Soft Matter

Size-Dependent Penetrant Diffusion in Polymer Glasses

Journal:	*Soft Matter*
Manuscript ID	SM-COM-04-2018-000701.R1
Article Type:	Communication
Date Submitted by the Author:	07-May-2018
Complete List of Authors:	Meng, Dong; Mississippi State University Zhang, Kai; Columbia University, Chemical Engineering Kumar, Sanat; Columbia University,

SCHOLARONE™
Manuscripts

Size-Dependent Penetrant Diffusion in Polymer Glasses

Dong Meng,# Kai Zhang, Sanat K. Kumar

Department of Chemical Engineering, Columbia University, New York, NY 10027

Abstract

Molecular Dynamics simulations are used to understand the underpinning basis of the transport of gas-like solutes in deeply quenched polymeric glasses. As found in previous work, small solutes, with sizes smaller than 0.15 times of the chain monomer size, move as might be expected in a medium with large pores. In contrast, the motion of larger solutes is activated and is strongly facilitated by matrix motion. In particular, solute motion is coupled to the local elastic fluctuations of the matrix as characterized the Debye-Waller factor. While similar ideas have been previously proposed for the viscosity of supercooled liquids above their glass transition, to our knowledge, this is the first illustration of this concept in the context of solute mass transport in deeply quenched polymer glasses.

#Current address: *Dave C. Swalm School of Chemical Engineering, Mississippi State University, Starkville, MS 39762*

The growing demand for clean energy creates a need for more efficient and commercially viable technologies. Many of these emergent technologies, such as CO_2 capture and natural gas purification, rely on the selective and efficient transport of gases. Polymeric membranes present an efficient solution to these separation needs, while being lightweight and low-cost.[1-6] There have been many advances in this field, but most of these have been performed empirically – consequently, a quantitative understanding of the molecular principles that control the separation ability of these membrane materials is still under development. For example, the most widely used quantity to understand separation is the venerable concept of *free-volume*, originally a statically defined metric.[7-14] An overwhelming body of experimental and theoretical work has established that this concept does not fully explain gas diffusion, and that the local dynamics of the matrix play a critical role.[7,15-21] Pioneering work by Gusev,[16-17] based on a solid-like model,[22-23] implies that solute motion is driven by the local elastic thermal motion of dense polymers, which is separate from the structural relaxation of the chains. We are motivated here to probe this conjecture and thus to (i) see if indeed matrix motions facilitate solute transport and if so (ii) to define the matrix motions that are relevant in this case.

In the solution diffusion model applicable to these situations, gas permeability is defined as the product of solubility and diffusivity.[24] It is now well accepted that differences in diffusion coefficients underpin the ability of glassy polymer membranes to separate gas mixtures.[25] In this short communication, we use Molecular Dynamics simulations to show that solute diffusion is decoupled from the long-range structural dynamics of the polymer (which are frozen in a glassy matrix). Going well beyond this well-accepted fact, our new finding is that the local, vibrational dynamics of the glassy polymer, as characterized by the long-time plateau value of the mean-squared displacement of the frozen matrix ("Debye-Waller factor"),[26] defines the appropriate "*dynamic free-volume*" metric. Beyond these applications in supercooled liquids[27] and glasses, the Debye-Waller factor also appears to be a useful metric that leads to universal scaling behavior of viscosity at higher temperatures.[28]

In this work, polymer chains are modeled by the Kremer-Grest model,[29] namely as a string of chemically identical monomers, each with a mass m and diameter σ. All monomers including bonded monomers interact through the truncated and shifted Lennard-Jones (LJ) potential:

$$U_{m,m}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - 4\varepsilon\left[\left(\frac{\sigma}{r_{mm}}\right)^{12} - \left(\frac{\sigma}{r_{mm}}\right)^{6})\right] & r \leq r_{mm} \\ 0 & r > r_{mm} \end{cases} \quad (1)$$

where ε is the well-depth. The cutoff distance $r_{mm} = 2.5\sigma$ ensures that the potential includes inter-bead attractions. Bonded monomers are connected using the finitely extensible nonlinear elastic (FENE) potential, with spring constant $k = 30\varepsilon/\sigma^2$ and a maximum bond extent R_0 $=1.5\sigma$.[30] This gives an average bond length $l_b = 0.97\sigma$. The penetrants are modeled as LJ spheres of diameter σ_s, interacting with polymers through the potential:

$$U_{m,s}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma+\sigma_s}{2r}\right)^{12} - \left(\frac{\sigma+\sigma_s}{2r}\right)^{6}\right] - 4\varepsilon\left[\left(\frac{\sigma+\sigma_s}{2r_{ms}}\right)^{12} - \left(\frac{\sigma+\sigma_s}{2r_{ms}}\right)^{6})\right] & r \leq r_{ms} \\ 0 & r > r_{ms} \end{cases} \quad (2)$$

The cutoff distance $r_{ms} = \sqrt[6]{2}(\sigma + \sigma_s)/2$ is chosen so that interaction between a penetrant and a chain monomer is purely repulsive. Interactions among penetrants are turned off since we focus on the tracer solute limit. All simulations are performed using the LAMMPS package.[31]

Initially, 20 penetrant particles are randomly placed inside a simulation cell under the constraint of no overlap between any two solutes. Then a total of $n = 144$ matrix polymer chains, each of length *N*=10 are created inside the box using the method of Auhl *et al.*[32] In all cases no overlap is allowed between the monomers and the penetrants. Overlapping monomers in the initial states are pushed off each other using a soft potential until they are far enough apart for the LJ interaction to be switched on. Further equilibration is carried out in the *NPT* ensemble at pressure $P = 0$ and $T = 1.0\,\varepsilon/k_B$ for 10^6 τ, where $\tau = \sigma\sqrt{m/\varepsilon}$ is the LJ time unit. This equilibration process is followed by isobaric quenching to one of the operating temperatures, namely $T = 0.3, 0.2, 0.15$ and $0.1\,\varepsilon/k_B$, respectively, at a cooling rate of $0.0004\varepsilon/k_B\tau$. The apparent glass temperature T_g, as determined from the break in slope of the density vs. temperature following this protocol, is estimated to be 0.36-$0.38\varepsilon/k_B$ for all samples. Therefore, the final operating temperatures are below the apparent T_g; no effort is made to further equilibrate these quenched glassy states. The Nose-Hoover equations of motion were solved for polymer segments,[33] while Newton's equations of motion are solved for the penetrants. An integration time step of 0.001 and 0.005τ was used, depending on σ_s. For comparison, a set of simulations with a "frozen matrix" are also conducted. After the quench to the desired temperature, the equations of motion for the polymer segments are not integrated so that they stay fixed at their original locations, while the Nose-Hoover equations of motion were solved for the penetrants at the corresponding temperature. The solute diffusion coefficients are calculated from the Einstein relation $D = \lim_{t\to\infty} \langle r^2(t)\rangle/6t$, where $\langle r^2(t)\rangle$ is the mean square displacement of penetrants.

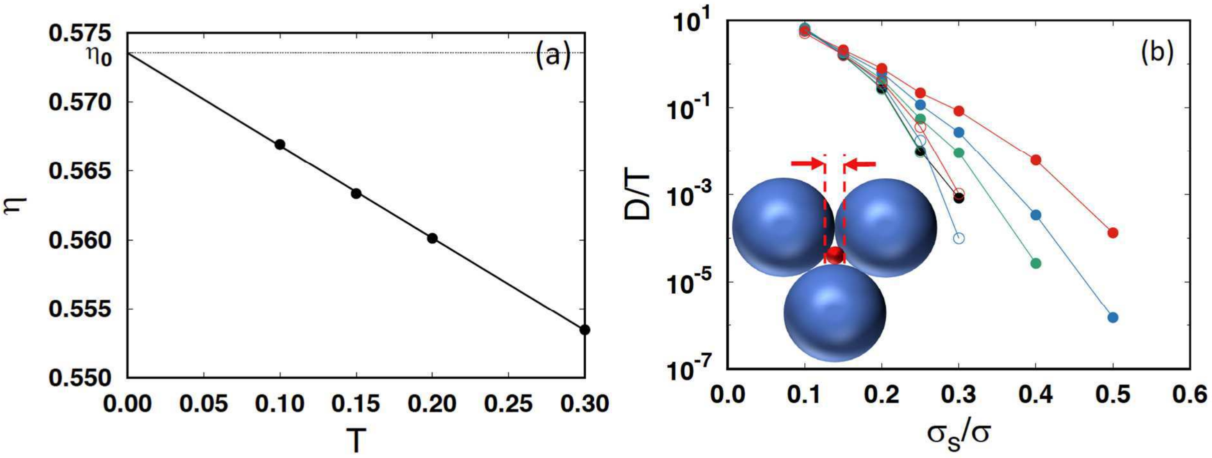


Figure 1. (a) Segmental packing fraction of polymer glass matrix as function of T, which extrapolates to η_0 at $T = 0$; (b) D/T as function of penetrant size σ_s; solid and open symbols represent results from "mobile" and "frozen" matrix simulations, respectively; data for $T = 0.3, 0.2, 0.15$, and 0.1 are shown in red, blue, green and black, respectively; inset in (b) schematically illustrates the "minimum porosity" of a closely-packed hard sphere medium and the critical penetrant size $\sigma_c \sim 0.15\sigma$.

Figure 1(a) shows the segmental packing fraction $\eta = \pi/6\,\sigma^3 nN/V$ of a quenched polymer matrix as a function of temperature. A linear temperature dependence is observed with an extrapolated T=0 intercept of $\eta_0 = 0.574$. Presumably, this value of η_0 depends on the choice of particle diameter σ and the cooling rate used in preparing the quenched sample, since we expect $\eta_0 = 0.58$ for a colloidal glass.[34] Figure 1(b) shows the reduced diffusion coefficients D/T as a function of penetrant diameter σ_s measured at various T. For penetrants smaller than $\sigma_c \sim 0.15\sigma$, the D/T collapses on a common curve, i.e., $D \propto T$. Further, penetrant diffusion does not seem to depend on whether the matrix is "frozen" or "mobile", suggesting that the solute moves without any matrix facilitation, and without the need for any activation. The critical size of 0.15σ reflects the *smallest* possible gap between three close-packed spheres [inset to Figure 1(b)]. Motions of penetrants smaller than σ_c occur without involving motions of matrix segments, and therefore the difference in matrix dynamics (e.g. "mobile" or "frozen") does not affect the results obtained in this regime.

As penetrant size increases to $\sigma_s > \sigma_c$, the D/T curves "separate" from each other, exhibiting a stronger dependence on σ_s at lower T. Since it is unlikely that voids comparable to σ_s (or larger) are present in static snapshots, the translational motion of these larger penetrants must be facilitated by local matrix motions.[16-17] Thus, we expect that penetrants only perform local motions in the cage defined by the matrix, followed by relatively rare *nonlocal* motions– the localized-hop mode of solute transport. To illustrate this point, Figures 2(a)-(b) compares the self-part of the van Hove function of penetrants of size $\sigma_s = 0.1\sigma$ and $\sigma_s = 0.3\sigma$, respectively, at the same temperature T=0.2. For $\sigma_s = 0.1\sigma$, there is a single prominent peak in the van Hove function that continuously evolves to larger distances with increasing time. In contrast, the van Hove function for the larger particle size develops a distinct second peak with increasing time, with the first peak staying at its original location. These two peaks correspond, respectively, to the localized and hopping species, respectively. While the location of the first peak changes little with time, more expectedly, its magnitude decreases with time. Since penetrant motion corresponds to "hopping" from one cage to the next one, diffusion in this regime should be an "activated" process. Figure 1(b) further shows that D/T obtained from the "frozen" matrix simulations are one to two order magnitude smaller than that from the "mobile" matrix ones at corresponding temperatures and penetrant sizes (even though matrix densities are kept the same), indicating that in this "activated" regime diffusion is inherently facilitated by the "*motions*" of matrix. (The diffusion regime can only be reached at T>0.2 for penetrant size $\sigma_s = 0.3\sigma$, and no diffusion regime can be reached for $\sigma_s > 0.3\sigma$ within simulation time.)

The self-part of the van Hove function at the different (glassy) temperatures [Figure 2(c)] are well fit by the Maxwell distribution function $b\sqrt{\frac{2}{\pi}}\frac{r^2 e^{-r^2/\alpha^2}}{\alpha^3}$, where b and α are fitting parameters. Except at early times, the distributions do not vary with time in any significant way, suggesting that motions of matrix segments are only of a "local" nature in these deeply quenched states.

The parameter α represents the "width" of the van Hove distribution, often reported as the effective cage size or the Debye-Waller factor of matrix. Plots of the mean squared displacement of chain monomers show a temporal plateau at longer times, and the square root of the height of this plateau scales directly with α. Figure 2(d) shows that α exhibits a linear dependence on T, and its extrapolated value at $T = 0$ is $\alpha_0 = 0.046$. (Interestingly, an admittedly long extrapolation yields that $\alpha = 0$ for $\eta \approx 0.583$, which is close to the extrapolated glass transition volume fraction for colloidal spheres, Figure 2(e).) Thus, the α_0 being nonzero is likely a consequence of the method used to prepare the matrix glass.

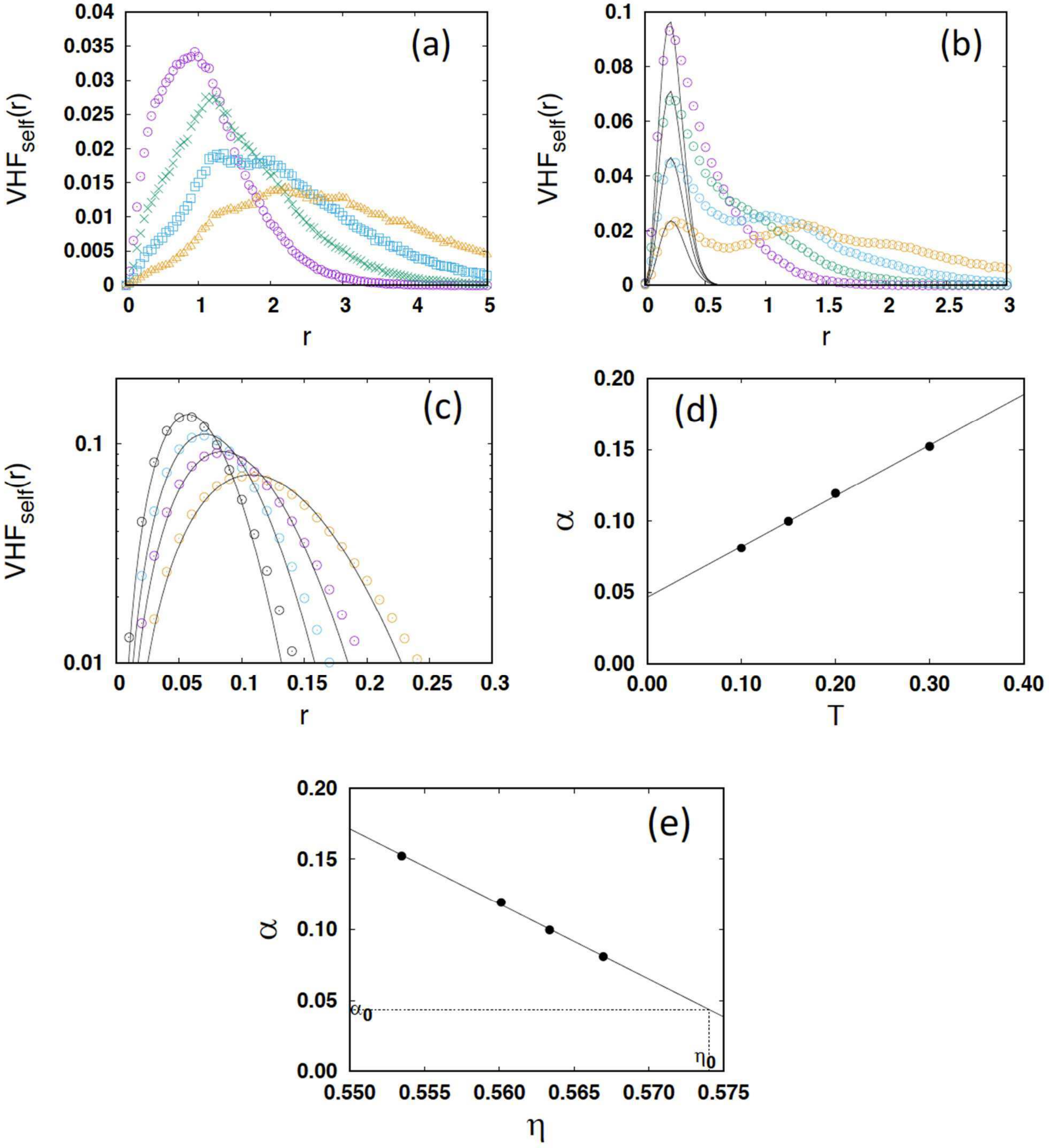


Figure 2. The self-part van-Hove function measured at $T = 0.2$ for penetrants of size (a) $\sigma_s = 0.1\sigma$ at time of 0.2, 0.4, 0.8 and 1.6 τ (from left to right); (b) $\sigma_s = 0.3\sigma$ at time of 1, 4, 16 and 64 τ (from top to bottom); (c) the self-part van-Hove function of polymer segments at $T = 0.1, 0.15, 0.2$ and 0.3(from left to right); the dashed lines in (b) and (c) show the fitting by the Maxwell distribution function; (d)-(e) dependence of the fitting parameter α on temperature and matrix segmental volume fraction.

Transition state theory has been proposed to account for such activated diffusion processes, i.e., $D \propto P_{cross} \propto e^{-E_a/T}$, where $P_{cross}$is the probability of barrier crossing and E_a is the temperature independent apparent "activation energy". By plotting D/T as function of $1/T$ in Figures 3(a)-(b), and fitting the resulting Arrhenius plots we obtain the apparent "activation energy" E_a for "mobile" and "frozen" matrix simulations [Figure 3(c)]. Based on the deduced values of E_a two regimes can be identified, and like in Figure 1 the transition occurs at $\sigma_s{\sim}\sigma_c$. For $\sigma_s \lesssim \sigma_c$, $E_a$is practically zero and indistinguishable between "frozen" and "mobile" matrix simulations. For $\sigma_s > 0.15\sigma$, E_a is observed to increase linearly as the function of σ_s, with the slope being significantly greater for the "frozen" matrix simulations. Since the segmental density is kept the same between the two types of simulations, the drastic difference in the apparent activation energy between the mobile and frozen solute simulations is solely a result of local matrix *dynamics* rather than the static properties of the polymer matrices.

Based on the transition state theory, we further exploit the relation of $T \propto \alpha - \alpha_0$ and $E_a \propto \sigma_s - \sigma_c$ as suggested in Figure 2(d) and Figure 3(c), respectively, and plot the reduced diffusion coefficient D/T as function of $(\sigma_s - \sigma_c)/(\alpha - \alpha_0)$ (for $\sigma_s > \sigma_c$). Figure 3(d) shows that D/T exhibits an apparently universally exponential dependence on $(\sigma_s - \sigma_c)/(\alpha - \alpha_0)$ for all temperatures studied. We believe that Figure 3(d) represents a physically based understanding of the activated diffusion process. The parameter $(\sigma_s - \sigma_c)/(\alpha - \alpha_0)$ which is the ratio of the "excess" size of penetrants relative to the degree of "dynamic" matrix fluctuations serves as a measure of "effective" activation energy in this situation.

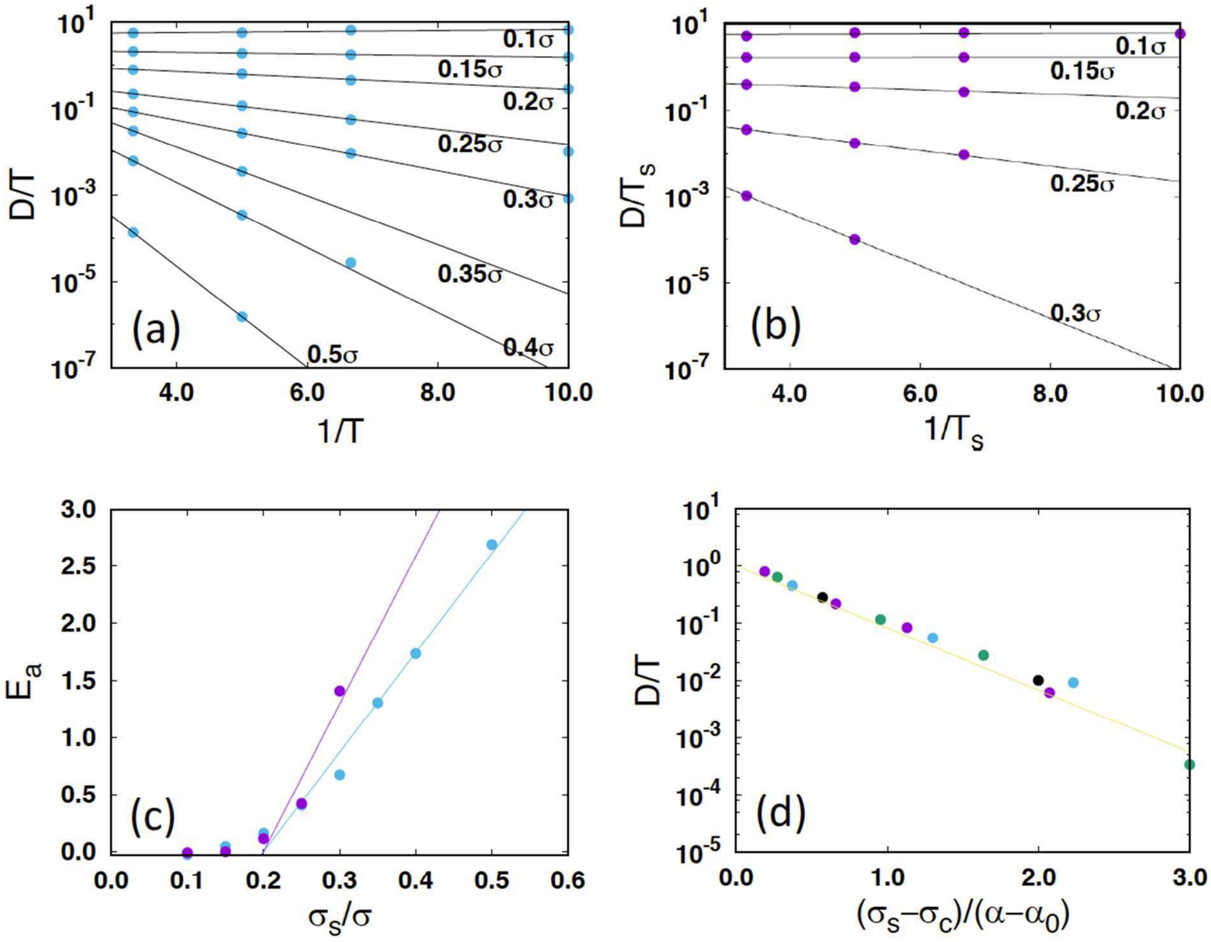


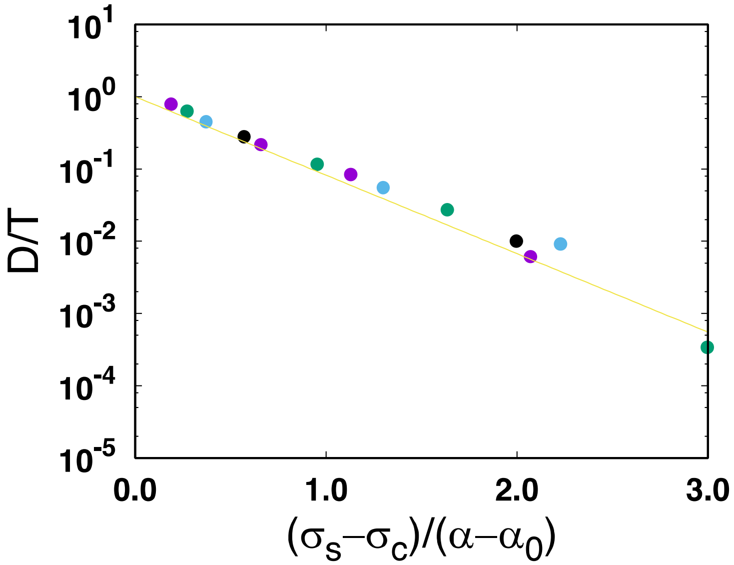
Figure 3. The Arrhenius plot of the reduced diffusion coefficients D/T from the (a) "mobile-" and (b) "frozen-" matrix simulations; (c) dependence of the apparent activation energy E_a from "mobile-" (blue) and "frozen-" (purple) matrix simulations as the function of penetrant size; (d) The universal dependence of the reduced diffusion coefficients D/T as a function of the "effective" penetrant size $(\sigma_s - \sigma_c)/(\alpha - \alpha_0)$, at different temperatures.

We take a moment here to relate this work to the earlier conjecture of Gusev, who suggested that the solute motion was facilitated by the local elastic fluctuations of the matrix molecules.[16-17] Our results agree with this model, and further show that the Debye-Waller factor is the appropriate measure that is relevant to describing these elastic fluctuations. Analogously, the diffusion of large nanoparticles through certain rubbery polymers can also follow a hopping mechanism.[35] Here, the constraint on solute motion originates either from cross-linked networks or from strong chain entanglement. Similar phenomena are also observed in non-polymeric disparate-size mixtures, in which the coupling between the diffusion of small particles and the movement of the large obstacles gives rise to interesting delocalized phases and anomalous dynamics.[27,36] However, in absence of polymer bonds, the glass transition of these obstacle matrices often couples with their packing fraction, which leads to different critical penetrant size for its activated motion.

We thank Kenneth Schweizer for helpful discussions and careful reading of this manuscript. We acknowledge primary financial support from the National Science Foundation under grant DMR-1507030.

1. Baker, R. W., Future directions of membrane gas separation technology. *Industrial & Engineering Chemistry Research* **2002,** *41*, 1393-1411.
2. Rowe, B. W.; Robeson, L. M.; Freeman, B. D.; Paul, D. R., Influence of temperature on the upper bound: Theoretical considerations and comparison with experimental results. *Journal of Membrane Science* **2010,** *360*, 58-69.
3. Robeson, L. M.; Freeman, B. D.; Paul, D. R.; Rowe, B. W., An empirical correlation of gas permeability and permselectivity in polymers and its theoretical basis. *Journal of Membrane Science* **2009,** *341*, 178-185.
4. Paul, D. R.; Robeson, L. M., Polymer nanotechnology: Nanocomposites. *Polymer* **2008,** *49*, 3187-3204.
5. Robeson, L. M., CORRELATION OF SEPARATION FACTOR VERSUS PERMEABILITY FOR POLYMERIC MEMBRANES. *Journal of Membrane Science* **1991,** *62*, 165-185.
6. Mahajan, R.; Koros, W. J., Factors controlling successful formation of mixed-matrix gas separation materials. *Industrial & Engineering Chemistry Research* **2000,** *39*, 2692-2696.
7. Cohen, M. H.; Grest, G. S., LIQUID-GLASS TRANSITION, A FREE-VOLUME APPROACH. *Phys Rev B* **1979,** *20*, 1077-1098.
8. Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. J., Ultrapermeable, reverse-selective nanocomposite membranes. *Science* **2002,** *296*, 519-522.
9. Wang, X. Y.; Lee, K. M.; Lu, Y.; Stone, M. T.; Sanchez, I. C.; Freeman, B. D., Cavity size distributions in high free volume glassy polymers by molecular simulation. *Polymer* **2004,** *45*, 3907-3912.
10. Wang, X. Y.; Raharjo, R. D.; Lee, H. J.; Lu, Y.; Freeman, B. D.; Sanchez, I. C., Molecular simulation and experimental study of substituted polyacetylenes: Fractional free volume, cavity size distributions and diffusion coefficients. *J Phys Chem B* **2006,** *110*, 12666-12672.
11. Ramesh, N.; Davis, P. K.; Zielinski, J. M.; Danner, R. P.; Duda, J. L., Application of Free-Volume Theory to Self Diffusion of Solvents in Polymers Below the Glass Transition Temperature: A Review. *J Polym Sci Pol Phys* **2011,** *49*, 1629-1644.
12. Yampolskii, Y., Polymeric Gas Separation Membranes. *Macromolecules* **2012,** *45*, 3298-3311.
13. Xi, L.; Shah, M.; Trout, B. L., Hopping of Water in a Glassy Polymer Studied via Transition Path Sampling and Likelihood Maximization. *J Phys Chem B* **2013,** *117*, 3634-3647.
14. Janes, D. W.; Bilchak, C.; Durning, C. J., Decoupling energetic modifications to diffusion from free volume in polymer/nanoparticle composites. *Soft Matter* **2017**.
15. Cohen, M. H.; Turnbull, D., MOLECULAR TRANSPORT IN LIQUIDS AND GLASSES. *J Chem Phys* **1959,** *31*, 1164-1169.
16. Gusev, A. A.; Suter, U. W., DYNAMICS OF SMALL MOLECULES IN DENSE POLYMERS SUBJECT TO THERMAL MOTION. *J Chem Phys* **1993,** *99*, 2228-2234.
17. Gusev, A. A.; Mullerplathe, F.; Vangunsteren, W. F.; Suter, U. W., DYNAMICS OF SMALL MOLECULES IN BULK POLYMERS. *Atomistic Modeling of Physical Properties* **1994,** *116*, 207-247.
18. Mullerplathe, F., DIFFUSION OF PENETRANTS IN AMORPHOUS POLYMERS - A MOLECULAR-DYNAMICS STUDY. *J Chem Phys* **1991,** *94*, 3192-3199.
19. Mullerplathe, F.; Rogers, S. C.; Vangunsteren, W. F., COMPUTATIONAL EVIDENCE FOR ANOMALOUS DIFFUSION OF SMALL MOLECULES IN AMORPHOUS POLYMERS. *Chem Phys Lett* **1992,** *199*, 237-243.
20. Eslami, H.; Muller-Plathe, F., Molecular dynamics simulation of sorption of gases in polystyrene. *Macromolecules* **2007,** *40*, 6413-6421.
21. Zhang, R.; Schweizer, K. S., Correlated matrix-fluctuation-mediated activated transport of dilute penetrants in glass-forming liquids and suspensions. *J Chem Phys* **2017,** *146*, 13.
22. Frenkel, J., *Kinetic Theory of Liquids*. Dover: 1955.

23. Argon, A. S., *The Physics of Deformation and Fracture of Polymers*. Cambridge University Press: Cambridge, 2013.
24. Wijmans, J. G.; Baker, R. W., THE SOLUTION-DIFFUSION MODEL - A REVIEW. *Journal of Membrane Science* **1995,** *107*, 1-21.
25. Galizia, M.; Chi, W. S.; Smith, Z. P.; Merkel, T. C.; Baker, R. W.; Freeman, B. D., 50th Anniversary Perspective: Polymers and Mixed Matrix Membranes for Gas and Vapor Separation: A Review and Prospective Opportunities. *Macromolecules* **2017,** *50*, 7809-7843.
26. Larini, L.; Ottochian, A.; De Michele, C.; Leporini, D., Universal scaling between structural relaxation and vibrational dynamics in glass-forming liquids and polymers. *Nature Physics* **2008,** *4*, 42-45.
27. Bosse, J.; Kaneko, Y., SELF-DIFFUSION IN SUPERCOOLED BINARY LIQUIDS. *Phys Rev Lett* **1995,** *74*, 4023-4026.
28. Puosi, F.; Pasturel, A.; Jakse, N.; Leporini, D., Communication: Fast dynamics perspective on the breakdown of the Stokes-Einstein law in fragile glassformers. *J Chem Phys* **2018,** *148*, 5.
29. Grest, G. S.; Kremer, K., Molecular-Dynamics Simulation for Polymers in the Presence of a Heat Bath. *Phys Rev A* **1986,** *33*, 3628-3631.
30. Kalathi, J. T.; Grest, G. S.; Kumar, S. K., Universal Viscosity Behavior of Polymer Nanocomposites. *Phys Rev Lett* **2012,** *109*.
31. Plimpton, S., FAST PARALLEL ALGORITHMS FOR SHORT-RANGE MOLECULAR-DYNAMICS. *J. Comput. Phys.* **1995,** *117*, 1-19.
32. Auhl, R.; Everaers, R.; Grest, G. S.; Kremer, K.; Plimpton, S. J., Equilibration of long chain polymer melts in computer simulations. *J Chem Phys* **2003,** *119*, 12718-12728.
33. Allen, M. P.; Tildesley, D. J., *Computer Simulation of Liquids*. Oxford University Press: 2017; Vol. 2nd Edition.
34. Ediger, M. D.; Angell, C. A.; Nagel, S. R., Supercooled liquids and glasses. *Journal of Physical Chemistry* **1996,** *100*, 13200-13212.
35. Cai, L. H.; Panyukov, S.; Rubinstein, M., Hopping Diffusion of Nanoparticles in Polymer Matrices. *Macromolecules* **2015,** *48*, 847-862.
36. Sentjabrskaja, T.; Zaccarelli, E.; De Michele, C.; Sciortino, F.; Tartaglia, P.; Voigtmann, T.; Egelhaaf, S. U.; Laurati, M., Anomalous dynamics of intruders in a crowded environment of mobile obstacles. *Nature Communications* **2016,** *7*, 8.



The universal scaling behavior of the diffusion coefficients D/T as a function of the "effective" penetrant size $(\sigma_s - \sigma_c)/(\alpha - \alpha_0)$.