Effective medium theory of permeation through ideal polymer networks

Yong Wu
Department of Physics, Virginia Tech, Blacksburg, VA 24061-0435
E-mail: wuyong@vt.edu

Abstract. The diffusion process through an ideal polymer network is studied by applying the effective medium theory (EMT) to a lattice-gas model. Polymers are modeled by random walks on the lattice bonds, across which molecules can hop with a certain probability. The steady state current of the system is calculated using the EMT and the results are compared to the simulations.
1. Introduction

In this paper I apply the effective medium theory (EMT) to a prototype lattice-gas model simulating the permeation process in polymer networks. The permeation through polymer networks has been studied in a number of experiments and simulations. Experiments are usually performed on a thin polymer film subject to a constant gas pressure. The current is measured at the steady state and its relation to the temperature, the cooling rate, the size of molecules and so on are studied. A prototype lattice-gas model, using random walks on lattice bonds to model the polymers, has been constructed in simulation studies. This simple model is equivalent to a resistor network, in which the probability distribution of resistor on a bond is highly correlated to its neighbors. The correlations differ this model from the well-known randomly distributed resistor network and make it much harder to study.

The EMT is a powerful tool to calculate the effective properties of random media. It has been successfully used in calculating effective conductance of the completely randomly distributed resistor network when far away from percolation. In this case, the Bruggeman formula of the EMT provides sufficiently accurate results, meaning that, when applied to our polymer systems, the Bruggeman formula yields excellent approximation when the polymer length is 1. When the polymer length gets longer, however, the error of the Bruggeman formula grows due to increasing correlations, and the theory needs be modified to account for the correlations. In this paper I develop a method to calculate the effective diffusivity, which gives fairly good results when the polymer length is relatively short (but greater than 1). Unfortunately, this method suffers from its fast growing complexity when the correlation increases, and thus is difficult to apply to very long polymer networks, or system close to percolation.

2. Model and Theory

Consider a d-dimensional lattice. We use coordinates $\mathbf{x} = (x_1, \ldots, x_d)$, where $x_1, \ldots, x_d$ are integers, to label the lattice cells, and $\mathbf{e}_i$ ($1 \leq i \leq d$) to denote the base vectors. Polymers are randomly placed in the lattice, whose segments occupy the lattice bonds. In a numerical simulation the polymers are generated by random walks. A particle can occupy a lattice cell and can jump to one of its neighboring cells, across the polymer segments sitting between the two cells. The jumping probability depends on the number of polymer segments. Similar to the Ohm’s law in a resistor system, the steady state current $J_i(\mathbf{x})$, which flows from $\mathbf{x} + \mathbf{e}_i$ to $\mathbf{x}$, is related to the concentration drop $E_i(\mathbf{x}) = c(\mathbf{x} + \mathbf{e}_i) - c(\mathbf{x})$ by

$$J_i(\mathbf{x}) = \sigma_{ij}(\mathbf{x})E_j(\mathbf{x}),$$

where $\sigma_{ij}(\mathbf{x})$ is the diffusivity. The diffusivity is a diagonal matrix, whose diagonal elements $\sigma_{ii}(\mathbf{x})$ are the jumping probability of particles across the bond separating cell $\mathbf{x} + \mathbf{e}_i$ and cell $\mathbf{x}$. Throughout this section we adopt the Einstein summation convention
that sums over repeated indices from 1 to \(d\). The conservation of the number of molecules is written as
\[
\nabla_i [\sigma_{ij}(x) \Delta_j c(x)] = 0,
\]
where \(\Delta_i\) is the forward finite difference such that, for any function \(f(x)\), \(\Delta_i f(x) = f(x + e_i) - f(x)\), and \(\nabla_i\) is the backward finite difference defined by \(\nabla_i f(x) = f(x) - f(x - e_i)\).

In a typical permeation experiment, a constant gradient of concentration \(\eta(x)\) is applied on the system. It is convenient to define the effective diffusivity \(\Sigma_{ij}\) by the proportionality between the average current and the applied field.

\[
\langle J_i \rangle = \Sigma_{ij} (E_0)_j.
\]
where \(\langle \cdot \rangle\) denotes the spatial average. Assuming the system is isotropic, then we should have \(\Sigma_{ij} = \sigma_{\text{eff}} \delta_{ij}\), where \(\delta_{ij}\) is the Kronecker delta.

Let \(\eta_{ij}(x) = \sigma_{ij}(x) - \Sigma_{ij}\). Eq. [2] can be solved using the Green function technique.

\[
c(x) = (E_0)_i x_i + \sum_{x'} G(x, x') \nabla_i \left( \eta_{ij}(x') \Delta_j c(x') \right),
\]
where \(G(x, x')\) is the Green function satisfying
\[
\sigma_{\text{eff}} \cdot \nabla_i \Delta_j G(x, x') = -\delta(x - x')
\]
and vanishing on the boundary. Then \(E(x)\) is given by
\[
E_i(x) = (E_0)_i + \sum_{x'} \tilde{G}_{ij}(x, x') \eta_{jk}(x') E_k(x')
\]
where the \(d \times d\) matrix \(\tilde{G}(x, x')\) is given by
\[
\tilde{G}_{ij}(x, x') = -\Delta_i \Delta_j' G(x, x').
\]

We also define susceptibility \(\chi(x)\) as a matrix such that
\[
\chi_{ij}(x)(E_0)_j = \eta_{ij}(x) E_j(x),
\]
which describe the field \(\eta(x)E(x)\) as a response to the applied field \(E_0\). Since \(\langle \eta E \rangle = \langle J - \Sigma E \rangle = \Sigma (\langle E_0 \rangle - \langle E \rangle) = 0\), the average of susceptibility is zero,
\[
\langle \chi(x) \rangle = 0.
\]

Rewriting Eq. [4] in terms of \(\chi(x)\), we get the following Dyson equation
\[
\chi(x) = \eta(x) + \eta(x) \sum_{x'} \tilde{G}(x, x') \chi(x'),
\]
Decomposing the diagonal term
\[
\chi(x) = \eta(x) + \eta(x) \tilde{G}(x, x) \chi(x) + \eta(x) \sum_{x' \neq x'} \tilde{G}(x, x') \chi(x').
\]
and introducing
\[
\chi^E(x) = [1 - \eta(x) \tilde{G}(x, x)]^{-1} \eta(x),
\]
Eq. [11] can be simplified
\[
\chi(x) = \chi^E(x) + \chi^E(x) \sum_{x' \neq x'} \tilde{G}(x, x') \chi(x').
\]
Expanding the right hand side of the above equation and taking the average, we get
\[
\langle \chi (x) \rangle = \langle \chi^E(x) \rangle + \sum_{x \neq x'} \langle \chi^E(x) \tilde{G}(x, x') \chi^E(x') \rangle \\
+ \sum_{x \neq x'} \sum_{x'' \neq x'} \langle \chi^E(x) \tilde{G}(x, x') \chi^E(x') \tilde{G}(x', x'') \chi^E(x'') \rangle + \cdots \quad (14)
\]

We classify the cells by the number of polymer segments sitting on its bonds. For example, when the dimension \(d = 2\), if each bond can only be occupied by one polymer segment at most, and if the probability of jumping across a polymer segment is \(q\), then there are 4 different types of cells whose diffusivity matrices are
\[
\sigma_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} q & 0 \\ 0 & q \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & q \end{pmatrix}, \quad \sigma_4 = \begin{pmatrix} q & 0 \\ 0 & q \end{pmatrix},
\]
respectively. Noticing that \(\chi^E(x)\) is determined by the type of cell at \(x\), and in a homogeneous system, \(\tilde{G}(x, x')\) only depends on \(x - x'\), Eq. 14 can thus be rewritten in terms of statistics of different type of cells
\[
\langle \chi \rangle = \sum_i f_0(i) \chi_i^E + \sum_{i,j} f_1(x' - x; i, j) \chi_i^E \tilde{G}(x' - x) \chi_j^E \\
+ \sum_{i,j,k} f_2(x' - x, x'' - x'; i, j, k) \chi_i^E \tilde{G}(x' - x) \chi_j^E \tilde{G}(x'' - x') \chi_k^E \\
+ \cdots \quad (16)
\]
where \(f_0(i)\) is the fraction of the type \(i\) cells, \(f_1(x' - x; i, j)\) is the joint probability distribution of seeing a type \(i\) cell and a type \(j\) cell resting at \(x\) and \(x'\), respectively, and \(f_2, f_3, \cdots\) are defined similarly. The function \(\tilde{G}(x) = \tilde{G}(0, x)\) can be easily calculated using the continuous Green function \(G_c(x, x')\) of the entire \(d\)-dimensional space
\[
\tilde{G}_{ij}(x) = \Delta_i \nabla_j G(0, x) \\
= \Delta_i \left[ \int_{x_1 - \frac{1}{2}}^{x_1 + \frac{1}{2}} dx_1' \cdots \int_{x_d - \frac{1}{2}}^{x_d + \frac{1}{2}} dx_d' \frac{\partial G_c(0, x')}{\partial x_j'} \delta \left( x_j' - \left( x_j - \frac{1}{2} \right) \right) \right],
\]
where \(\delta(x)\) is the delta function.

In principle, the probability distributions \(f_i\) can be determined by doing statistics for a numerically generated polymer system. The computer resource required to do the statistics, however, increase exponentially with \(i\) and \(|x - x'|, |x' - x''|\), etc. Therefore in practice we are only able to calculate the right hand side of Eq. 16 up to 3 terms, with the constrictions that \(|x - x'| < R, |x' - x''| < R, \cdots\), where \(R \geq 1\) is some constant integer we pick. Neglecting of the correlations outside the range \(R\) and higher order terms are justified by the fact that \(\tilde{G}(x)\) decreases as \(|x|^{-d}\).

Combining Eq. 16 and Eq. 9 we get an equation that can be used to solve for the effective diffusivity \(\Sigma_{ij}\). If only the first order term of the right hand side of Eq. 16 is kept, then it is only needed to solve \(\langle \chi^E \rangle = 0\), which yields the classical EMT solution for the effective diffusivity. Noticing that \(\tilde{G}_{ij}(0) = -(1/d)\delta_{ij}\), the equation produces the well-known Bruggeman formula
\[
\frac{(1 - p)(1 - \sigma_{eff})}{1 + (d - 1)\sigma_{eff}} + \frac{p(q - \sigma_{eff})}{q + (d - 1)\sigma_{eff}} = 0,
\]
(18)
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Table 1. Current measured in simulations $J_{\text{sim}}$ and current $J_i$ calculated by Eq. 16, which includes up to $i$ higher order terms, as a function of the polymer length $l$. Also shown in the brackets are the errors of each calculated current relative to the measurement. Note that $J_0$ gives the classical EMT solution, which is independent of the polymer length. The probability to jump across an occupied bond is $q = 0.1$, and the occupation is $p = 0.25$.

| $l$ | $J_{\text{sim}}$  | $J_0$ (error) | $J_1$ (error) | $J_2$ (error) | $J_3$ (error) |
|----|-------------------|--------------|--------------|--------------|--------------|
| 1  | 156.4             | 155.7 (-0.45%) | 155.7 (-0.45%) | 155.9 (-0.32%) | 155.9 (-0.32%) |
| 2  | 149.6             | 155.7 (4.1%)  | 151.5 (1.3%)  | 151.3 (1.1%)  | 151.1 (1.0%)  |
| 4  | 144.5             | 155.7 (7.8%)  | 150.5 (4.2%)  | 148.9 (3.0%)  | 148.7 (2.9%)  |
| 8  | 141.0             | 155.7 (10.4%) | 149.7 (6.2%)  | 147.1 (4.3%)  | 146.7 (4.0%)  |
| 16 | 138.9             | 155.7 (12.1%) | 149.4 (7.6%)  | 145.8 (5.0%)  | 145.4 (4.7%)  |
| 32 | 137.7             | 155.7 (13.1%) | 150.1 (9.0%)  | 146.0 (6.0%)  | 145.5 (5.7%)  |
| 64 | 137.2             | 155.7 (13.5%) | 150.6 (9.8%)  | 146.1 (6.5%)  | 145.6 (6.1%)  |

where $p$ is the fraction of occupied bonds in the system.

In a previous study it has been shown that for a system with the polymer length $\ell = 1$, Eq. 18 gives an excellent approximation to $\sigma_{\text{eff}}$. However, if the polymer length $\ell > 1$, the higher order terms, which describe the correlation between cells, significantly revise the results. It is also worthy of noting that this method of calculating the effective diffusivity works best when the system is far away from the percolation threshold, which means either the temperature has to be high, or the mass density be very low. Only in this regime the correlation is not crucial. and this method can be a good approximation.

For long polymers or system not so far away from percolation, or, in other word, when correlations are important, one could improve the result of the EMT by including more higher order terms in Eq. 16. This is illustrated by our calculation result shown in Table 1 where we list the current at $q = 0.1$ and $p = 0.25$ calculated through Eq. 16 using up to 3 higher order terms in the expansion, in comparison with both the current measured by numerical simulations (for details of the simulation, see [5]) and the current calculated by the classical EMT approximation. The correlation range $R$ used in the calculation is 3. Only single occupation on bonds is allow in the calculation, because multiple occupation produces too many types of cells to do statistics for $R > 1$ or include more than one higher order terms.

The results clearly show that the classical EMT yields extremely accurate result for $\ell = 1$, but produces considerable errors when $\ell > 1$. Taking account of correlations by including the higher order terms can significantly improve the calculation.

3. Summary and discussion

In this paper I have used the EMT to calculate the effective diffusivity of a lattice-gas model simulating permeation through polymer networks. Such a model is equivalent to resistor network, which is described by a Laplace Equation at the steady state. The
solution of this equation can be expressed by a Dyson expansion. One needs to include higher order terms in the expansion to account for the correlations of the distribution of polymer segments. When system is far away from percolation, we have calculate the steady state current using up to 4 terms in the expansion and get reasonably good result compared to simulations. The error of the calculation increases with the polymer length, since longer polymers have stronger correlations.

From Table 1 one can see that the current is decreasing function of the polymer length. It can be qualitatively explained by considering the blob (the set of cells that carry current at $q = 0$) size, which also decrease with the polymer length. A possible future work would be using the EMT to provide some quantitative insight to this phenomenon.

4. Acknowledgment

This research is supported in part by the US National Science Foundation through grant DMR-0414122.

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