Inter-diffusion of solvent into glassy polymer films: An example for disorder and fluctuations in non-equilibrium statistical mechanics

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Introduction

Using the continuity equation of flux :

$$\frac{\partial c(z,t)}{\partial t} = -\frac{\partial J(z,t)}{\partial z} \tag{1}$$

c : Concentration in units of mass per unit volume
J : Flux of matter defined as the amount of substance per unit area per unit time

Fick's first law :

$$J(z,t) = -D\frac{\partial c}{\partial z} \tag{2}$$

D : Diffusion coefficient in units of area per unit time

MD simulations

Molecular Dynamics (MD) simulate classical motion of particles in time.
We consider a Canonical ensemble (NVT).
Here we used the LAMMPS software.
It can be understood as a "virtual experiment".

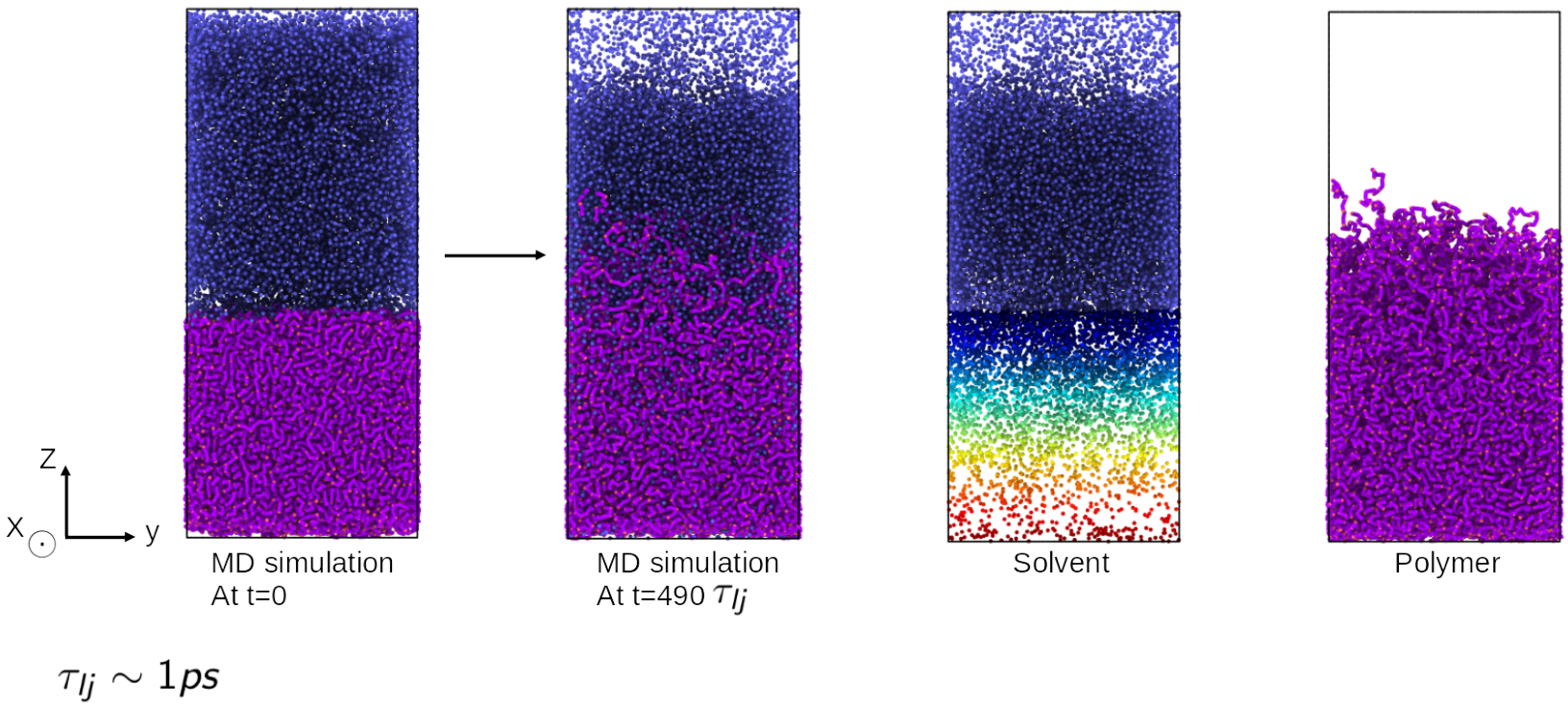


Figure – MD simulation of the inter-diffusion of solvent into polymer film

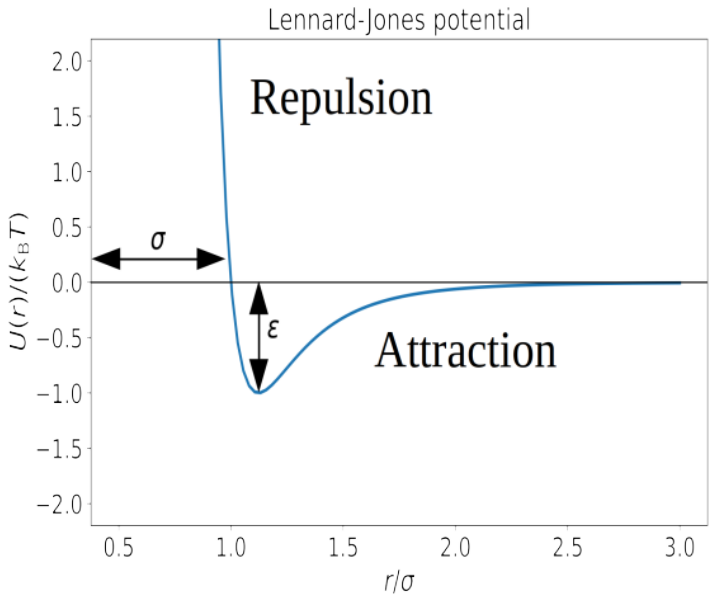
Lennard-Jones potential

Lennard-Jones potential :

$$U_{ij}(r) = 4\epsilon_{ij}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

ϵ_{ij} : well depth of two particles i and j
σ : distance at which the intermolecular potential is zero
$r_{ij} = |\vec{r}_i - \vec{r}_j|$: distance between both particles

In the following, (i, j) refer to p for polymer and s for solvent.



Concentration profiles

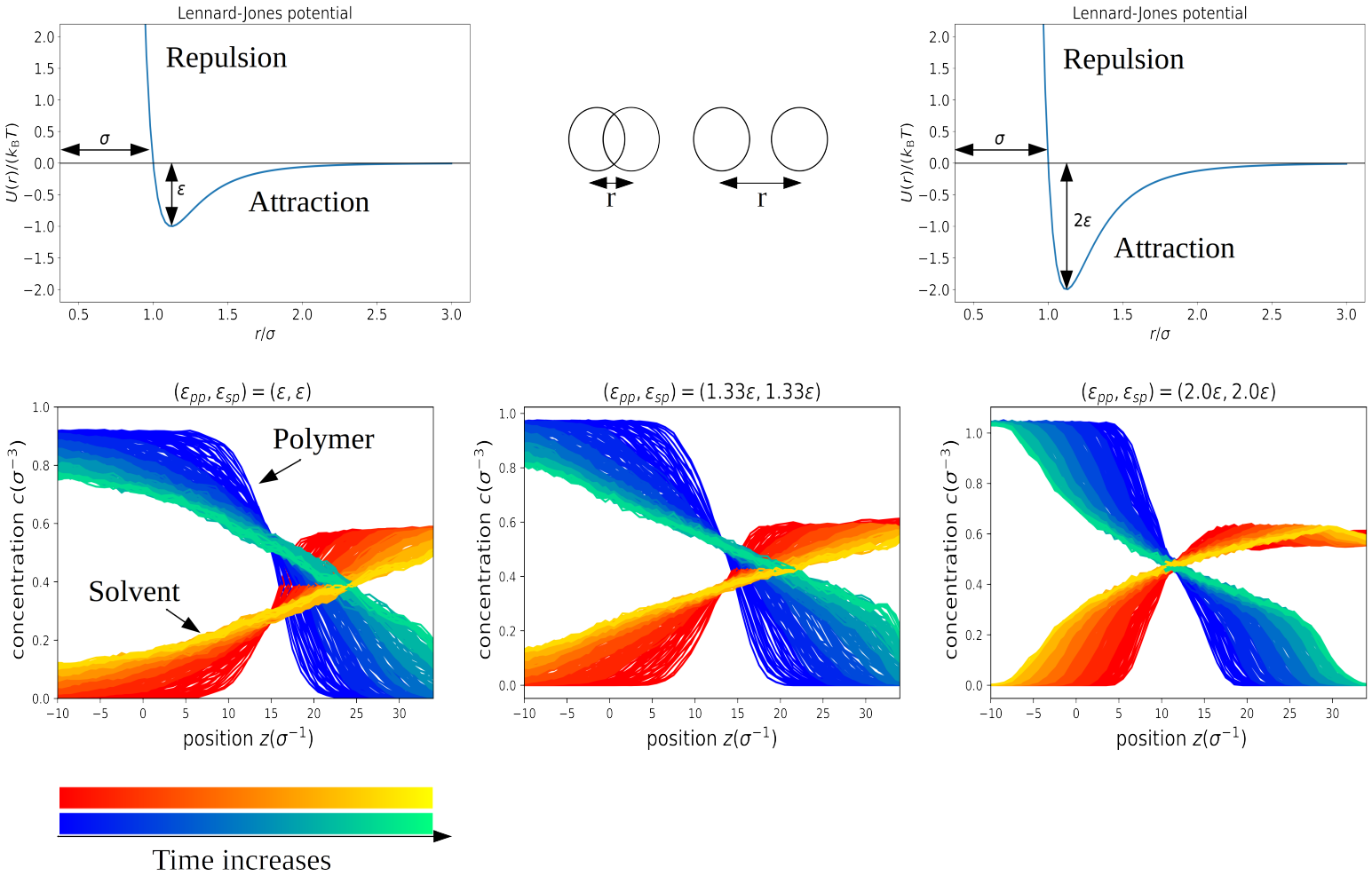


Figure – Solvent and polymer concentration profiles as a function of time for different cases of polymer-polymer and solvent-polymer interactions. Values of ϵ inspired by J. Chem. Phys. **121**, 7513 (2004).

Fick's Law

Fick's first law :

$$J(z,t) = -D(c)\frac{\partial c}{\partial z} \tag{3}$$

$D(c)$: Diffusivity assumed to depend only on (z,t) via solvent concentration $c(z,t)$

Diffusion equation for inter-diffusion of solvent into polymer film :

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left[D(c)\frac{\partial c}{\partial z}\right] \tag{4}$$

From which we see that :

$$t \sim z^2 \Leftrightarrow z \sim \sqrt{t}$$

Diffusivity expression

Using Boltzmann transformation of Eq. (3) :

$$u = \frac{z}{\sqrt{t}} \quad \Longrightarrow \quad \frac{\partial u}{\partial z} = \frac{1}{\sqrt{t}} \quad \Longrightarrow \quad \frac{\partial}{\partial z} = \frac{1}{\sqrt{t}} \frac{\partial}{\partial u} \tag{5}$$

$$\Longrightarrow \quad \frac{\partial u}{\partial t} = -\frac{1}{2} \frac{z}{t^{3/2}} \quad \Longrightarrow \quad \frac{\partial}{\partial t} = -\frac{u}{2t} \frac{\partial}{\partial u} \tag{6}$$

u : Scaling variable

Putting (4) and (5) into diffusion equation gives :

$$D(c) = -\frac{1}{2} \left[\left(\frac{dc'}{du} \right) \right]_c^{-1} \int_0^c u(c') dc' \tag{7}$$

where $c = c(u)$. By inversion, we get $u = u(c)$.

Scaled solvent concentration profiles

In order to follow the theory, we shifted the positions to set the 0 position to the inter-diffusion interface.

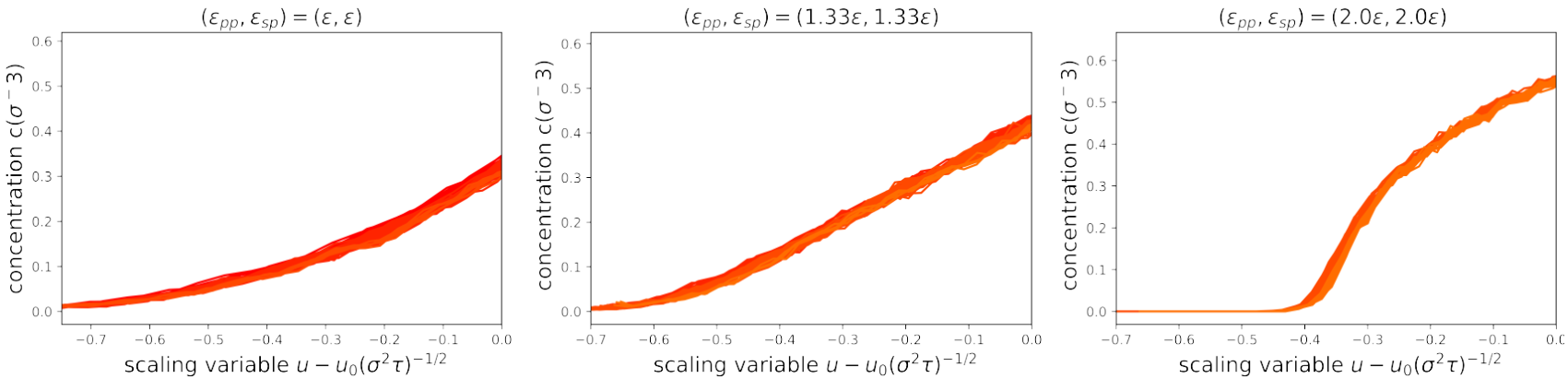


Figure – Solvent concentration profiles as a function of the scaling variable for different cases of polymer-polymer and solvent-polymer interactions

Diffusion coefficient

The diffusivity calculated numerically using Eq.6 :

$$D(c) = -\frac{1}{2}\left[\left(\frac{dc'}{du}\right)\right]^{-1}_{c}\int_{0}^{c} u(c')dc'$$

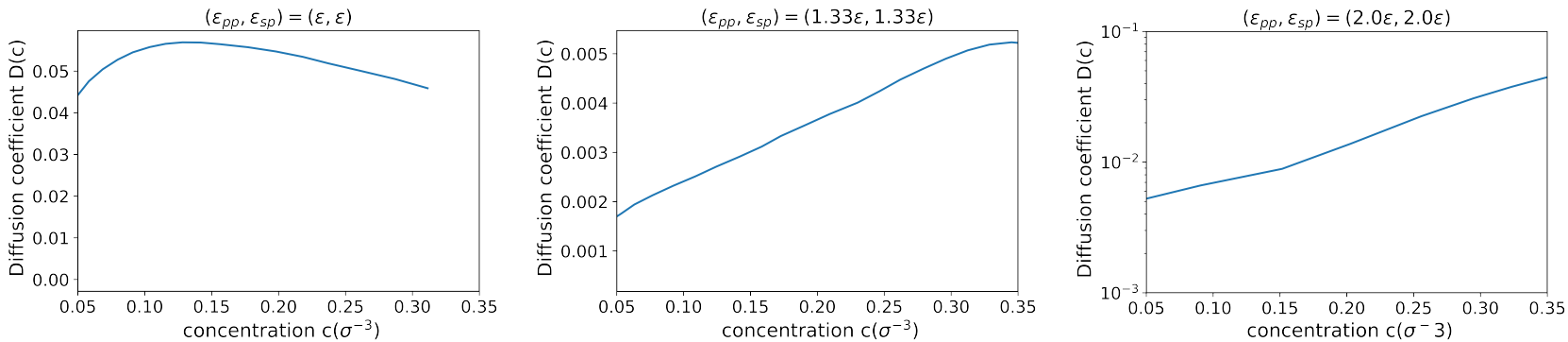


Figure – Diffusivity as a function of solvent concentration for different cases of polymer-polymer and solvent-polymer interactions

Theoretical approach for concentration

For constant diffusion coefficient, we can represent the concentration profiles using :

$$c(z,t) = \frac{c_0}{2}\left[1 + erf\left(\frac{z}{2\sqrt{Dt}}\right)\right] \quad \begin{cases} c(z=0,t) & = \frac{c_0}{2} \\ c(z\to\infty,t) & = c_0 \end{cases}$$

$erf()$: Error function
D : Mean value of diffusion coefficient

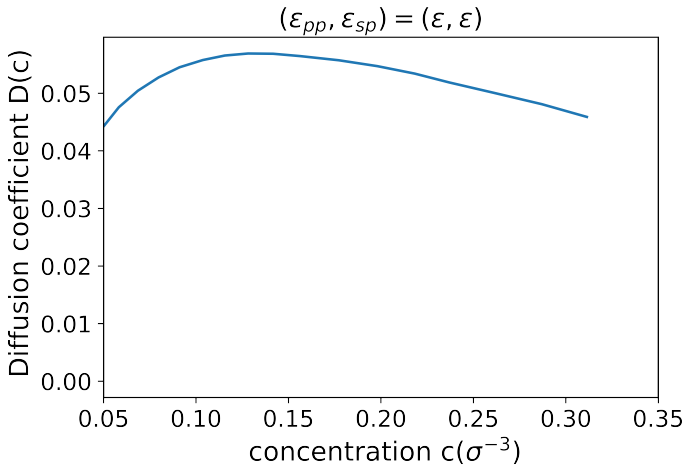


Figure – Diffusivity as a function of solvent concentration

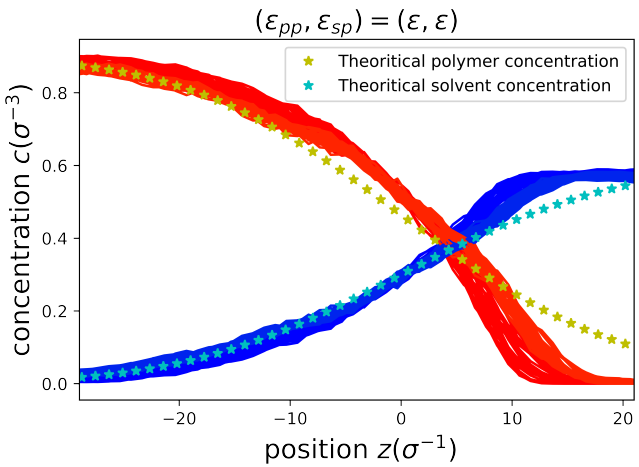


Figure – Numerical and theoretical concentration profiles

Conclusion

We used molecular dynamics method to simulate the inter-diffusion of solvent into polymer film, with collected data, we managed to evaluate diffusivity using Fick's law.

Diffusion coefficient has different behavior according to the chosen parameters.

As a further step, we can try to find some suitable theoretical approaches for concentration in cases where polymer-polymer and solvent-polymer interactions are : $(1.33\epsilon, 1.33\epsilon)$ and $(2.0\epsilon, 2.0\epsilon)$

Appendix

Here so-called *(reduced) Lennard-Jones units* have been introduced:

- All lengths are measured in units of σ: $r^* = r/\sigma$.
- All energies are measured in units of ε: $U^*_{\mathrm{LJ}} = U_{\mathrm{LJ}}/\varepsilon$.
- Temperature (T): With the Boltzmann constant k_{B} temperature is measured in units of:
  $T^* = T/(\varepsilon/k_{\mathrm{B}}) = k_{\mathrm{B}}T/\varepsilon$.
- Particle number density (ρ): ρ is measured in units of $1/\sigma^3$:
  $\rho^* = \rho/(1/\sigma^3) = \rho\sigma^3$.

References

J. Chem. Phys. 121, 7513 (2004)

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Primer of Diffusion Problems book by R. Ghez (Wiley, 1988)