Computer simulation of polymer networks: swelling by binary Lennard-Jones mixtures

Enno Oyen and Reinhard Hentschke ‡∗

Fachbereich Mathematik und Naturwissenschaften
and
Institut für Materialwissenschaften,
Bergische Universität,
D-42097 Wuppertal, Germany
(Dated: April 21, 2005)

Abstract

The swelling of regular, tightly meshed model networks is investigated by a molecular dynamics-Monte Carlo hybrid technique. Chemical equilibrium between two simulation boxes representing the gel phase and a solvent bath, respectively, is obtained by subjecting the Lennard-Jones particles of a binary mixture, serving as explicit solvent, to the particle transfer step of Gibbs Ensemble-Monte Carlo. The swelling behaviour, especially preferential absorption of a single component, whose dependence on temperature, pressure and fluid composition is studied, also depends significantly on the size of the central simulation cell. These finite size effects correlate well with those exhibited by the density of solvent-free (dry) networks. A theoretical expression, whose derivation is based on network elasticity (of dry networks), yields finite size scaling behaviour in good accord with simulation results for both dry networks and gels in contact with solvent baths. This expression can be used to extrapolate the swelling behaviour of simulated finite systems to infinite system size.

‡ Author to whom correspondence should be addressed.
I. INTRODUCTION

Polymer networks have been generally accessible to computer simulations for about fifteen years, i.e. the frequency of papers on computer simulation of polymer networks increased from roughly a dozen by a factor of ten comparing the decades before and after 1990. But already a number of earlier works discuss the possibilities offered by computer simulation of polymer networks addressing network formation, network structure, and mechanical properties (e.g.,\textsuperscript{1}) or the dynamics of entangled polymers (e.g.,\textsuperscript{2}). Much of the earlier history of polymer network simulation is discussed in the following reviews\textsuperscript{3,4}. More recently topics of interest were mainly the kinetics of formation and topological effects (e.g.,\textsuperscript{7-10}). A strong focus has developed on polyelectrolyte networks triggered by their importance as superabsorbing materials widely used in hygiene products or in construction materials (e.g.,\textsuperscript{11-15}).

Since 1997 a number of works have appeared looking at polymer networks in chemical equilibrium with explicit sorbates (e.g.,\textsuperscript{16,18,19} (see also\textsuperscript{4} and the additional references therein)\textsuperscript{12,20-23}). There are several reasons why explicit inclusion of solvent in a molecular simulation investigating the swelling of a polymer network may be desirable. The technical difficulties associated with explicit solvents, i.e. establishing the equilibrium between the gel phase and the bulk solution, are of interest in their own right. In addition solvents do have their own phase behavior, and crossing a phase boundary in the bulk solvent may induce pronounced changes in the gel phase. This aspect has been investigated in a recent experimental study on the swelling of poly(ethylenoxide)-gels in aqueous solution\textsuperscript{5}. Another point is the coupling between network swelling and the molecular structure of the solvent. A striking example is the swelling of superabsorbing materials. The mass of absorbed water to the absorbing material my exceed two orders of magnitude. But if the water is substituted by, for instance ethanol with a similar dipole moment, the absorption reduces to essentially zero\textsuperscript{6}. Finally, solvents may be mixtures composed of several molecular species. Simulation of the relative fractions in the gel phase as compared to the bulk solution thus requires the explicit inclusion of solvent particles in the model.

In this work we study preferential sorption in case of a binary solvent in thermal equilibrium with a regular model network. To our knowledge, this problem has been treated by computer simulation only once for the case of hard sphere interaction by de Pablo and coworkers\textsuperscript{16}. Here the solvent consists of particles interacting via Lennard-Jones potentials.
The two solvent species differ exclusively in size, i.e. we use two different $\sigma$-parameters. The network chains consist of harmonically bonded LJ particles identical to the large solvent species. The technique is a hybrid combining molecular dynamics translation moves of all particles with Gibbs Ensemble Monte Carlo transfer of solvent particles between the network and the bulk solvent. In particular we study the dependence of the swelling ratio and the separation factor on thermodynamic conditions as well as on solvent composition. The paper is structured as follows. In section II we discuss the methodology. In the next section we focus on finite size effects, which are important because the inclusion of explicit solvent imposes severe limitations on the system size. Based on the self-consistent field approach to polymer conformation we find a general scaling form followed by all quantities of interest. Section IV compiles our bulk results for the swelling and separation behavior of the network. Section V is the conclusion.

II. METHOD

The method used here is a molecular dynamics–Monte Carlo hybrid technique. The system consists of two simulation volumes; one containing the network including solvent, the other one containing solvent only. Due to the usual periodic boundary conditions employed here the central simulation cells are unit cells of infinite lattices. The non-bonding interaction acting between all particles is the usual Lennard-Jones (LJ) potential, $u_{LJ}(r) = 4\epsilon \left( \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right)$. Cross interactions between different species are computed using the Lorentz mixing rule, $\sigma_{\alpha\beta} = \frac{1}{2} (\sigma_\alpha + \sigma_\beta)$. Notice that in this work all particles possess the same $\epsilon$ value and the same mass, $m$. The $\sigma$ values of the network and the two solvents are given in Tab. I together with the other model parameters. In addition the usual long-range corrections (LRC) to potential energy (required in the Monte Carlo part) and pressure based on the LJ potential are employed throughout. In general, we use a cutoff radius $r_{cut} = 2.5$ LJ units (unless stated otherwise). Increasing $r_{cut}$ from 2.5 to 5.0 does not change any result significantly. The networks consist of linear chains of LJ sites connected via harmonic springs, $u_{bond} = \frac{k}{2} (r - r_0)^2$. Note that $\sigma_{net} = \sigma_1 = r_0$ (cf. Tab. I). The fully extended chains form simple cubic lattices in which every $n_c$th LJ site along a chain also belongs to two other chains (cf. Fig. 1a).

The motions of all particles in the two boxes, whether part of the network or part of the
solvent, are computed via the molecular dynamics (MD) technique using the velocity Verlet algorithm\textsuperscript{24} to integrate the equations of motion (with a time step $\Delta t = 0.002$). The weak coupling method due to Berendsen et al.\textsuperscript{25} is used to adjust temperature and pressure in each box ($\tau_T = 0.1$, $\tau_P/kT = 20$). So both boxes are separately equilibrated and kept in thermal and mechanical equilibrium with heat and pressure baths by MD techniques. The MD runs are interrupted every 50 time steps, and the current configurations are exposed to Gibbs Ensemble Monte Carlo (GEMC) particle exchange moves\textsuperscript{26,27}, which serve to establish chemical equilibrium between both boxes. Each exchange attempt consists of the following steps:

- One box $B_{rm}$ is chosen for particle removal at random (and the other box $B_{ad}$ for particle addition), i.e., each box is as likely to be $B_{rm}$ as $B_{ad}$.

- The kind of particles (solvent 1 or 2) to be transferred is chosen so that each kind is selected with an arbitrary but fixed probability. Here the probability for solvent 1, which ranges from 0.6 (at the highest temperature) to 0.9 (at the lowest temperature), is chosen so that the number of successful exchange attempts is roughly the same for both solvents.

- One of the particles of the selected kind located in box $B_{rm}$ is chosen at random for removal.

- A position in box $B_{ad}$ is selected at random for particle insertion.

- The particle exchange is accepted with probability

$$\min \left(1, \frac{V_{ad} \cdot N_{rm}}{V_{rm} \cdot (N_{ad} + 1)} \cdot \exp \left(- \frac{\Delta U_{rm} + \Delta U_{ad}}{T}\right) \right),$$

where $\Delta U_{rm}$ is the potential energy difference associated with the attempted removal, and $\Delta U_{ad}$ is the potential energy difference due to the attempted insertion. In addition $V_{rm}, V_{ad}, N_{rm},$ and $N_{ad}$ refer to the corresponding simulation box volumes and particle numbers before the transfer.

The number of such particle exchange attempts carried out within one MC block between two partial MD runs varies from one (in case of the smallest system with 270 network
particles at the highest temperature) to 20,000 (in case of the largest system containing 5120 network particles at the lowest temperature). So the overall numbers of particles of each kind are conserved, but the particle numbers in each box are not.

The effect of particle insertion on one of the key quantities of interest, the swelling ratio, $q$, defined as the ratio of the network volume in the swollen state to the volume of the dry network at the same thermodynamic conditions, is shown in Fig. 1b. The figure exemplifies the dependence of $q$ on the number of accepted particle transfers per LJ time unit for the case of swelling by a one-component LJ fluid instead of a mixture. The model parameters used in this case are listed in Tab. II. The primary simulation volume of the fully extended network comprises $4^3$ cubic unit cells (corresponding to 256 network beads). The total number of solvent particles is 1000. At sufficiently high temperature, i.e., $T = 2.7$, there is no discernible effect, whereas at the low temperature, $T = 1.15$, the effect of particle insertion becomes rather pronounced beyond 10 accepted particle transfers per LJ time unit, i.e., the equilibrium distribution is perturbed strongly by particle exchanges. Of course the magnitude of the effect depends on the system parameters. Therefore, the number of attempted particle exchanges has to be chosen carefully at low temperatures. While too many accepted exchanges lead to poor results due to systematic error, too few exchanges cause slow equilibration and low frequency oscillations which require extraordinarily long simulation times.

III. DISCUSSION OF FINITE SIZE EFFECTS

Computer simulation studies of polymer networks focus on rather small volumes resulting in finite size effects, which may not be negligible. Fig. 2 shows molecular dynamics simulation results for the density of a perfectly regular model network as function of system size, $N^{1/3}$, where $N$ denotes the number of LJ sites, which here, because we consider a dry network, is equal to the number of network beads. The model parameters are the ones for the network swollen by the binary mixture (cf. Tab. I), except $n_c = 15$ (instead of 4), i.e., the network of Fig. 2 has a comparatively large mesh size. Notice that the network density increases with increasing number of unit cells (every unit cell contains 43 LJ sites). We note that simulations on networks with different $n_c$ and at different temperatures and pressures show completely analogous behaviour (cf. Fig. 1 in Ref.28).
Physical quantities computed from atomic or molecular computer simulations usually are linked to either the volume or the typical linear dimension of the simulation cell. Leading finite size corrections to the chemical potential in simple liquids for instance are proportional to $N^{-1}$, where $N$ is the number of particles in the system. Close to the critical point, however, spatial density fluctuations dominate the behavior, and finite size effects are described in terms of the fluctuation correlation length cutoff at a linear dimension $L \propto N^{1/3}$. But even away from criticality many quantities are coupled to the linear expanse of the simulation cell rather than to its volume. Recent examples are simulations focusing on the thermal conductivity in crystalline systems, where the phonon mean free path is limited by $L$, and the finite size corrections are found to be proportional to $L^{-1}$.\(^{31,32}\)

Fig. 2 includes two approximations to the simulation data representing these two $N$-dependencies. Neither curve convincingly explains the $N$-dependence of the data. In particular, there is not explicit motivation why the data should scale as $N^{-1}$ or $N^{-1/3}$ (or as power laws thereof). In a previous paper\(^{28}\) we derive a formula for the $N$-dependence of $\rho$, given by

$$\rho = \rho_{\infty} - C \exp[-aN^{1/3}]$$

(cf. Eq. (7) in Ref.\(^{28}\)). Here $C$ and $a$ are parameters. The resulting approximation to the data in Fig. 2, given by the solid line, is excellent. The agreement is not limited to the conditions simulated in Fig. 2. Excellent agreement is obtained also for a wide range of different temperatures, pressures and network mesh sizes (cf. Figs. (1) and (3) in Ref.\(^{28}\)). Eq. (2) is derived using the self-consistent field approach for the network chains including contributions beyond the so called ground state dominance approximation (e.g. section IX.2 in Ref.\(^{34}\)). The main value of Eq. (2) is that it allows to estimate the bulk density, $\rho_{\infty}$, based on a number of simulations for small systems, which requires a fraction of the time necessary to complete the simulations for the larger systems. Thus Eq. (2) may greatly reduce the effort which has to be spent in order to obtain reliable bulk results.

In the following we are interested mainly in networks swollen by solvents, even though we continue to use dry networks when we determine the swelling ratio, $q$, defined as the ratio of the volume of the gel to the volume of the dry network at the same thermodynamic conditions. The two panels in Fig. 3 show the dependence of the swelling ratio, $q$, on system
size at different thermodynamic conditions. Here the system size is defined in terms of \( N_{\text{net}}^{1/3} \), where \( N_{\text{net}} \) is the number of network beads. Notice that the finite size effect, which in case of the density was about 6% over the range of system sizes considered, has increased up to 35%. Nevertheless the form of Eq. (2), i.e.

\[
Y = Y_\infty - C_Y \exp[-a_Y N^{1/3}],
\]

(3)

can still be applied to the swelling ratio \((Y = q)\). The resulting curves yield perfect description of the simulation data. The applicability of Eq. (3) to other quantities than the network density is not too surprising, because this form of the finite size correction term appears in the free energy of the network (cf. Eq. (3) in Ref. 28), i.e. every quantity derived from this free energy or from a free energy containing this contribution will, at least to first order, also exhibit this particular finite size dependence. Notice that the finite size effects do vary little comparing the two pressures. However, when the temperature is varied, we observe pronounced finite size effects at low temperatures. For the highest temperature only the smallest system exhibits discernible deviation from the bulk result, i.e. the result in the thermodynamic limit of infinite system size. This means that reliable high temperature results can be obtained by simulating a few systems of moderate size. Nevertheless, simulation data from systems of varying size are required at lower temperatures in order to carry out the extrapolation according to Eq. (3).

Another useful quantity is the separation factor defined via

\[
\alpha = \frac{x_{\text{net}}^2}{x_{\text{solv}}^2} / \frac{x_{\text{net}}^1}{x_{\text{solv}}^1}.
\]

(4)

(e.g., Ref. 29) Again the finite size behavior of \( \alpha \) may be described via Eq. (3) with \( Y = \alpha \). This is shown in Fig. 4, where \( \alpha \) is plotted as function of \( N_{\text{net}}^{1/3} \) for the same temperatures and pressures as in Fig. 3. Note that our comments on Fig. 3 also apply to Fig. 4. While the finite size effects are clearly visible at low temperatures, the results at the highest temperature are dominated by statistical errors. The quality of the fit may be represented more clearly. Fig. 5 shows scaled swelling ratios and separation factors at \( T = 1.2 \) and \( P = 0.2, 0.5 \) using the values for \( q_\infty \) and \( \alpha_\infty \) extracted from Figs. 3a and 4a.

7
IV. BULK RESULTS

Selected bulk results for $q$ and $\alpha$, i.e. $q_\infty$ and $\alpha_\infty$, are compiled in Fig. 6. While the results for low temperatures ($T = 1.2$ to $1.8$) are obtained from extrapolation, the results for $T = 2.0$ and $3.0$ are simply averages from simulations of sufficiently large systems. The swelling ratio decreases monotonically as the temperature increases. Note that an analogous monotonic decrease was found previously for single component solvent$^{21}$. It is also worth noting that a decreasing $q$ with increasing $T$ is found experimentally for poly(ethylenoxide) gels swollen in water$^5$. The corresponding separation factor, $\alpha$, shown in the bottom panel, also exhibits a monotonous decrease as the temperature increases (except at the lowest temperature). Error bars show the standard error of the mean based on a number of independent runs in case of the highest temperatures ($T = 2.0, 3.0$). In the low temperature cases, however, the error bars are rough estimates, based on the differences of the results of independent simulations of identical system sizes (two to three runs in each case). Note also that an increase in pressure leads to an increase of the swelling ratio (cf. the discussion of the pressure dependence of $q$ for one-component solvents via lattice calculations in Refs.$^{21}$ and$^{22}$ (2001)).

Of course, the results shown in Fig. 6 for $x_{solv}^1 \approx 1/3$ can depend on the composition of the bulk solvent mixture. The influence of the composition of the bulk solvent mixture, expressed in terms of $x_{solv}^1$, is considered in Fig. 7 at $T = 1.2/3.0$ and $P = 0.5$. Notice that $q$ and $\alpha$ exhibit no discernible dependence on the composition of the bulk solvent at $T = 3.0$. At the lowest temperature studied here, however, we do find a noticeable dependence of $q$ and $\alpha$ on composition, even though the effect on $\alpha$ still appears to be rather weak.

Before looking at the solvent separation in more detail, it is useful to briefly consider the gas-liquid phase behavior of a solvent mixture similar to the one employed in the swelling simulations. The top panel in Fig. 8 shows the gas-liquid coexistence in the $P-x_1$-plane computed at $T = 1.15$. Besides the simulations at predefined pressures (like the network swelling experiments), we also carry out runs subject to the conditions of constant overall volume of both simulation boxes and equality of pressures. The data include results obtained in previous simulations by Panagiotopoulos et al.$^{26,27,33}$ as well as in this work. Note that coexistence curves computed at other (subcritical) temperatures will look similar. Especially the pressure range of the coexistence region is limited by the vapor pressures of the pure
fluids. In the network swelling experiments, we always have taken care to not straddle gas-liquid coexistence, even though the effect of the phase transition on the swelling behavior is of interest of course (cf. Ref.⁵). The bottom panel in Fig. 8 shows the separation factor plotted vs. pressure computed analogous to Eq. (4) (gas and liquid phase instead of network and solvent) applied to the mole fractions at coexistence in the upper panel. The data obtained in this work indicate a near linear increase of \( \alpha \) with rising \( P \). Note that the overall magnitude of \( \alpha \) obtained for the bulk solvent mixture at coexistence is the same as in the case of the network in contact with the homogeneous solvent at similar temperatures and pressures. Note also that the vertical lines in the bottom panel of Fig. 8 indicate the vapor pressures of the pure fluids, \( P_1 \) and \( P_2 \). The horizontal line indicates \( \alpha = P_2/P_1 \), which follows if we assume the validity of the laws of Dalton and Raoult.

Fig. 9 illustrates the separation of the two solvent species via sorption. The open squares are obtained by direct simulation at \( T = 3.0 \). The short dashed line, which is an excellent approximation to the data, is obtained by solving Eq. (4) for \( x_{1}^{\text{net}} \) and inserting the value of \( \alpha \), obtained at the respective temperature, from the bottom panel in Fig. 6. This of course assumes that \( \alpha \) is independent of composition (as shown in the bottom panel in Fig. 7), an approximation which is well known from adsorption onto solid substrates (cf. Ref.²⁹, section 3.10). Based on this assumption Fig. 9 includes another example, the long dashed line, for \( \alpha = 1.7 \) corresponding to \( T = 1.2 \) in the bottom panels of Fig. 6 and Fig. 7. The simulation results indicated by the open circles and the filled diamonds again fall on the predicted line. The open circles are obtained from single simulations of the largest systems, whereas the filled diamonds correspond to extrapolated thermodynamic limits calculated in the following manner: \( x_{1}^{\text{solv}} \) are averaged simulation results from systems of varying size, but similar composition (i.e., \( x_{1}^{\text{solv}} \approx 1/3 \) and \( x_{1}^{\text{solv}} \approx 2/3 \), respectively); \( \alpha \) are obtained from extrapolation (filled diamonds in bottom panel of Fig. 7); \( x_{1}^{\text{solv}} \) and \( \alpha \) are inserted in Eq. (4), which is solved for \( x_{1}^{\text{net}} \). The situation is not so clear cut at low temperatures - a point we discuss in the context of the next figure. Overall, however, the sorption of the smaller species is preferred. This is in agreement with Ref.¹⁶, where the authors study the equilibrium swelling of athermal (hard-core) polymeric gels. Here we find in addition that the depletion of large particles in the network relative to the bulk solution diminishes as the temperature increases. Again we return to the discussion of this point in the context of Fig. 10.
Fig. 10 finally shows the site absorbability, defined via

$$A = \frac{N_{solv}}{N_{net}}. \quad (5)$$

Here $N_{solv}$ is the number of solvent particles inside the network containing $N_{net}$ network particles. Notice that $A$ increases strongly with decreasing temperature. This behavior is easily understood in terms of the thermodynamics of adsorption at solid substrates. The site absorbability is closely related to excess amount adsorbed per accessible surface area, $\Gamma$, i.e. $\Gamma \sim A/a_s$, where $a_s$ is a typical area per molecule. At low gas pressure, $P$, one has a Henry’s law type relation, $\Gamma = k_H P + \mathcal{O}(P^2)$, where $k_H$ is Henry’s constant (for a one component gas). $k_H$ is related to the isosteric heat of adsorption, $q_{st}$, via $q_{st} = \frac{\partial \ln k_H}{\partial 1/T}$ (using LJ units), where the index $o$ indicates that the formula is derived in the limit of small coverage. $q_{st}$ is given by the difference between the molar enthalpy in the gas and at the surface, i.e. $q_{st} = h_{gas} - h_{surf}$. Consistent with the above level of approximation we replace $h_{gas}$ by $\frac{3}{2}T + T$ (translational motion + ideal gas law). Likewise we replace $h_{surf}$ by $-\epsilon + T + T$, i.e. we assume that the particles experience a one-dimensional oscillator potential with a depth given by $-\epsilon$ and free translation in the perpendicular directions. In addition we use $PV \approx 0$ (relative to the gas phase). Thus we obtain $\epsilon + \frac{1}{2}T = \frac{\partial \ln k_H}{\partial 1/T}$. Integration yields $k_H \propto T^{-1/2}e^{\epsilon/T}$. Consequently we may write $A \sim T^{-1/2}e^{\epsilon/T}$ for different temperatures, $T$. Using $T = 3.0$, $A \approx 0.13$ and $T = 1.2$, $A \approx 1.3$ at $x_{solv}^1 = 0$, i.e. only the smaller particles are present, we obtain $\epsilon \approx 3.7$. Similarly we use $T = 3.0$, $A \approx 0.1$ and $T = 1.2$, $A \approx 0.4$ at $x_{solv}^1 = 1$, i.e. only the larger particles are present, to obtain $\epsilon \approx 1.9$. Even though the approximations made here are rather crude the result is appealing. It ties the observed reduction of $A$ with increasing temperature (at $x_{solv}^1 = 0, 1$) to reasonable $\epsilon$-values. If we replace the one-dimensional oscillator potential in the above reasoning by a three-dimensional oscillator (appropriate for a particle in an isotropic cage) the corresponding $\epsilon$-values are 5.5 and 3.7. This increase is consistent with the idea of a particle interacting with many neighbors. Even though the numbers are model dependent, we always find that $\epsilon$ comes out smaller for the larger species, i.e. there is an energetic advantage favoring the sorption of the smaller species as already expressed in Fig. 9.

In Ref.16, where the authors present results for the sorption of a binary hard sphere solvent by a hard-core polymeric gel, the preferential sorption of the smaller species is explained.
in terms of a packing argument. The latter is based on the virtual removal of all solvent particles from the gel. If the resulting cavities are refilled, so the argument, it is easier to insert a small particle. However, this intuitive argument may equally be applied to a region inside the bulk solvent (without a network!), where it clearly fails. Probably the preferential sorption of the smaller species (in the hard core case) is due to a compromise between the translational entropic disadvantage an empty cavity imposes and the additional conformational freedom such a cavity gives to the polymer chains. In our case the same effect will contribute to the preferential sorption of the smaller LJ particles. But in addition there appears to be an energetic advantage as well.

At intermediate composition, i.e., for $0 < x_{1}^{solv} < 1$, the behavior of $A$ is close to ideal for the high temperature, i.e., the site absorbability is related to the mole fractions, $x_{1}^{solv}$ and $x_{2}^{solv}$, via a Raoult’s law type behavior extending over the entire range of mole fractions. Note that $A \cdot x_{i}^{net}$ ($i = 1, 2$) is a kind of site absorbability w.r.t. solvent $i$ only. At the low temperature, however, deviations from the ideal behavior do occur. This has important implications. At the high temperature we may obtain $\alpha$ for an arbitrary $x_{1}^{solv}$ simply by computing the site absorbabilities for pure solvents, because the straight (dashed) lines in the upper panel of Fig. 10 are in excellent agreement with the data. For $T = 3.0$ this yields $\alpha = 1.4$ in complete accord with Fig. 7. In the lower panel of Fig. 10 the (dashed) lines do not describe the simulation data. In this case we obtain $\alpha \approx 3.2$ from the site absorbabilities of the pure solvents. This value is not in accord with Fig. 7, and the corresponding dashed-dotted curve in Fig. 9 does not describe the data.

V. CONCLUSION

In this work we simulated the preferential sorption for the case of binary LJ mixtures consisting of species distinguished by different $\sigma$ in contact with model networks consisting of harmonically bonded LJ sites of the larger type. We find that the finite size effects are important and must be eliminated carefully. In order to estimate the importance of finite size effects we apply a method developed previously, which is based on the self-consistent field approach to polymer conformation. We obtain bulk results for the swelling ratio and the separation factor which turn out to be rather insensitive to the bulk solvent composition at the highest (but not at the lowest) temperature considered here. We find that the
smaller solvent species is preferentially found inside the network. This effect diminishes with increasing temperature for the two pressures investigated here.

In a wider context the present work might be of interest for the separation of physical mixtures via sorption and diffusion in membranes, which is of great technological importance. Even though we have not studied the relation between equilibrium sorption and diffusion, the present work allows to estimate the effort involved if such simulations are to be carried out for more realistic systems.

* Electronic address: hentschk@uni-wuppertal.de; URL: http://constanze.materials.uni-wuppertal.de

TABLE I: Model parameters employed for network swelling by binary mixture (in LJ units).

<table>
<thead>
<tr>
<th>quantity</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_{net}$</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>0.8</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
</tr>
<tr>
<td>$r_0$</td>
<td>1.0</td>
</tr>
<tr>
<td>$k$</td>
<td>10 000</td>
</tr>
<tr>
<td>$n_c$</td>
<td>4</td>
</tr>
</tbody>
</table>

TABLE II: Model parameters employed for network swelling by a single LJ fluid (in LJ units).

<table>
<thead>
<tr>
<th>quantity</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_{net}$</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>0.788</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
</tr>
<tr>
<td>$r_0$</td>
<td>1.245</td>
</tr>
<tr>
<td>$k$</td>
<td>7842</td>
</tr>
<tr>
<td>$n_c$</td>
<td>2</td>
</tr>
</tbody>
</table>
FIG. 1: Top: Example of a regular model network with $n_c = 4$ in the absence of solvent. Upper left - initial configuration; lower right - crumpled configuration obtained during simulation. The shading of the balls distinguishes ordinary network beads, network crosslinks, and (open) bonds connecting the shown network segments to periodic images. These bonds are not shown in the crumpled configuration. Bottom: Effect of particle exchange, characterized by the number of accepted particle transfers per LJ time unit, $N_{acpt}$, on the swelling ratio, $q$, in case of a single solvent. Left triangles: $T = 2.7, P = 0.219$; right triangles: $T = 2.7, P = 3.82$; circles: $T = 1.15, P = 0.219$; diamonds: $T = 1.15, P = 3.82$; $r_{cut} = 2.36$ in all cases. Squares: $T = 1.15, P = 3.82$, $r_{cut} = 1.97$. Note that $P = 0.219 \left(0.107 \frac{\sigma}{\epsilon}\right)$ is less than and $P = 3.82 \left(1.87 \frac{\sigma}{\epsilon}\right)$ is greater than the critical pressure of the solvent.
FIG. 2: Density of the dry network, $\rho = N/V$, vs. system size, $N^{1/3}$. Here $N$ is the number of LJ sites contained in the simulation box. Symbols: Simulations results for network of Tab. I with $n_c = 15$ at $T = 1.2$, and $P = 0.2$ ($r_{cut} = 3.0$). Long dashed line: fit to the data according to $\rho = \rho_\infty - aN^{-1/3}$; short dashed line: fit to the data according to $\rho = \rho_\infty - aN^{-1}$. The quantity $a$ is an adjustable parameter. Solid line: approximation to the data using Eq. (2).
FIG. 3: Swelling ratio, $q$, vs. system size, $N_{net}^{1/3}$, expressed via the number of network beads, $N_{net}$. Symbols are simulation data (averaged over two to three runs each). The solid lines are fitted using Eq. (3). Dashed lines indicate the bulk swelling ratios. Top: variation of pressure $P$ at temperature $T = 1.2$. Bottom: variation of $T$ at $P = 0.5$. Considering the overall number of solvent particles in both boxes, there are twice as many small particles (solvent 2) as big particles (solvent 1) in all cases. The mole fraction of solvent 1 in the solvent box, $x_{solv}$, varies from 0.34 to 0.38.
FIG. 4: Separation factor, $\alpha$, vs. system size, $N_{net}^{1/3}$, expressed via the number of network beads, $N_{net}$. Symbols are simulation results obtained from the same runs used to produce Fig. 3. The solid lines are fitted using Eq. (3). Dashed lines indicate the bulk separation factors. Top: variation of $P$ at $T = 1.2$. Bottom: variation of $T$ at $P = 0.5$. 
FIG. 5: Top: \( q - q_\infty \) on logarithmic scale vs. \( N_{\text{net}}^{1/3} \) corresponding to Fig. 3a \((T = 1.2)\). Bottom: \( \alpha - \alpha_\infty \) on logarithmic scale vs. \( N_{\text{net}}^{1/3} \) corresponding to Fig. 4a \((T = 1.2)\).
Error bars (not shown) are smaller than the symbols. Considering the overall number of solvent particles in both boxes, there are twice as many small particles (solvent 2) as big particles (solvent 1) in all cases. The mole fraction of solvent 1 in the solvent box, $x_1^{\text{solv}}$, varies from 0.33 to 0.38. The line is meant to guide the eye. Bottom: same for the separation factor, $\alpha$ (with error bars).
FIG. 7: Composition dependence of the swelling ratio, $q$, (top) and the separation factor, $\alpha$, (bottom) at two temperatures and $P = 0.5$; $x^{\text{solv}}_1$ is the mole fraction of the larger LJ particles (solvent 1) in the solvent box. The lines are meant to guide the eye. Note that the ordinates of both panels are drawn to the same scale as those in Fig. 6. The data for $T = 1.2$ are thermodynamic limits obtained by extrapolation (simulations with 270 to 5120 network beads). The data for $T = 3.0$ result from single runs employing 640 and 2160 network particles, respectively.
FIG. 8: Liquid-gas coexistence of a binary Lennard-Jones mixture (without network) with $\sigma_2 = 0.769\sigma_1$ at $T = 1.15$ ($\epsilon_2 = \epsilon_1$). Top: Pressure, $P$, (in LJ units in terms of fluid 1) vs. mole fraction in the liquid and in the gas phase, $x_{1\text{, liquid}}$ and $x_{1\text{, gas}}$, respectively. Open circles are taken from Ref.\textsuperscript{26,27,33}. Solid circles are simulation results obtained in this work. Here we always employ overall 600 particles in the mixture simulations, but only 300 and 500 particles, respectively, in case of a single LJ fluid. Bottom: Separation factor, $\alpha$, vs. pressure $P$ (in LJ units in terms of fluid 1). The symbols correspond to those in the top panel. The vertical lines indicate the vapor pressures of the pure fluids. The ratio of vapor pressures is marked by the horizontal line.
FIG. 9: Mole fraction $x_1^{\text{net}}$ in the network vs. mole fraction $x_1^{\text{solv}}$ in the pure solvent. The symbols are simulation results obtained at two temperatures, $T$, and $P = 0.5$. Open squares: $T = 3.0$, single runs with 640 and 2160 network particles, respectively; open circles: $T = 1.2$, single simulation runs with 5120 network particles (largest systems); filled diamonds: $T = 1.2$, extrapolated thermodynamic limits ($x_1^{\text{solv}}$ and $x_1^{\text{net}}$ obtained as described in the text). The straight dotted line serves to guide the eye. The short dashed, long dashed, and dashed-dotted lines correspond to the equation $x_1^{\text{net}} = x_1^{\text{solv}}/(\alpha + x_1^{\text{solv}}(1 - \alpha))$ where $\alpha = 1.35$, $\alpha = 1.7$, and $\alpha = 3.2$, respectively.
FIG. 10: Site absorbability, $A$, vs. mole fraction in the solvent box, $x_{1}^{\text{solv}}$, at two temperatures, $T$, and $P = 0.5$. Top: $T = 3.0$, single simulations with 640 and 2160 network particles, respectively. Bottom: $T = 1.2$, extrapolated thermodynamic limits ($x_{1}^{\text{solv}}$ and $x_{1}^{\text{net}}$ obtained as described in the discussion of Fig. 9). The lines correspond to ideal (Raoult’s law type) behaviour.