret effect [1–4]. The Soret coefficient S_T relates the steady state concentration gradient to the imposed temperature gradient. By convention, the Soret coefficient of component i is positive if component i is enriched in the cooler region [5]. Thermal diffusion has long been used as an effective tool for separating mixtures of isotopes [4]. More recently, the effect has been used to characterize mixtures of complex fluids (see for example Refs. 5–8).

In liquid mixtures whose components differ widely in molecular mass, such as polymer solutions [6, 7] and colloidal suspensions [8], it is typically the heavier component that migrates to the cold region. There are, however, exceptions. In 1977, Giglio and Vendramini found a negative Soret coefficient for poly(vinyl alcohol) in water [9]. Very recently, de Gans *et al.* [10, 11] reported results of thermal diffusion forced Raleigh scattering (TDFRS) measurements on solutions of poly(ethylene oxide) (PEO) in mixtures of ethanol and water. In pure water, PEO shows the expected migration to the cold region of the fluid ($S_T > 0$). However, in solutions with low water content, PEO is found to migrate to the warmer region of the fluid ($S_T < 0$). Although changes in sign of the Soret coefficient have been reported for a number of liquid mixtures of small-molecule fluids, including alcohol solutions [12–16], the PEO/ethanol/water system appears to be the first polymer solution for which such a sign change has been observed.

Thermodiffusion in a binary fluid mixture is described by the flux of one of the components in response to a temperature and concentration gradient.[1] The flux is given by

$$J_1 = -\rho D \nabla c_1 - \rho c_1 (1 - c_1) D' \nabla T, \quad (1)$$

where D is the mutual diffusion coefficient, D' the thermal diffusion coefficient of component 1, ρ the total mass density, c_1 the mass fraction of component 1, and T is the temperature. Here the pressure is assumed to be constant throughout the mixture and the flux J_1 describes the flow of component 1 with respect to the center of mass of the system.[1] Eventually, the system reaches a stationary state in which the flux J_1 vanishes. Inserting $J_1 = 0$ into Eq. (1) yields

$$-\frac{1}{c_1(1 - c_1)} \frac{\nabla c_1}{\nabla T} = \frac{D'}{D}. \quad (2)$$

The Soret coefficient of component 1 is the ratio of thermal and mutual diffusion coefficients

$$S_T = \frac{D'}{D}. \quad (3)$$

More generally, we define the Soret coefficient of component i of a mixture as

$$S_T = -\frac{1}{c_i(1 - c_i)} \frac{dc_i}{dT}. \quad (4)$$

For ternary mixtures, such as PEO in a mixed solvent, concentration gradients and fluxes of two of the components are considered. While Eqs. (1)–(3) are generalized [1, 17] the Soret coefficient of component i can still be defined through Eq. (4).

Thermal diffusion in liquid mixtures is not well understood and even the sign of the Soret coefficient cannot generally be predicted (see e.g. Refs. 4–6). Due to the complexity of the task, attempts to extend the kinetic gas theory [18] of thermodiffusion to the liquid state have so far been unsuccessful [4, 6]. Molecular dynamics simulations (for a review see Ref. 19) have become an important tool in the investigation of thermodiffusion in small-molecule liquids. Long computation times make it difficult, however, to address thermodiffusion in polymeric systems.

In this work, we investigate the Soret effect in dilute polymer solutions and liquid mixtures with the aid of a recently developed [20, 21] two-chamber lattice model. Following traditional experimental methods [1–4], we consider a system divided into two chambers of equal size that are maintained at slightly different temperatures. Particles are free to move between the chambers, which do not otherwise interact. If the pressure differences between the chambers are small enough to be neglected, the Soret coefficient can be determined from the difference in composition of the solutions in the two chambers [1–4]. We start by describing the lattice model for PEO in ethanol-water mixtures in Section II. In Section III we introduce our two-chamber lattice model to determine Soret coefficients of liquid mixtures. Results of our calculations are presented in Section IV and compared with experimental data, where available. In Section V we discuss the work presented here.

II. LATTICE MODEL FOR PEO IN ETHANOL/WATER MIXTURES

Solutions of high molecular weight poly(ethylene oxide) (PEO) in ethanol and water have interesting properties. Hydrogen bonding between PEO and water molecules plays an important role in aqueous solutions of PEO (see e.g. Refs. 22, 23). Water is a good solvent for PEO at standard temperature and pressure. However, the solvent quality decreases with temperature and a miscibility gap opens above a lower critical solution temperature [23]. Ethanol, on the other hand, is a poor solvent for PEO at room temperature but the solubility increases with temperature [10]. In mixtures of ethanol and water at standard temperature and pressure, the water content determines the solubility of PEO. For the molecular weight considered in this work, the transition between poor and good solvent condition appears between a water content of 5% and 10% by weight [10, 11]. Light scattering experiments [10] show that the PEO chains expand with increasing water content, indicating that the addition of water improves the solvent quality.

In order to describe dilute solutions of poly(ethylene oxide) (PEO) in mixtures of ethanol and water, we have developed a simple lattice model for a polymer chain in a mixed compressible solvent. At a given temperature, pressure, and composition, the solution is represented by a simple cubic lattice with N sites, of which N_c , N_s , and N_w are occupied by the polymer (PEO), the first solvent (ethanol), and the second

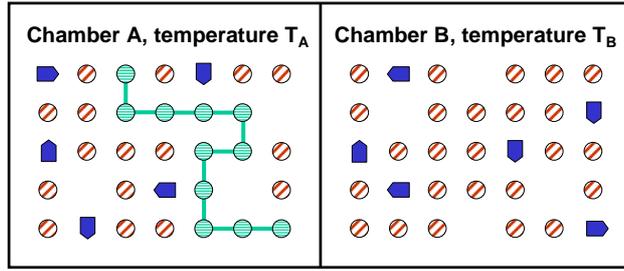


FIG. 1: Two-dimensional illustration of the two-chamber lattice model for the PEO in mixtures of ethanol and water. In this figure, chamber A contains the polymer chain, indicated by circles connected by line segments. The unconnected circles represent sites occupied by ethanol, while the angular shapes represent sites occupied by water.

solvent (water), respectively. In order to account for compressibility, we allow sites to be unoccupied so that $N = N_c + N_s + N_w + N_v$, where N_v is the number of voids. The total volume of the lattice is $V = v_0 N$, where v_0 is the volume of one elementary cube.

Interactions between occupied nearest neighbor sites are described by interaction energies ϵ_{ij} , where the subscripts indicate the occupants of the sites (p for polymer, s and w for the solvents; voids are assumed to have zero interaction energies). In aqueous solutions, hydrogen bonding between PEO and water plays an important role (cf. Ref. 22). In order to account for these specific interactions, we introduce an orientational degree of freedom in the description of water. Each elementary cube occupied by water is assumed to have one special face. If this face is exposed to a polymer segment, the interaction energy is $\epsilon_{pw;s}$ (strongly attractive) otherwise $\epsilon_{pw;n}$ (non-specific), see the left panel of Fig. 1 for an illustration.

From an exact enumeration of all self-avoiding walks of length $N_c - 1$ on a simple cubic lattice (cf. [24, 25]), we determine the number $c(m)$ of chain conformations with m segment pair contacts and the average squared radius of gyration $\bar{R}_g^2(m)$ as a function of m . In this work, $N_c = 17$. In solution, a chain conformation with m pair contacts has $n_n = 4N_c + 2 - 2m$ nearest neighbor (nn) sites, which are occupied by n_i , $i \in \{s, w, v\}$ solvent particles and voids. With the aid of the random mixing approximation for all but the polymer contacts, the canonical partition function of the system can be written as

$$\begin{aligned}
 Z_{\text{pol}}(N, T, N_w, N_s) = & \quad (5) \\
 & N \sum_m c(m) \sum_{[n_w]} 6^{N_w - n_w} \binom{n_n}{n_w} \binom{N - n_n - N_c}{N_w - n_w} \\
 & \times \sum_{[n_s]} \binom{n_n - n_w}{n_s} \binom{N - n_n - N_c - (N_w - n_w)}{N_s - n_s} \\
 & \times e^{-\beta(m\epsilon_{pp} + n_s\epsilon_{ps})} (5e^{-\beta\epsilon_{pw;n}} + e^{-\beta\epsilon_{pw;s}})^{n_w} e^{-\beta E_T},
 \end{aligned}$$

where, as before, $c(m)$ is the number of chain conformations with m polymer-polymer contacts. The square brackets around the summation indices indicate that the summation is performed consistent with the available nearest neighbor sites and the total filling of the lattice. The energy E_r denotes the contribution to the total energy due to solvent-solvent interactions evaluated in random mixing approximation [26], cf. Eq. (9) below.

The pressure of the system is calculated from

$$P = \frac{k_B T}{v_0} \left(\frac{\partial \ln Z_{\text{pol}}}{\partial N} \right)_{N_s, N_w, N_c}. \quad (6)$$

By performing partial summations over the terms in Eq. (5) the probabilities for specific sets of states can be determined. If we write the partition function as

$$Z_{\text{pol}} \equiv \sum_{m, [n_w], [n_s]} Z_{m, n_w, n_s}, \quad (7)$$

the average radius of gyration $\langle R_g^2 \rangle$ is given by

$$\langle R_g^2 \rangle = Z_{\text{pol}}^{-1} \sum_{m, [n_w], [n_s]} \bar{R}_g^2(m) Z_{m, n_w, n_s}. \quad (8)$$

In order to describe properties of ethanol-water mixtures and in order to perform the two-chamber calculations discussed below, the canonical partition function of a chamber without polymer is required. Consider a lattice of N sites occupied by the two types of solvent and voids, $N = N_s + N_w + N_v$. Denoting the filling fractions of ethanol and water by $\phi_s = N_s/N$ and $\phi_w = N_w/N$ and assuming random mixing, the internal energy is given by [26]

$$E_{\text{nop}} = \frac{z}{2} N (\epsilon_{ss} \phi_s^2 + \epsilon_{ww} \phi_w^2 + 2\epsilon_{ws} \phi_s \phi_w). \quad (9)$$

Accordingly, the canonical partition function of the lattice without polymer takes the form

$$\begin{aligned} Z_{\text{nop}}(N, T, N_s, N_w) \\ = 6^{N_w} \binom{N}{N_w} \binom{N - N_w}{N_s} e^{-\beta E_{\text{nop}}}. \end{aligned} \quad (10)$$

Our lattice model for PEO in ethanol-water mixtures has eleven system-dependent parameters. The determination of these parameters and the relation between physical properties and model variables is described in detail in Ref. [20]. Seven of the system-dependent parameters describe the thermodynamics of the pure components and are determined from a comparison with equation-of-state data of the pure components. The remaining four parameters are needed for the description of the mixtures. In Ref. [20] we employed a geometric-mean approximation for ethanol-water interactions and

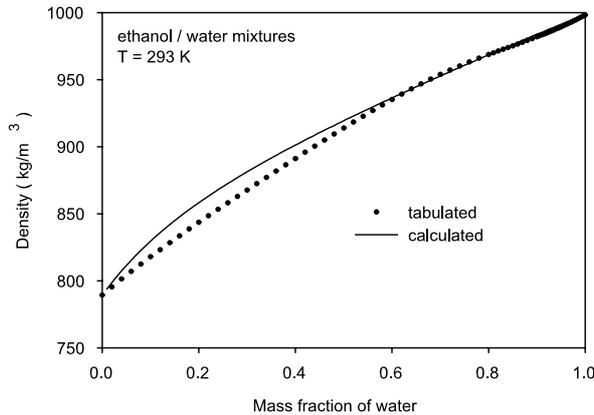


FIG. 2: Density of ethanol-water mixtures at $T = 293$ K and $P \approx 0.1$ MPa. The symbols represent tabulated values [27], the line represents densities calculated from our lattice model.

used the chain dimensions of the short PEO chains as an indicator for solvent quality to determine values for the polymer-solvent interaction energies. In this work we retain the system-dependent parameters of Ref. [20] except for the mixed interaction energy ϵ_{ws} that describes the ethanol-water interactions. The Soret coefficient of water in ethanol-water mixtures changes sign at a water concentration of around 72% by weight [14, 15]. In order to investigate thermodiffusion in ethanol-water mixtures, we determined a value of ϵ_{ws} from a comparison with tabulated values for the density of ethanol-water mixtures [27], weighted to insure a good fit at high water concentrations. In Fig. 2 we compare calculated and tabulated values for the density of ethanol-water mixtures. As expected, the agreement is very good for mixtures with high water contents. Deviations between tabulated and calculated values increase with decreasing water content but do not exceed 2%. The system-dependent parameters are presented in Table I. Since chain dimensions are an indicator for solvent quality, we present in Fig. 3 graphs for the chain dimensions calculated with the aid of the system-dependent parameters presented in Table I. The chain expands (solvent quality improves) with increasing water content of the solution, in qualitative agreement with experimental observation [10, 11]. For PEO in ethanol, the chain dimensions increase with increasing temperature while they decrease with temperature for PEO in water, in agreement with observed changes in solvent quality, cf. Ref. [23].

III. TWO-CHAMBER SYSTEM

Having established a model for the thermodynamic and structural properties of the mixtures, we turn to thermodiffusion. We consider a system of two chambers with slightly different temperatures and determine the probability to find the polymer in

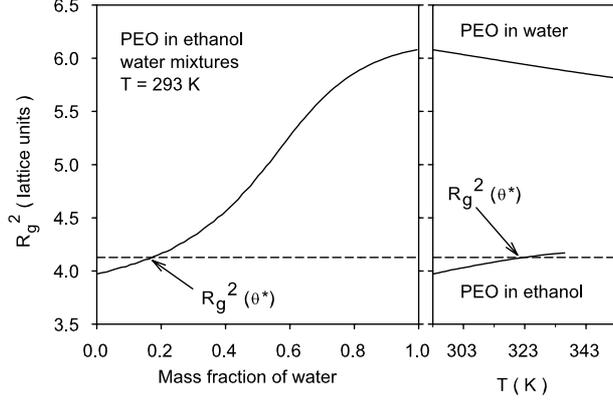


FIG. 3: Radius of gyration squared, R_g^2 , as calculated from Eq. (8). The left panel shows chain dimensions as a function of solvent composition at temperature $T = 293$ K, pressure $P \approx 0.1$ MPa, and a PEO concentration of 5 g/L. The right panel shows the temperature variation at constant pressure of the chain dimensions of PEO in the two pure solvents, ethanol and water. The dashed line indicates the chain dimensions, $R_g^2(\theta^*)$, of the isolated 17 bead chain at the θ temperature of the infinite chain.

TABLE I: System-dependent parameters for the PEO/ethanol/water system

lattice site volume $v_0 = 5.255 \times 10^{-5} \text{m}^3/\text{mol}$			
	ϵ_{ij} in J/mol		scale factors
ethanol	$\epsilon_{ss} = -2306$		$s_s = 1$
water	$\epsilon_{ww} = -3306$		$s_w = 0.3362$
PEO	$\epsilon_{pp} = -1153$		$s_p = 0.6318$
	mixed interactions		
ethanol/water	$\epsilon_{ws} = -3600$		
PEO/water	$\epsilon_{pw,n} = 2660$		
	$\epsilon_{pw,s} = -8020$		
PEO/ethanol	$\epsilon_{ps} = 2660$		

the warmer of the two chambers, see Fig. 1. Assuming that the chambers are non-interacting, the canonical partition function of the system for a given occupation of the chambers is the product of the individual partition functions. To ease notation for the two-chamber sum of states, we define the canonical partition for a single chamber as

$$\begin{aligned}
 Z(N, T, N_w, N_s, N_p) &= \begin{cases} Z_{\text{pol}}(N, T, N_s, N_w) & \text{for } N_p = 1 \\ Z_{\text{nop}}(N, T, N_s, N_w) & \text{for } N_p = 0 \end{cases} \quad (11)
 \end{aligned}$$

where $N_p \in \{0, 1\}$ is the number of polymer chains in the chamber.

For the mixed solvent system considered here, the concentration of the two solvents will generally be different in the warm and cold regions of a fluid. Since we have no a priori information about concentrations (or chemical potentials) of the solvents, we consider all distributions of particles consistent with fixed total particle numbers. The sum of states is then given by

$$Q = \sum_{N_{p,A}=0}^1 \sum_{[N_{w,A}]} \sum_{[N_{s,A}]} Z(N_A, T_A, N_{w,A}, N_{s,A}, N_{p,A}) \times Z(N - N_A, T_B, N_w - N_{w,A}, N_s - N_{s,A}, 1 - N_{p,A}), \quad (12)$$

where, as before, square brackets indicate summations consistent with the total numbers of particles and lattice sites. Chamber A is considered the warmer chamber so that $\delta T = T_A - T_B > 0$, and equal-sized chambers are used, $N_A = N_B = N/2$. As we are performing the calculation of the terms in the sum of states, we monitor for each chamber the composition and the pressure of the mixtures. This allows us to calculate the average quantities for each chamber by performing weighted sums. For example, the average mass fraction of component i in chamber A, is calculated from

$$c_{i,A} = \frac{1}{Q} \sum_{N_{p,A}=0}^1 \sum_{[N_{w,A}]} \sum_{[N_{s,A}]} c_i(N_{w,A}, N_{s,A}, N_{p,A}) \times Z(N_A, T_A, N_{w,A}, N_{s,A}, N_{p,A}) \times Z(N - N_A, T_B, N_w - N_{w,A}, N_s - N_{s,A}, 1 - N_{p,A}), \quad (13)$$

where c_i is the mass fraction of component i . For the case of the solvent mixture without polymer, the equation simplifies to

$$c_{i,A} = \frac{1}{Q} \sum_{[N_{w,A}]} \sum_{[N_{s,A}]} c_i(N_{w,A}, N_{s,A}, 0) \times Z(N_A, T_A, N_{w,A}, N_{s,A}, 0) \times Z(N - N_A, T_B, N_w - N_{w,A}, N_s - N_{s,A}, 0). \quad (14)$$

The probability to find the polymer in chamber A in this model is given by

$$q_A = \frac{1}{Q} \sum_{[N_{w,A}]} \sum_{[N_{s,A}]} Z_{\text{pol}}(N_A, T_A, N_{w,A}, N_{s,A}) \times Z_{\text{nop}}(N - N_A, T_B, N_w - N_{w,A}, N_s - N_{s,A}). \quad (15)$$

This probability is related to an internal energy difference of two chambers at the same temperature:

$$q_A - \frac{1}{2} \simeq -\frac{1}{4} \frac{\langle U_{\text{nop}} \rangle - \langle U_{\text{pol}} \rangle}{k_B T} \frac{\delta T}{T}. \quad (16)$$

The angular brackets indicate an average over all configurations of particles in two chambers at the same temperature T , where the polymer is confined to one of the chambers. U_{pol} and U_{nop} are the average internal energies of the chamber with and without polymer at fixed composition. For the small temperature differences $\delta T = 10^{-4}$ K, corresponding to $\delta T/T \simeq 3 \times 10^{-7}$, employed in our calculations, values for the probability q_A calculated from Eqs (15) and (16) agree to more than five digits. The excess probability $q_A - 1/2$ is proportional to the temperature difference and independent of the polymer concentration for dilute solutions. Relations similar to Eq. (16) can be derived for the probability of finding a given number of solvent particles in the warmer chamber A. They show that the difference between the average numbers of particles in chambers A and B is proportional to δT .

IV. RESULTS

We have applied our lattice model to ethanol-water mixtures and to solutions of PEO in ethanol/water mixtures under a variety of conditions. As noted above, calculated values for composition differences in the two chambers are expected to be proportional to the temperature difference $\delta T = T_A - T_B$ for sufficiently small values of δT . We find this to be the case for a large range of δT values and used $\delta T = 10^{-4}$ K throughout the calculations.

In Fig. 5 we present values for the Soret coefficient of water in ethanol-water mixtures calculated according to Eqs. (14) and (4). For comparison, we include experimental data by Kolodner *et al.* [14], Zhang *et al.* [15], and Dutrieux *et al.* [16]. Both experiment and theory show a change in sign of the Soret coefficient as the water content of the solution is increased. The deviations between calculated values and experimental data are smallest at high water concentrations. This illustrates the importance of a good description of the thermodynamic properties of the mixture. In our earlier work [20], where we employed a geometric mean approximation for the mixed interactions, we found no sign-change for the Soret coefficient of water.

In Fig. 5 we present values for the Soret coefficient of PEO at room temperature (293 K), atmospheric pressure (0.1 MPa), and a PEO concentration of 5 g/L, calculated according to Eqs. (13) and (4). For comparison, we include experimental data by Wiegand and coworkers [10, 28]. Both experiment and theory show a change in sign of the Soret coefficient as the water content of the solution is increased. For low water concentrations of the solution, the polymer is more likely to be found in the higher temperature chamber; for high water concentrations the opposite is true. Differences between theory and experiments are most pronounced at low water concentrations, where our calculations overestimate the Soret effect. This is a consequence of our choosing a mixed interaction parameter ϵ_{ps} that emulates for short chains the poor solvent conditions that long PEO chains experience in ethanol [21]. A comparison of Fig. 5 with the chain-dimension graph Fig. 3 shows a correlation between solvent quality and thermodiffusion. In general, as the solvent quality increases, indicated by an increase in chain dimensions, the Soret coefficient becomes more positive.

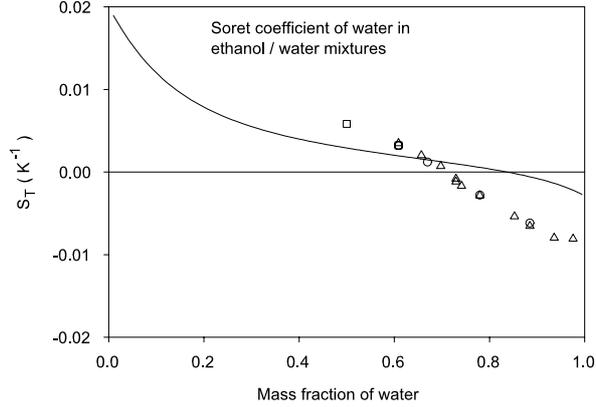


FIG. 4: Soret coefficient of water in mixtures of ethanol and water at approximately 20° Celsius. The symbols indicate experimental data (triangles: Kolodner *et al.* [14], circles: Zhang *et al.* [15], squares: Dutrieux *et al.* [16]), the line represents values calculated from our lattice model.

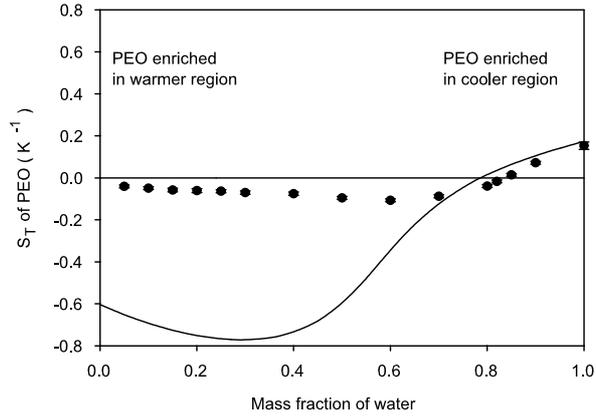


FIG. 5: Soret coefficient of PEO in mixtures of ethanol and water at room temperature and atmospheric pressure. The symbols represent experimental data by de Gans *et al.*[10] and Kita *et al.*[28], the line is the result of our lattice model calculations.

V. DISCUSSION

In this work, we have presented a two-chamber lattice-model approach to determine Soret coefficients of liquid mixtures. A dilute polymer solution is represented by a simple cubic lattice occupied by a single polymer chain, solvent particles and voids. Exact enumeration results for an isolated chain allow us to construct partition functions for the polymer-solvent system without invoking a random mixing approximation for contacts with polymer sites. Interactions between solvent particles, on the other hand, are evaluated in a random-mixing approximation. Enumeration results

are also used to calculate the radius of gyration of the chain in solution, which allows us to monitor the solvent quality of the solution. In order to investigate thermodiffusion, we assume that the lattice is divided into two non-interacting sublattices of equal size that are maintained at slightly different temperatures. For a given occupation of the sublattices, the partition function of the combined system is a product of the canonical partition functions of the sublattices. We consider all possible distributions of polymer chain and solvent particles among the sublattices. The sum of states of the system is calculated by adding up the total partition functions for all distributions, while average quantities are calculated by performing the appropriate weighted sums. The Soret coefficient of component i is determined from the difference between the average concentration of component i in the warm and cold chambers. As in the earlier work on heat of transport (cf. Denbigh [29]) kinetic energy contributions are neglected in our calculations. However, we do not approximate the heat of transport by a difference in potential energy. Instead, the probability to find the polymer in the warmer of the two chambers can be related to a difference in average internal energy that reflects both enthalpic and entropic contributions.

We have investigated the Ludwig-Soret effect in mixtures of ethanol and water. Values for the Soret coefficient of water calculated from our lattice mode change sign as the water concentration increases in qualitative agreement with experimental data [14–16]. Since our model for ethanol and water is very simple, we should not expect quantitative agreement between theory and experiment. We are currently working on a model that includes specific interactions between the molecules which may improve the description of both ethanol-water mixtures and solutions of PEO in such mixtures.

Our model reproduces some of the important thermodynamic properties of the PEO/ethanol/water system. In particular, for PEO in mixed solvents, the solvent quality as monitored by the radius of gyration increases as the water content of the solution increases [10, 11]. Similarly, increasing the temperature increases the solvent quality for mixtures with low water content. For mixtures with high water content, on the other hand, increasing the temperature reduces the solvent quality in agreement with observations on PEO in water (cf. Ref. 23). Our two-chamber approach allows us to calculate Soret coefficients of PEO for given temperature, pressure and composition of the solvent. As expected for dilute solutions [30], the results are independent of the polymer concentration. In qualitative agreement with experimental data of de Gans *et al.* [10, 11] and Kita *et al.* [28], the calculated Soret coefficients are negative for solutions with low water content and positive for solutions with high water content.

A comparison of the results for the radius of gyration of the chain and the values of the Soret coefficients reveals a close relationship between the solvent quality and the partitioning of the polymer between the chambers. In general, the Soret coefficient of the polymer becomes more positive as the solvent quality increases. A typical experiment on polymers in good solvents is thus expected to yield positive Soret coefficients. We expect negative Soret coefficients to be observed for polymers that would be insoluble were it not for specific interactions between solvent molecules and sites on the polymer. It appears that both polymer systems for which negative Soret coefficients have been observed, the solutions of PEO in a mixed ethanol/water

solvent[10, 11, 28] and the solution of poly(vinyl alcohol) in water [9, 31], belong to this category.

Acknowledgments

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