Correlated matrix-fluctuation-mediated activated transport of dilute penetrants in glass-forming liquids and suspensions

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We formulate a microscopic, force-level statistical mechanical theory for the activated diffusion of dilute penetrants in dense liquids, colloidal suspensions, and glasses. The approach explicitly and self-consistently accounts for coupling between penetrant hopping and matrix dynamic displacements that actively facilitate the hopping event. The key new ideas involve two mechanistically (at a stochastic trajectory level) coupled dynamic free energy functions for the matrix and spherical penetrant particles. A single dynamic coupling parameter quantifies how much the matrix displaces relative to the penetrant when the latter reaches its transition state which is determined via the enforcement of a temporal causality or coincidence condition. The theory is implemented for dilute penetrants smaller than the matrix particles, with or without penetrant-matrix attractive forces. Model calculations reveal a rich dependence of the penetrant diffusion constant and degree of dynamic coupling on size ratio, volume fraction, and attraction strength. In the absence of attractions, a near exponential decrease of penetrant diffusivity with size ratio over an intermediate range is predicted, in contrast to the much steeper, non-exponential variation if one assumes local matrix dynamical fluctuations are not correlated with penetrant motion. For sticky penetrants, the relative and absolute influence of caging versus physical bond formation is studied. The conditions for a dynamic crossover from the case where a time scale separation between penetrant and matrix activated hopping exists to a “slaved” or “constraint release” fully coupled regime are determined. The particle mixture model is mapped to treat experimental thermal systems and applied to make predictions for the diffusivity of water, toluene, methanol, and oxygen in polyvinylacetate liquids and glasses. The theory agrees well with experiment with values of the penetrant-matrix size ratio close to their chemically intuitive values. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983224>]

I. INTRODUCTION

The diffusion of dilute “penetrants” in atomic, molecular, and polymer supercooled liquids and glasses, and also their transport in dense colloidal mixture suspensions, is of high interest in diverse areas of science and engineering.^{1–5} Relevant applications include gas and molecule separations,⁶ water purification membranes,⁷ barrier materials, self-healing systems based on microcapsules,^{8–10} ion and solute transport in polymeric materials and biological systems,¹¹ and the flow of colloids in porous media.^{12,13} Penetrants are here, by definition, smaller than the elementary species that constitutes the matrix, but they can still vary over a wide range of absolute and relative size and shape and the extent of attractive interactions with the matrix material. Such variations can result in distinct transport regimes. For dense colloidal suspensions with strong short range attractions, slow glassy dynamics due to steric caging competes with “attractive glass” formation associated with strong physical bonding.^{14,15} In molecular and polymeric systems, strong enough penetrant-matrix attractions can induce matrix particle separated bridging configurations.

A number of theoretical and computational studies of penetrant diffusion in the high temperature “normal liquid” regime have been reported, including various empirical relations based on the modification of the Stokes-Einstein equation^{17,18} (e.g., the Wilke–Chang model¹⁶), first-principles dynamic mode-coupling theory (MCT),¹⁸ and molecular simulations.¹⁹ However, penetrant diffusion in deeply supercooled liquids, very dense suspensions, and glasses is a distinct and even more challenging problem since transport is typically a highly activated process involving the correlated motion in space and time of the penetrant and its surrounding matrix. Multiple time and length scales are now important, and the existence of high barriers means that standard molecular dynamics or Monte Carlo simulations are difficult or impossible.^{20,21} The limited existing models for activated penetrant diffusion are typically highly phenomenological, often built on ill-defined “free volume” ideas replete with adjustable fit parameters usually of unclear physical meaning.^{22–24}

Recently, we heuristically formulated a microscopic, force level, self-consistent nonlinear Langevin equation (SCNLE) theory²⁵ for activated barrier hopping and non-hydrodynamic diffusion of a hard sphere penetrant in dense hard sphere fluids. Based on an *a priori* mapping of

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chemical complexity to an effective sphere mixture,^{25,26} activated diffusion in atomic, molecular, and polymer liquids was studied.^{25,26} Calculations for specific systems of highly variable penetrant-matrix particle size ratio and strength of attraction agreed reasonably well with experiments.^{25,26}

The key new idea of the prior SCNLE theory is a time-dependent dynamic free energy that controls penetrant motion which is related to the bare forces, equilibrium pair structure, thermodynamic state, and *pure* matrix fluid space-time relaxational dynamics as encoded in its collective density fluctuation dynamic structure factor, $S(k,t)$.²⁵ An essential (linear response or “Gaussian-like”) approximation is that the matrix motions that influence penetrant hopping are unaffected by its presence. Thus, the matrix surrounding a penetrant enters as a constraining force field that relaxes in time per the bulk system via its own activated dynamics. The latter is described by the accurate Elastically Collective Nonlinear Langevin equation (ECNLE) theory^{27,28} of one-component glass-forming liquids. Self-consistency is enforced by requiring the equality of the mean time scale for penetrant hopping and degree of matrix collective relaxation.

Despite significant successes, the SCNLE approach ignores all explicit (trajectory-level) dynamic correlations between the penetrant hopping event and matrix fluctuations. Although in an ensemble-averaged sense adding one penetrant to the matrix liquid does not modify the bulk matrix dynamics, on the local scale of the penetrant hopping event this is not true. Rather local dynamic cooperativity between facilitating matrix motions and penetrant hopping must exist and is expected to depend on all system and thermodynamic state variables. Our present goal is to address this issue by formulating a more advanced theory that self-consistently includes the active matrix dynamical facilitation of penetrant diffusion. This requires an explicit treatment of matrix displacements and their coupling to penetrant motion at a trajectory level. The dynamic free energy concept is again employed, but now in a coupled manner for penetrants and matrix.

The basic new idea is sketched in Figure 1. There is some resemblance to the classic condensed matter physics problems of interstitial small atom hopping transport or polaron formation and diffusion in crystalline and amorphous solids.²⁹ In essence, the dynamical transition state for a penetrant hop (displacement to its barrier location) is coupled with a coordinated dynamical fluctuation of the matrix particles on a length scale below that corresponding to its activated relaxation (alpha process). We shall quantify the degree of dynamic coupling by a single dimensionless parameter, γ , which is the ratio of the penetrant jump distance to reach its barrier to the associated correlated matrix displacement. This fluctuation “costs” dynamic free energy, but by creating extra space around the penetrant it lowers the barrier for penetrant hopping. This is the physics we imply when using the word “facilitation.” The precise degree of matrix displacement (value of γ) is self-consistently determined by requiring temporal causality or coincidence, i.e., the mean time for the penetrant to reach its barrier (transition state) equals the time scale for the matrix particles to undergo their facilitating displacement. We call this new approach “self-consistent cooperative hopping theory” (SCCHT).

FIG. 1. Schematic of key ingredients of SCCHT. Matrix facilitation of penetrant hopping is formulated based on the concept of a dimensionless dynamical coupling parameter γ , defined as the ratio of the penetrant jump distance Δr_p to the matrix facilitating displacement $\Delta r_{m,c}$. The penetrant dynamic free energy (left graph) depends on γ , which is uniquely determined based on a temporal causality or coincidence condition that the penetrant mean barrier hopping time equals the mean time for a matrix particle to displace by $\Delta r_{m,c} = \Delta r_p / \gamma$. The central image schematically illustrates a coupled penetrant-matrix activated hopping event.

The SCCHT formulation has three general advantages relative to the prior SCNLE theory²⁵ that we believe allows it to capture more of the essential physics. First, it explicitly accounts for the dynamic cooperativity of penetrant-matrix motion not contained in the prior approach. Hence, a “penetrant hop” becomes a coupled penetrant-matrix activated re-arrangement event. Second, it has no free parameters, in contrast to the SCNLE theory which required information about the form of the nonexponential relaxation function of the pure matrix fluid, $S(k,t)$, that was treated as external input. Third, the SCNLE approach did not exactly reduce to the ECNLE theory of one-component liquids in the limit that the penetrant and matrix particles become identical, but the new SCCHT does. We will show that the SCCHT makes distinctive predictions for how penetrant diffusion depends on the size ratio which are in better agreement with simulations than the SCNLE theory, and preliminary applications to penetrant diffusion in polymer melts and glasses reveal that the SCCHT also captures experimental observations better than the SCNLE approach.

Section II briefly reviews theoretical background concerning the model employed, ECNLE theory, and SCNLE theory. The new SCCHT approach is formulated in Section III. Section IV compares the predictions of SCNLE theory and SCCHT for the diffusivity of repulsive and sticky penetrants. Sections V and VI present numerical results based on the new theory for purely repulsive penetrants and sticky penetrants, respectively. Quantitative application to experiments on water, toluene, methanol, and oxygen diffusion in a polymer melt and glass is given in Section VII. The article concludes in Section VIII with a summary and discussion.

II. THEORETICAL BACKGROUND

To set the stage for formulating SCCHT, we briefly review the foundational elements of our prior work. All technical details and discussion of theoretical approximations are given in prior papers.^{25,26}

A. Model and ideal mode coupling theory foundation

We consider a dilute spherical particle mixture composed of a single penetrant (diameter, d) in a fluid of matrix particles (number density ρ_m) of diameter σ at a temperature T . In this article, subscripts p and m refer to the penetrant and matrix, respectively. The dynamical approach is formulated for arbitrary pair interaction potentials. The starting point for the pure fluid matrix is a standard generalized Langevin equation (GLE) for single particle motion.^{30–32} The central quantity is the time correlation (memory) function of the slowly relaxing component of the total forces on a tagged sphere, $K_m(t)$. This object is determined based on the mode-coupling theory (MCT) approximation^{25,31,33} of projecting forces onto the bilinear field of matrix and tagged particle density fluctuations, the required 4-point correlations are factorized as a product of 2-point functions, and projected dynamics is replaced by the real dynamics. The result in Fourier space is²⁵

$$K_m(t) \equiv \frac{1}{3} \langle \vec{f}_m(0) \cdot \vec{f}_m(t) \rangle \approx \int \frac{d\vec{k}}{(2\pi)^3} \rho_m C_{mm}^2(k) S_{mm}(k) \times F_{s,m}(k, t) F_{c,m}(k, t). \quad (1)$$

Here, $S_{mm}(k)$ is the matrix static structure factor, $C_{mm}(k) = \rho_m^{-1} (1 - S_{mm}^{-1}(k))$ is the direct correlation function,³¹ and $F_{s,m}(k, t)$ and $F_{c,m}(k, t) \equiv S_{mm}(k, t)/S_{mm}(k)$ are the (normalized to unity at $t = 0$) single particle and collective density fluctuation dynamic structure factors or propagators, respectively. Force relaxation occurs in a parallel manner via a spatially resolved single particle and collective time-dependent density fluctuations.

The analog of Eq. (1) for the dilute penetrant is²⁵

$$K_p(t) \equiv \frac{1}{3} \langle \vec{f}_p(0) \cdot \vec{f}_p(t) \rangle \approx \int \frac{d\vec{k}}{(2\pi)^3} \rho_m C_{mp}^2(k) S_{mm}(k) \times F_{s,p}(k, t) F_{c,m}(k, t). \quad (2)$$

The matrix collective dynamic density fluctuations are encoded in $F_{c,m}(k, t)$ and enter in an external field manner, i.e., independent of the presence of the penetrant. Effective forces (via the dynamic vertex, $\rho_m C_{mp}^2(k) S_{mm}(k)$) are quantified by the penetrant-matrix pair correlation function, $g_{mp}(r) = h_{mp}(r) + 1$, and matrix structure factor. The former obeys²⁵

$$h_{mp}(k) = C_{mp}(k) S_{mm}(k). \quad (3)$$

To treat slow dynamics, the first step is to determine the ideal (naïve MCT) localization transition.^{25,30,33} The arrested state is modeled as a harmonic Einstein solid with a de Gennes-Vineyard form of the collective Debye-Waller factor.^{25,32} Taking the long time limit of the force-force time correlation function, and enforcing self-consistency, yields two decoupled localization length equations for the matrix and penetrant,²⁵

$$r_{loc,m}^{-2} = \frac{1}{18\pi^2} \int_0^\infty dk \rho_m k^4 C_{mm}^2(k) S_{mm}(k) e^{-k^2 r_{loc,m}^2/6} \times e^{-k^2 r_{loc,m}^2/6 S_{mm}(k)}, \quad (4)$$

$$r_{loc,p}^{-2} = \frac{1}{18\pi^2} \int_0^\infty dk \rho_m k^4 C_{pm}^2(k) S_{mm}(k) e^{-k^2 r_{loc,p}^2/6} \times e^{-k^2 r_{loc,m}^2/6 S_{mm}(k)}. \quad (5)$$

B. Matrix ECNLE theory and penetrant hopping in the frozen matrix limit

To go beyond ideal MCT and treat hopping, ECNLE theory ideas^{27,28} are invoked. For the pure matrix fluid, the relevant equations for the dynamic free energy as a function of the dynamical displacement of a matrix particle, r_m , the collective elastic barrier, $F_{elastic,m}$, the effective elastic fluctuation induced cage expansion length scale, $\Delta r_{eff,m}$, and the corresponding mean Kramers³⁰ hopping time, $\tau_{hop,m}$, are given by the following four equations:^{25,28}

$$\frac{F_{dyn,m}(r_m)}{k_B T} = -3 \ln \left(\frac{r_m}{\sigma} \right) - \frac{1}{2\pi^2} \int_0^\infty dk \frac{\rho_m k^2 C_{mm}^2(k) S_{mm}(k)}{1 + S_{mm}^{-1}(k)} \times \exp \left[-\frac{k^2 r_m^2}{6} (1 + S_{mm}^{-1}(k)) \right], \quad (6)$$

$$F_{elastic,m} = 12 \phi_m \frac{r_{cage,m}^3}{\sigma^3} \Delta r_{eff,m}^2 K_{0,m}, \quad (7)$$

$$\Delta r_{eff,m} = \frac{3}{r_{cage,m}^3} \left[\frac{r_{cage,m}^2 \Delta r_m^2}{32} - \frac{r_{cage,m} \Delta r_m^3}{192} + \frac{\Delta r_m^4}{3072} \right], \quad (8)$$

$$\tau_{hop,m} = \frac{2\tau_{s,m} e^{F_{elastic,m}/k_B T}}{\sigma^2} \int_{r_{loc,m}}^{r_{loc,m} + \Delta r_m} dr_m e^{F_{dyn,m}(r_m)/k_B T} \times \int_{r_{loc,m}}^{r_m} dr'_m e^{-F_{dyn,m}(r'_m)/k_B T}. \quad (9)$$

In Eqs. (6) and (7), k_B is Boltzmann's constant, $\phi_m \equiv \rho_m \pi \sigma^3/6$ is the fluid volume fraction, $K_{0,m} = 3k_B T/r_{m,loc}^2$ is the harmonic spring constant of the ideal MCT localized state, the matrix cage radius is $r_{cage,m} = r_{min,mm}$ (where $r_{min,mm}$ corresponds to the first minimum of $g_{mm}(r)$), and Δr_m is the microscopic matrix particle jump distance. The solution of Eq. (4), $r_{loc,m}$, corresponds to the minimum of the matrix dynamic free energy; a schematic is shown in Fig. 1. It is well established³³ that the dynamical constraints that enter the dynamic free energy are dominated by the local cage scale wavevectors in Eq. (6). This feature will be conceptually important when formulating the new SCCHT approach below.

Penetrant hopping in the “frozen matrix” (no relaxation) limit is controlled by the penetrant dynamic free energy,²⁵

$$\frac{F_{dyn,p}(r_p)}{k_B T} = -3 \ln \left(\frac{r_p}{\sigma} \right) - \frac{1}{2\pi^2} \int_0^\infty dk \rho_m k^2 C_{pm}^2(k) S_{mm}(k) \times F_{c,m}(k, r_{loc,m}) e^{-k^2 r_p^2/6}, \quad (10)$$

where the matrix collective propagator satisfies the relation $F_{c,m}(k, r_{loc,m}) = e^{-k^2 r_{loc,m}^2/6 S_{mm}(k)}$. The minimum of this function obeys the naïve mode coupling theory (NMCT) self-consistent ideal localization in Eq. (5).

C. General SCNLE penetrant hopping theory

In reality, the matrix is not a harmonic amorphous solid. To account for the effect of anharmonic matrix motion on penetrant hopping, we previously heuristically constructed the SCNLE theory by arguing that $F_{c,m}$ in Eq. (10) can be replaced by its pure matrix fluid ensemble-averaged dynamic analog,²⁵

$$F_{c,m}(k, r_{loc,m}) \rightarrow e^{-k^2 r_{loc,m}^2 / 6 S_{mm}(k)} \cdot \frac{S_{mm}(k, t)}{S_{mm}(k)} \Big|_{\text{slow}}, \quad (11)$$

where the subscript “slow” indicates matrix alpha relaxation dynamics. Hence, matrix motion enters in an effectively incoherent manner as a time-dependent “external field” that serves as a parallel channel of relaxation of forces on the penetrant. There is no explicit coupling to, or feedback with, penetrant displacement. To implement this idea, we adopted an approximate analytic form of $S_{mm}(k, t)$,^{25,35,36}

$$S_{mm}(k, t) \approx S_{mm}(k) e^{-k^2 r_{loc,m}^2 / 6 S_{mm}(k)} \exp \left[- \left(\frac{t}{\tau_m(k)} \right)^{\beta_K} \right], \quad (12)$$

where the wavevector dependent collective relaxation time, $\tau_m(k)$, is^{25,35,36}

$$\frac{\tau_{hop,m}}{\tau_m(k)} = e^{-k^2 \sigma^2} + \left(\frac{(k/k^*)^2 R}{S_{mm}(k)[1 + (k/k^*)^2 R]} \right)^{1/\beta_K}. \quad (13)$$

Self-consistency enters by requiring that the penetrant mean hopping time $\tau_{hop,p}$ computed using the Kramers theory is identical to the time that enters the penetrant dynamic free energy of Eq. (10) with Eq. (11). Full details of the SCNLE theory can be found in Ref. 25.

The SCNLE formulation includes two *a priori* unknown parameters: the matrix liquid Kohlrausch-Williams-Watts (KWW) exponent β_K and the dimensionless parameter R that quantifies decoupling of diffusion and relaxation in the pure matrix liquid.^{25,35,36} Our previous studies revealed that the influence of R on penetrant diffusivity prediction is very weak, and $\beta_K = 1/3$ yields rather good results when applying the SCNLE to penetrant diffusion in polymers.²⁶ But conceptually, the SCNLE theory is not free of unknown input parameters.

III. SELF-CONSISTENT COOPERATIVE HOPPING THEORY

A. Formulation

Our goal is to go beyond describing the effect of matrix collective dynamics on penetrant hopping as an effective external time-dependent mean field which temporally decays via the pure matrix relaxation function, $S_{mm}(k, t)$. Rather, we aim to explicitly capture mechanical coupling of matrix and penetrant displacements in determining the hopping event, which in essence requires going beyond a literal dynamic Gaussian factorization approximation. The basic idea was briefly explained in the Introduction and is schematically illustrated in Fig. 1. Two coupled dynamic free energies are introduced where an instantaneous matrix displacement (below barrier) modifies the penetrant dynamic free energy. The simplest, but self-consistent, quantification of the coupling is adopted to quantify the degree of matrix displacement from its

localized state that facilitates the penetrant barrier hopping event: temporal causality or coincidence. This corresponds to the mean time for the penetrant to reach its barrier being exactly equal to the mean time required for the facilitating matrix displacement to be achieved. This criterion yields a relation for determining the precise degree of cooperative facilitating matrix displacement (denoted as $\Delta r_{m,c}$, see Fig. 1), which depends on all system variables and the thermodynamic state. Broadly, the physical picture is that the “reactive” penetrant trajectory is controlled by a dynamic free energy that evolves with instantaneous matrix displacement. After the penetrant transits over its barrier, the matrix is assumed to return to its localized position, i.e., dynamically re-equilibrates. The statistical mechanical formulation of this idea defines the SCCHT.

The heuristic “local equilibrium” idea of NLE theory^{25,32,33} is invoked for treating the matrix and penetrant dynamic displacement variables (r_m, r_p). This results in a penetrant dynamic free energy that depends explicitly on the matrix displacement variable as

$$\begin{aligned} \frac{F_{dyn,p}(r_p)}{k_B T} = & -3 \ln \left(\frac{r_p}{\sigma} \right) - \frac{1}{2\pi^2} \int_0^\infty dk \rho_m k^2 C_{pm}^2(k) S_{mm}(k) \\ & \times e^{-k^2 r_p^2 / 6} e^{-k^2 r_m^2 / 6 S_{mm}(k)}. \end{aligned} \quad (14)$$

Equation (14) may “look like” the penetrant and matrix dynamics are again Gaussian factorized, but this is not true since the dynamical trajectory variables (r_m, r_p) enter, not ensemble-averaged Debye-Waller factors or propagators. Thus, some aspects of beyond 2-point space-time correlations are approximately taken into account. Given the penetrant is at infinite dilution, we assume the matrix particle displacements are controlled by the pure system dynamic free energy.

We now introduce a trajectory level coupling between matrix particle and penetrant displacements in terms of a dimensionless “dynamical coupling parameter,” γ . Effectively, this is a simple model for the “reactive eigenvector” that defines the coupled matrix-penetrant activated event. This parameter quantifies how much matrix particles displace from their localization well as the inverse fraction of how much the penetrant displaces and is defined by

$$r_m = r_{loc,m} + (r_p - r_{loc,p})/\gamma, \quad r_p \geq r_{loc,p}. \quad (15)$$

In general, γ quantifies the ratio of the penetrant displacement from its localization length, $(r_p - r_{loc,p})$, to the matrix displacement from its localized position, $(r_m - r_{loc,m})$. Note from Eqs. (14) and (15) that any matrix displacement beyond the harmonic limit will *reduce* the caging constraints felt by the penetrant, and in this sense it “facilitates” penetrant hopping. If this coupling parameter diverges ($\gamma \rightarrow \infty$), Eq. (14) corresponds to the frozen matrix limit where there is no instantaneous causal coupling between matrix displacement and penetrant motion. On the other hand, the smaller γ is, the stronger coupling is between penetrant and matrix dynamics. Using Eq. (15), the γ -dependent penetrant dynamic free energy

function is

$$\frac{F_{dyn,p}(r_p, \gamma)}{k_B T} = -3 \ln \left(\frac{r_p}{\sigma} \right) - \frac{1}{2\pi^2} \int_0^\infty dk \rho_m k^2 C_{pm}^2(k) S_{mm}(k) \times e^{-k^2 r_p^2 / 6} e^{-k^2 [r_{loc,m} + (r_p - r_{loc,p})/\gamma]^2 / 6} S_{mm}(k). \quad (16)$$

Importantly, Eq. (16) guarantees that the condition $\partial F_{dyn,p}(r_p, \gamma) / \partial r_p = 0$ exactly reduces to the penetrant harmonic localization Eq. (5).

The temporal causality or coincidence condition is adopted to uniquely determine γ . The penetrant jump distance (left side of Fig. 1) corresponding to $F_{dyn,p}(r_p, \gamma)$ is denoted as $\Delta r_p(\gamma)$. Then, based on Eq. (15), $\Delta r_{m,c}(\gamma) = \Delta r_p(\gamma) / \gamma$. The self-consistent condition is as follows:

$$\tau_{hop,p}(\gamma) = \tau_{dis,m}(\Delta r_{m,c}(\gamma)), \quad (17)$$

where the mean penetrant hopping time is computed using $F_{dyn,p}(r_p, \gamma)$ and the Kramers theory,³⁰

$$\tau_{hop,p}(\gamma) = \frac{2\tau_{s,p} e^{F_{elastic,p}(\gamma)/k_B T}}{d^2} \int_{r_{loc,p}}^{r_{loc,p} + \Delta r_p(\gamma)} dr_p e^{F_{dyn,p}(r_p, \gamma)/k_B T} \times \int_{r_{loc,p}}^{r_p} dr'_p e^{-F_{dyn,p}(r'_p, \gamma)/k_B T}. \quad (18)$$

The mean time required for the matrix particles to displace a distance $\Delta r_{m,c}(\gamma)$ (see Fig. 1) is denoted as $\tau_{dis,m}(\Delta r_{m,c}(\gamma))$, which is estimated from the Kramers first passage time³⁴ equation,

$$\tau_{dis,m}(\Delta r_{m,c}) = \frac{2\tau_{s,m} e^{F_{elastic,p}(\gamma)/k_B T}}{\sigma^2} \int_{r_{loc,m}}^{r_{loc,m} + \Delta r_{m,c}} dr_m e^{F_{dyn,m}(r_m)/k_B T} \times \int_{r_{loc,m}}^{r_m} dr'_m e^{-F_{dyn,m}(r'_m)/k_B T}. \quad (19)$$

We now elaborate on our discussion of the elastic component ($F_{elastic,p}(\gamma)$) of the activation barrier for the coupled matrix-penetrant hopping event. The underlying physical picture is correlated displacements of the penetrant and matrix particles exist on the penetrant cage length scale. To allow large amplitude hopping to occur requires some cage expansion corresponding to an elastic distortion of the matrix particles outside this cage. Physically, the *same* elastic dynamic free energy cost applies to both the time scale for penetrant and matrix displacements. In the dilute penetrant limit of present interest, the penetrant is (on average) at the center of its cage of matrix neighbors. Thus, even after hopping, its position is predicted to not exceed its original cage radius. Thus, given the single particle mean field foundation of the NLE theory of hopping, and the prior ECNLE analysis,^{27,28} the penetrant jump does not contribute to the average cage expansion (Fig. 1), which is associated solely with the facilitating displacements of the surrounding matrix cage particles. Hence, precisely the same ECNLE theory analysis employed for the 1-component liquid²⁸ again applies (see Eqs. (7) and (8), except that the cage expansion displacement depends on the degree of dynamic

coupling between the matrix and penetrant particles, and the cage radius is $r_{cage,p} = r_{min,pm}$, where $r_{min,pm}$ corresponds to the first local minimum of $g_{pm}(r)$. The elastic barrier results then become

$$F_{elastic,p}(\gamma) = 2\pi \rho_m r_{cage,p}^3 \Delta r_{eff,m}^2(\gamma) K_{0,m}, \quad (20)$$

$$\Delta r_{eff,m}(\gamma) = \frac{3}{r_{cage,p}^3} \left[\frac{r_{cage,m}^2 \Delta r_{m,c}^2}{32} - \frac{r_{cage,m} \Delta r_{m,c}^3}{192} + \frac{\Delta r_{m,c}^4}{3072} \right]. \quad (21)$$

Note that since the *same* elastic barrier enters the mean displacement times of the penetrant and matrix particles, it cancels out of the temporal self-consistency relation of Eq. (17).

The penetrant hopping diffusion constant is estimated per the simple Fickian treatment employed before,²⁵

$$D_{hop,p} = \Delta r_p^2(\gamma) / 6\tau_{hop,p}(\gamma). \quad (22)$$

It is often non-dimensionalized by $D_0(\phi_m)$, which is the pure matrix Enskog diffusivity defined in Ref. 25.

B. Limiting behavior and relation to prior formulations

We note that the SCCHT exactly reduces to the 1-component ECNLE theory in the limit the penetrant and matrix particles are *identical* ($d = \sigma$ and no penetrant-matrix interactions beyond hard core) where the dynamic coupling parameter $\gamma = 1$, by construction. Recall that the ECNLE theory describes single particle activated motion, which is influenced by two barriers associated with local cage constraints and the facilitating long range elastic fluctuation of the liquid outside the cage. The above $d = \sigma$ “consistency reduction” is not exactly obeyed by the prior SCNLE theory, nor our prior conceptually appealing approach based on a dynamic free energy surface idea constructed for spherical particle mixtures in the NLE framework.^{37,38} Furthermore, construction of a dynamic free surface involves some ambiguity associated with an “integration path dependent” issue.³⁹ The new SCCHT approach does not incur this potential difficulty.

In the presentation of the SCCHT idea above, the penetrant was viewed as the dynamically “faster species” corresponding to the physical picture that when the penetrant hops, the accompanying matrix displacement has not reached its own barrier, $\Delta r_{m,c} \leq \Delta r_m$, cf. Fig. 1, per a “sub-reactive” matrix trajectory fluctuation. The matrix hopping time, $\tau_{hop,m}$, is thus independent of the presence of a dilute penetrant. Subsequent hops by the penetrant are influenced by the same dynamical matrix environment as the first hop, and in this sense the space-time “dynamic facilitation” idea discussed in the context of 1-component supercooled fluids⁴⁰ is not taken into account.

If a self-consistent solution for the temporal coincidence condition that determines γ does not exist, it implies the assumption that penetrant is the “faster species” is not true. This situation then corresponds to the emergence of a dynamic crossover to a new “constraint release” (CR) regime where the matrix and penetrant hopping events become slaved with identical mean hopping time scales. In practice, the mechanism for entering this regime (which is *a priori* predicted) is that the size of the penetrant and matrix particles becomes “close enough” and/or there are strong penetrant-matrix attractions

giving rise to dynamic bond formation. In our earlier studies using the SCNLE theory,²⁵ this CR situation was called regime 3. In this article, we focus primarily on systems not in this regime, as relevant to gas and small molecule diffusion in polymers or nanoparticle motion in colloidal suspensions. We note that when $d \gg \sigma$, penetrant diffusivity will be dominated by hydrodynamics and is described by the Stokes-Einstein relation $D_{\text{penetrant}} = k_B T / 3\pi\eta_{\text{matrix}}d$, where η_{matrix} is the matrix viscosity. We are not interested in this regime, and our non-hydrodynamic SCCHT focuses on systems where the penetrant size is comparable or (much) smaller than the matrix particle size, a regime where a hydrodynamic description is not applicable.

C. Mixture models

We consider a minimalist mixture model of spheres that interact via additive hard core repulsions plus a penetrant-matrix (p-m) exponential attraction beyond contact,

$$u_{pm}(r) = \varepsilon e^{-(r-d_{pm})/a}, \quad r \geq d_{pm}, \quad (23)$$

where $d_{pm} = (d + \sigma)/2$, and ε and a define the attraction strength (in units of $k_B T$ unless otherwise noted) and range, respectively. All calculations use $a/d_{pm} = 0.4$, and the required structural pair correlations are determined using the Percus-Yevick integral equation theory.³¹ This model is directly relevant to colloidal suspensions, and as a toy model of thermal liquids. It also serves as a foundational model to apply the dynamical theory to thermal molecular and polymer liquids via the well-documented mapping^{41,42} employed previously.^{25,26}

The other key system variables are the size ratio, d/σ , and matrix fluid volume fraction, ϕ_m . For context, if one is interested in laboratory colloidal suspensions or computer simulations, then kinetic glass formation is typically associated with $\phi_m \approx 0.58 \pm 0.01$.⁴³ For thermal liquids, the kinetic glass transition temperature (mean alpha time of ~ 100 s) based on the ECNLE theory occurs at $\phi_m \approx 0.611$,⁴¹ while the dynamic crossover to the deeply supercooled regime where the collective elastic barrier becomes very important occurs at $\phi_m \approx 0.57$.⁴¹

IV. INCOHERENT VS. CORRELATED MATRIX DYNAMIC FLUCTUATIONS

We now present representative calculations that illustrate the differences in predictions of the SCNLE theory and SCCHT for penetrants that either do not attract or strongly attract the matrix particles. This comparison highlights how treating matrix dynamical fluctuations in an “incoherent external field” manner contrasts with the new results based on including the mechanistic coupling of matrix and penetrant displacements.

Figure 2 shows SCCHT and SCNLE theory calculations of the penetrant diffusivity for $\phi_m = 0.611$ and $\varepsilon = 0$ (main frame) and $\varepsilon = -2.5$ (inset), along with the analogous “frozen matrix” limit calculations. Recall that the latter follows from setting $\gamma = \infty$ in SCCHT. The frozen matrix calculations always yield the smallest penetrant diffusion constants, which is physically sensible since it ignores non-vibrational matrix

FIG. 2. Dimensionless penetrant diffusivity (in units of the pure matrix Enskog diffusivity, $D_0(\phi_m)$; see Ref. 25) as a function of the size ratio d/σ at a matrix volume fraction of 0.611, which is representative of one-component thermal liquids at their glass transition temperature. Solid curves are SCCHT calculations, dashed curves are the prior SCNLE theory²⁵ results employing $\beta_K = 1, 1/2$, or $1/3$ (R is fixed at 10), and dashed-dotted curves are “frozen harmonic matrix” limiting calculations. Main panel: $\varepsilon = 0$; inset: $\varepsilon = -2.5$.

dynamics which speeds up activated transport by reducing dynamical constraints on the penetrant. Since SCNLE theory requires the matrix KWW β_K parameter as input, we have performed calculations for three different values ($\beta_K = 1, 1/2, 1/3$) which span the range observed in real materials. The SCNLE theory results are essentially the same as the “frozen matrix” results in the relatively small d/σ range (narrower for smaller β_K). In contrast, the SCCHT results deviate from the “frozen matrix” results beginning at the smallest value of d/σ considered, which is close to its activated hopping onset value that defines when a local barrier first emerges in the penetrant dynamic free energy. Overall, there are rather large differences between the SCCHT and SCNLE predictions, especially for intermediate size ratios, and more so for sticky penetrants that form physical bonds (compare the inset and main panel). More generally, the functional form of the size ratio dependence predicted by the two theories is quite different. The SCCHT predicts a roughly exponential variation of diffusivity as a function of size ratio over a significant range, while the SCNLE theory predicts²⁵ a much sharper supra-exponential reduction.

Since the two theories treat the influence of matrix dynamics on penetrant diffusion differently, it presumably is not surprising to observe major differences of their predictions. One can physically argue on general grounds that active matrix facilitation, if properly described, should speed up penetrant diffusion, and SCCHT should capture more of the physics of activated transport. This deduction agrees with the results in Fig. 2 and will be further buttressed in Secs. V–VII when we compare SCCHT to simulations and experiments. At larger size ratios, however, one does see in Fig. 2 that there are curve crossings between the two theories. We believe that this is not fundamental, but rather is due to the new SCCHT properly going to the 1-component ECNLE theory result as the size ratio approaches unity (when $\varepsilon = 0$), while the SCNLE theory does not and over-predicts diffusivity.

V. ACTIVATED DYNAMICS IN REPULSIVE INTERACTION SYSTEMS

We now focus solely on the new SCCHT. In this section, only purely repulsive systems ($\varepsilon = 0$) are studied. Figure 3 shows calculations of dimensionless penetrant diffusivity, the ratio of the penetrant to matrix hopping time, and the dynamic coupling parameter γ , at five high matrix volume fractions. The penetrant diffusivity for all cases varies roughly exponentially over an intermediate range of size ratios up to $d/\sigma \sim 0.8$. The curves do not extend to below $d/\sigma \sim 0.2$ – 0.25 since penetrants are not transiently localized (vanishing barriers). For larger size ratios, the system enters the constraint release regime where penetrant and matrix particle hopping times are nearly equal. This crossover is the reason the penetrant diffusivity curves “bend down” in Fig. 3, a feature that is more dramatic as the matrix fluid becomes denser.

A clear size ratio dependence of the coupling parameter is evident, which depends only very weakly on matrix volume fraction. In accord with intuition, as a penetrant gets bigger, more facilitating matrix distortion is required corresponding to a smaller value of γ and a greater dynamical coupling. The γ values are always large (~ 10 , indicating a small amplitude of matrix distortion accompanying the penetrant hopping) for small values of d/σ , and more so at a higher matrix density. The latter trend likely reflects the more strongly localized nature of the matrix, which implies displacement fluctuations are more costly at a higher density. At $d/\sigma \sim 0.4$, γ decreases to ~ 4 , and for even larger d/σ values, the matrix density dependence becomes very weak (all five curves essentially collapse) and all go to the same limit of $\gamma = 1$ when $d/\sigma = 1$.

Another quantitative measure of the penetrant-matrix dynamic decoupling is the ratio of the penetrant to the matrix hopping times, $\tau_{hop,p}/\tau_{hop,m}$. The larger this number, the larger the penetrant-matrix hopping time scale separation, and the more decoupling of their dynamics. The bottom inset of Fig. 3 shows that at a fixed size ratio, the time scale

FIG. 3. Dimensionless hopping diffusivity for repulsive penetrants as a function of the size ratio d/σ at five matrix volume fractions of 0.57, 0.59, 0.6, 0.611, and 0.63 (spanning the onset of the deeply supercooled regime to below T_g for thermal liquids). Insets: corresponding results for the ratio of penetrant and matrix barrier hopping times and the dynamic coupling parameter.

FIG. 4. Penetrant dynamic free energy (solid curves) as a function of displacement r_p for five size ratios (0.2, 0.3, 0.4, 0.5, and 0.7) at $\phi_m = 0.611$ and $\varepsilon = 0$. The corresponding dynamic coupling parameter values are shown in the legend. The dashed curve is the corresponding matrix dynamic free energy (depends only on ϕ_m in the dilute penetrant limit) as a function of its displacement r_m , also in units of σ . The x-axis value associated with the left end (local F_{dyn} minimum) of each curve is the (penetrant or matrix) localization length. The filled symbols on each curve indicate the position of the penetrant hopping barrier. Corresponding open symbols on the $F_{dyn,m}$ curve indicate the position of correlated matrix displacement that facilitates penetrant hopping in a temporally casual manner. All curves are shifted vertically such that $F_{dyn} = 0$ at the localization length. Thus, the y-axis value corresponding to the local maximum of each curve is the penetrant or matrix hopping barrier height.

separation strongly increases as the matrix density grows and monotonically decreases as the size ratio increases.

To more vividly illustrate the mechanistic aspects of SCCHT, Figure 4 presents the self-consistently determined penetrant dynamic free energy and matrix dynamic free energy curves for five size ratios at $\phi_m = 0.611$; the corresponding γ values are stated in the legend. One sees that as the penetrant gets bigger, a larger matrix distortion is needed to facilitate its hopping. The penetrant localization length is smaller for a larger size ratio, but always bigger than the matrix localization length. In the $d/\sigma = 1$ limit, the dashed curve becomes identical to the solid curve.

The inset of Fig. 5 summarizes results for the penetrant jump distance and matrix facilitating displacement for the same five systems in Fig. 3. The former is larger at a higher matrix density and follows a non-monotonic size ratio dependence; this non-monotonic behavior is also present for the absolute value of the jump distance $\Delta r_p/\sigma$ (not shown). In our previous SCNLE work,²⁵ we identified the d/σ value corresponding to the maximal jump distance as indicating a change from a regime 1 to regime 2 behavior. While the new SCCHT results differ from their SCNLE analogs, this qualitative two-regime picture still applies at size ratios preceding the onset of the constraint-release regime. In contrast to the penetrant jump distance behavior, the facilitating matrix displacement always increases with d/σ . In the limit of $d/\sigma = 1$, these two quantities are the same, by construction.

The main panel of Fig. 6 shows the ratio of the elastic to local activation barriers for the five systems of Fig. 3 and the inset of Fig. 5. This ratio is a measure of dynamic cooperativity of the alpha process in ECNLE theory, and it increases for

FIG. 5. Penetrant jump distance (in units of d , solid curves) and accompanying matrix displacement (in units of σ , dashed curves) as a function of the size ratio d/σ . Main panel: results for the five p-m attraction strengths in the legend at $\phi_m = 0.611$. Inset: results for the five representative matrix volume fractions in the legend for the repulsive penetrant system ($\epsilon = 0$).

larger size ratios or denser matrices. The stronger “bending up” behavior that becomes more pronounced with growing matrix volume fraction is responsible for the “bending down” features of the penetrant diffusivity in Fig. 3.

It is desirable to test the new predictions of SCCHT for the size ratio dependence of penetrant diffusivity against simulations. The main panel of Fig. 7 highlights our predictions at three very high matrix volume fractions, just below, at, and above the laboratory kinetic vitrification value. We find a roughly exponential dependence that spans up to 10 decades of time scale if the size ratio is not too large. This rather striking result is a direct consequence of the self-consistently coupled penetrant-matrix motion encoded in SCCHT.

We note that Bosma and Wesseling¹⁷ formulated an empirical, free-volume-based equation for the penetrant diffusion coefficient, which exhibits a similar exponential

FIG. 6. Ratio of the penetrant elastic to local barrier height as a function of the size ratio d/σ . Main panel: results for five matrix volume fractions (see legend) for the repulsive penetrant system ($\epsilon = 0$). Inset: results for five p-m attraction strengths (see legend) at $\phi_m = 0.611$.

FIG. 7. Dimensionless penetrant diffusion constant as a function of the size ratio over the range $0.2 \leq d/\sigma \leq 0.8$ at three very high matrix volume fractions (0.6, 0.611, and 0.63) and $\epsilon = 0$. Here, D_{unit} is defined below Eq. (24). Inset shows that the high volume fraction $D_{\text{hop},p}$ results collapse well onto a master curve if d/σ is scaled by the matrix transient localization length. Circles represent results at discrete d/σ values: 0.2, 0.3, 0.4, 0.5, and 0.6. Regression of all 15 data points to an exponential form yields (dashed curve) $D_{\text{hop},p}/D_{\text{unit}} = 95e^{-0.66(d/r_{\text{loc},m})}$, with a correlation coefficient of 0.992.

dependence as we predict. Other empirical and diverse propositions for the $D-d$ relation have also been proposed in the high temperature “normal liquid” matrix regime^{16,19} (from power law to exponential law and with varied effective exponents). These relations all generally capture penetrant diffusion coefficients over roughly two decades of time scale ($D \sim 10^{-6} - 10^{-4}$ cm²/s). But all these phenomenological models seem largely unrelated to our work, which focuses on strongly activated penetrant transport.

To our knowledge, simulation data to test our predicted exponential variation of D with size ratio in glass-forming liquids are not in the literature. However, Meng and Kumar⁴⁴ have recently simulated repulsive penetrant diffusion in glassy bead-spring model polymer matrices. They find that the penetrant diffusivity is an exponential function of d/σ for intermediate size ratios, in qualitative agreement with our results. Remarkably, the simulations also find⁴⁴ that penetrant diffusivities collapse on a master curve as a function of the penetrant diameter scaled by the matrix mean vibrational amplitude ($\langle u^2 \rangle^{1/2}$) in its transiently localized cage state as determined from the near plateau of the dynamic mean square displacement. Motivated by this finding, we carry out a similar exercise by employing the theoretically computed matrix localization length, $r_{\text{loc},m}$, as a physically sensible surrogate of $\langle u^2 \rangle^{1/2}$. The inset of Fig. 7 shows that SCCHT predicts an excellent collapse, with a master function,

$$D_{\text{hop},p}/D_{\text{unit}} \propto \exp\left(-0.66 \frac{d}{r_{\text{loc},m}}\right), \quad (24)$$

where $D_{\text{unit}} \equiv \sigma \sqrt{k_B T/M}$ and M is the matrix particle mass. The slope of this exponential behavior is also in reasonable accord with the simulations.⁴⁴ Much more benchmark simulation studies are desirable to test our SCCHT predictions, including the multiple new features that are predicted to emerge for the sticky-penetrant systems discussed in Sec. VI.

VI. ACTIVATED DYNAMICS OF STICKY PENETRANTS: CAGING VS. BONDING

We now consider penetrants which attract the matrix particles. For the dense systems of interest, the physics involves both steric caging and transient penetrant-matrix physical bond formation. These two dynamical effects are not independent, and both are influenced by changes in equilibrium penetrant-matrix structure, $g_{pm}(r)$. Moreover, the number and strength of bond associations at fixed ε will vary with the relative penetrant size due to packing considerations, and in a manner that depends on the absolute magnitude of ε relative to the thermal energy and matrix volume fraction. Generically, such attractions always increase the contact value of $g_{pm}(r)$ and thus are expected to always slow down penetrant relaxation and diffusion. Since structural reorganization due to attractive interactions depends on the spatial range of the interaction, this parameter also matters. This aspect can be especially relevant for colloid-nanoparticle systems, but also for molecular systems if the attraction is due to a specific interaction such as a short range hydrogen or ionic bond. Here we consider only one spatial range, as explained in Section III C.

Figures 8 and 9 present representative results for the scaled penetrant diffusivity, the ratio of penetrant to matrix mean hopping time, and the dynamic coupling parameter γ for five different attraction strengths (including the repulsive case) at two high matrix volume fractions of 0.611 and 0.57, respectively. For $\phi_m = 0.611$, the corresponding penetrant jump distance and correlated matrix displacement distance results were shown in the main panel of Fig. 5, and the ratio of the penetrant elastic to local barrier height results were shown in the inset of Fig. 6.

Both Figs. 8 and 9 show that all diffusivity curves terminate at $d/\sigma < 1$ except for the purely repulsive penetrant system. This end point indicates that at this d/σ value, the self-consistent solution for $\Delta r_{m,c}(\gamma)$ reaches for the first time the matrix jump distance Δr_m required for its alpha relaxation (see upper insets in Figs. 8 and 9). Such a behavior signals the emergence of the constraint release (slaved) dynamical regime

FIG. 8. Dimensionless penetrant diffusion constant as a function of the size ratio d/σ at $\phi_m = 0.611$ for five p-m attraction strengths (0, -0.5, -1, -2, and -2.5). Insets: corresponding results for the ratio of penetrant and matrix barrier hopping times, and the dynamic coupling parameter.

FIG. 9. Dimensionless penetrant diffusion constant as a function of the size ratio d/σ at $\phi_m = 0.57$ for five p-m attraction strengths (0, -0.5, -1, -2, and -2.5). Insets: corresponding results for the ratio of the penetrant to matrix mean hopping time, and the dynamic coupling parameter.

for larger d/σ values. It is physically intuitive that, given the p-m attraction slows down penetrant transport, the end point d/σ value occurs below the onset of slaving at $d/\sigma = 1$ when $\varepsilon = 0$ and decreases with increasing attraction strength.

The detailed dependence of penetrant diffusivity on the p-m attraction shows a rather rich and complex behavior. At both matrix volume fractions (and confirmed for any high matrix density in the activated dynamical regime, not shown), the value of d/σ at the CR crossover does not monotonically decrease as ε increases. Instead, in both systems, it reaches a minimum at $\varepsilon = -2$ and then slightly increases at $\varepsilon = -2.5$. Consistent with this behavior, SCCHT predicts that for d/σ values close to the CR crossover, the penetrant diffusion constant can be slightly enhanced upon increasing the p-m attraction strength from $\varepsilon = -2$ to -2.5 . This seemingly counterintuitive behavior is likely due to subtle competing caging and bonding effects on the structure, and hence the effective forces, that impede penetrant motion. For example, stronger attractions can increase the matrix-penetrant contact value but can potentially reduce cage coherence (creating locally larger density fluctuations), which would weaken the steric blocking effects on transport.¹⁴ Overall, however, penetrant diffusivity is predicted to be smaller for larger p-m size ratios and stronger p-m attractions in most cases (Figs. 8 and 9).

Regarding the “exponential size scaling” predicted for repulsive penetrants (Figs. 3 and 7), we find that for the lower matrix density (e.g., $\phi_m = 0.57$, Fig. 9) or weak p-m attraction ($\varepsilon = -0.5$ and -1), a roughly exponential dependence still holds over a wide intermediate d/σ window. Interestingly, a roughly “double exponential” profile emerges for the strong p-m attraction and the highest matrix density system ($\varepsilon = -2.5$, $\phi_m = 0.611$). Here, penetrant diffusivity decreases nearly exponentially with size ratio (at similar rate) for $d/\sigma < 0.35$ and $d/\sigma > 0.5$ (until CR the regime is entered), with a weaker size dependence in the intermediate range $0.35 < d/\sigma < 0.5$.

The dynamic coupling parameter γ universally decreases with d/σ for different p-m attraction strengths and at a fixed

size ratio for a stronger p-m attraction. Thus, increasing penetrant size and/or p-m attraction strength induces stronger penetrant-matrix dynamic correlation in the activated event. We note that the penetrant jump distance is smaller than its matrix analog at the CR crossover (and thus $\gamma < 1$) for strongly attractive systems because the p-m bonding leads to a smaller penetrant localization length and barrier location. This behavior is reminiscent of colloidal systems that transiently arrest into physical gels due primarily to strong bonds.^{14,15} The dynamic coupling parameter being less than unity at the CR crossover also means that there exists a special p-m size ratio (smaller than the value of d/σ at the CR crossover) for which γ precisely equals unity. However, for p-m attractive systems, $\gamma = 1$ does not indicate that the penetrant and matrix degrees of freedom are dynamically equivalent. Rather, for this case the penetrant hopping jump distance is identical to the matrix displacement in order to facilitate its hopping (i.e., $\Delta r_p = r_{B,p} - r_{loc,p} = \Delta r_{m,c} = r_{dis,m} - r_{loc,m}$), but $r_{loc,p} \neq r_{loc,m}$ and $r_{B,p} \neq r_{dis,m}$.

Figure 10 more explicitly illustrates the origin of the SCCHT sticky penetrant diffusion results. The self-consistently determined penetrant and matrix dynamic free energies are shown for four size ratios at $\phi_m = 0.611$ and a strong attraction of $\varepsilon = -2.5$. The corresponding dynamic coupling parameter values are given in the figure legend. Two of the trends observed for repulsive penetrants (Fig. 4) continue to apply: (i) for larger p-m size ratios, more matrix displacement is needed to facilitate penetrant hopping and (ii) the corresponding localization length is smaller. But new “gel-like” features^{14,15} emerge in the penetrant dynamic free energy. For example, at $d/\sigma = 0.7$, the localization length is much smaller than its matrix analog, and the penetrant jump distance is only 60% of the matrix displacement because physical bonding plays a central role in determining the penetrant barrier location. In contrast, for repulsive systems, the penetrant localization length is always larger than the matrix analog, and the penetrant jump distance is always larger than the degree of matrix facilitating displacement.

FIG. 10. Same as Figure 4 but for $\phi_m = 0.611$, $\varepsilon = -2.5$, and $d/\sigma = 0.2, 0.3, 0.5$, and 0.7 .

We now return to the main panel of Fig. 5 to discuss more quantitatively how the p-m attraction strength influences the penetrant jump distance and matrix displacement. The penetrant jump distance varies non-monotonically with size ratio for all attraction strengths. Except at very small size ratios (~ 0.2), a stronger p-m attraction leads to a smaller penetrant jump distance. For the strongest p-m attraction considered ($\varepsilon = -2.5$), the penetrant jump distance never exceeds its diameter. The inset of Fig. 6 compares the ratio of the penetrant elastic to local barriers for five attraction strengths and $\phi_m = 0.611$. All curves again terminate at the CR crossover (where $\Delta r_{m,c}(\gamma) = \Delta r_m$). The relative contribution of the longer range elastic barrier is smaller for a stronger p-m attraction at this CR crossover. The qualitative reason is that stronger p-m bonds lead to tighter matrix packing around the penetrant, and thus a smaller $r_{cage,p}$ and $F_{elastic,p}$.

VII. PENETRANT DIFFUSION IN POLYMER MELTS AND GLASSES

In our previous work,^{25,26} we proposed a mapping scheme from a hard sphere mixture model to a thermal liquid mixture of penetrants plus molecules or polymers based on requiring that the effective sphere matrix system exactly reproduces the dimensionless long-wavelength density fluctuation amplitude of the real thermal matrix in the equilibrated liquid phase. The nonequilibrium below matrix T_g glass was treated by ignoring physical aging and assuming that the matrix volume fraction increases with cooling via its known thermal expansion coefficient.²⁶ Here, we employ exactly the same mapping approaches and revisit what the new SCCHT predicts for the diffusion constant of four chemically diverse penetrants (water, toluene, oxygen, and methanol) in the polymer polyvinylacetate (PVAC). We have chosen PVAC since the existing no-fit-parameter ECNLE theory of this pure polymer melt is very accurate for its glass transition temperature, dynamical fragility ($m \sim 95$), and temperature-dependent alpha relaxation time.^{42,45} As such, how well the penetrant diffusivity predictions compare with experiment directly reflects the reliability of our new theoretical ideas for penetrant diffusion.

To perform the quantitative comparisons, we proceed precisely as discussed in our prior work. All system parameters, including the strength of the attractive interaction between the penetrant and PVAC Kuhn segment, are *a priori* determined²⁶ with one exception: the effective penetrant-Kuhn segment size ratio, d/σ . This single numerical parameter is varied to best account for the experimentally measured temperature dependence of penetrant diffusion for water, toluene, and methanol in the deeply supercooled liquid, and from just above to below the matrix T_g for oxygen. We compare the SCCHT predictions with its previously determined SCNLE theory analogs. Metrics of success are as follows: (i) how well the theory quantitatively accounts for the absolute magnitudes and temperature dependences of penetrant diffusivity and (ii) how close the best fit (optimized) value of d/σ (given in Table I) is to *a priori* chemical estimates.

Figure 11 shows the results; the employed (extracted) optimized size ratios are given in Table I. First, one visually

TABLE I. Key parameters and theory optimization results for penetrant diffusion in PVAC. dev_{th-exp} is the theory-experiment deviation number defined in Ref. 26.

Penetrant	ε/k_B (K) ^a	<i>a priori</i> d/σ ^a	Optimal	dev_{th-exp}	Optimal	dev_{th-exp}
			d/σ ^a SCNLE ^a	(%) SCNLE ^a	d/σ ^a SCCHT	(%) SCCHT
H ₂ O	-1157	0.298	0.208	4.6	0.234	7.8
O ₂	-420	0.389	0.322	7.1	0.348	6.7
Methanol	-623	0.417	0.334	14.6	0.380	2.3
Toluene	0 ^b	0.775	0.982	6.7	0.758	3.9

^aNumbers quoted from our previous work (Ref. 26).

^bReasonable effective p-m attraction strength for the chemistry-matched system (see more discussion in Ref. 26).

sees that both theories predict rather well the experimental data for water and oxygen diffusion. For methanol, SCCHT yields better agreement with experiment. For toluene, we note that the filled triangle symbols are the experimental data used in our previous work²⁶ and serve as the basis for size ratio optimization (Table I) for both theories. The open triangle symbols are two additional experimental data points in the literature.⁴⁶ They serve as an *a priori* test of the ability of the theories to make a prediction. One sees that the SCCHT curve nicely agrees with these two data points, and a significant deviation occurs based on the SCNLE approach. Overall, the SCCHT consistently yields better accuracy than the prior SCNLE approach. Moreover, the optimized size ratio values (Table I) extracted from the SCCHT calculation are generally much closer to prior estimated values (see Ref. 26 for details) than those from the SCNLE analysis. Thus, the SCCHT improves physicochemical consistency.

Most of the experimental data in Fig. 11 are in the super-cooled matrix polymer liquid regime. The two theories make

FIG. 11. Theory versus experiment for the penetrant diffusion constant in absolute units. Theoretical results based on the best fit value of d/σ are shown for SCCHT (solid curves) and SCNLE theory (dashed curves) using $\beta_K = 1/3$, $R = 10$, for water, oxygen, methanol, and toluene self-diffusion constants in PVAC as a function of T_g/T ($T_g = 308$ K, pure PVAC). See Table I for relevant molecular parameters. Filled symbols represent experimental data (same as cited previously²⁶) that were analyzed to obtain the optimal d/σ values (see Table I) for both theories. The two open symbols represent additional experimental data in the literature⁴⁶ for toluene diffusivity in PVAC, which are not used in the fitting optimization exercise.

FIG. 12. SCCHT predictions for the ratio of the penetrant-to-matrix hopping time (main panel) and dynamical coupling parameter (inset) corresponding to the experimental systems in Fig. 11.

very different predictions in the glass. The SCCHT predicts a faster diffusion (e.g., by up to three decades for water well into the PVAC glass) than the SCNLE theory does. Moreover, the SCCHT predicts an apparent Arrhenius temperature dependence in the glass, while the SCNLE result is modestly supra-Arrhenius. Experimental tests of the SCCHT results over a wider temperature regime are highly desirable.

Finally, Figure 12 presents the corresponding ratio of the penetrant to matrix hopping times (main panel) and dynamical coupling parameters (inset) for the systems studied in Fig. 11. The former ratio varies in a strongly non-Arrhenius manner above the matrix T_g and in a nearly Arrhenius manner below it. Over all the temperatures and systems studied, the time scale ratio changes by 16 orders of magnitude. Weaker penetrant-matrix dynamic coupling (indicated by a smaller value of $\tau_{hop,p}/\tau_{hop,m}$) is found at lower temperatures and also for smaller size ratios which vary in the order of water < oxygen < methanol < toluene. The dynamical coupling parameter exhibits a rich behavior, reflecting the competing caging and physical bonding effects. For toluene, where only caging is present (since $\varepsilon = 0$, see Table I), γ slightly increases upon cooling. But for the other three penetrants which do attract the PVAC Kuhn segment, γ varies non-monotonically with temperature. This behavior likely reflects that with decreasing (increasing) temperature ($\varepsilon/k_B T$), the physical bonding effect becomes more important relative to the steric caging effect. This suggestion is supported by our results in Figs. 8 and 9, which show that γ decreases as $\varepsilon/k_B T$ becomes larger if all other parameters are fixed.

VIII. SUMMARY AND DISCUSSION

We have re-formulated our prior force-level SCNLE theory²⁵ of dilute penetrant activated diffusion in dense liquids and glasses, which was based on treating matrix dynamical fluctuations per an average “external dynamic field.” The new, more advanced SCCHT explicitly and self-consistently accounts for coupling between penetrant hopping and matrix

dynamical displacements that facilitate the activated event. The key new ideas are two mechanistically (at a trajectory level) coupled dynamic free energy functions for the matrix and penetrant, a single dynamic coupling parameter that quantifies how much the matrix displaces relative to the penetrant when the latter reaches its transition state, and the enforcement of a temporal causality or coincidence condition. Besides containing more physics, the SCCHT involves no unknown parameters and exactly reduces to the one-component liquid ECNLE theory of activated relaxation^{27,28} in the limit the penetrant and matrix becomes identical.

The SCCHT approach was implemented for the foundational model of a dilute penetrant smaller than the matrix particles, with or without penetrant-matrix attractive forces. Model calculations reveal a rich dependence of the penetrant diffusion constant and degree of matrix-penetrant dynamic coupling as a function of size ratio, volume fraction, and attraction strength. For all situations, the correlated motion included in the SCCHT results in a faster diffusivity compared to the SCNLE theory, consistent with our physical intuition. Since the differences between the two theories depend on all the system variables, qualitative trends can also change. For example, the SCCHT predicts a near exponential decrease of penetrant diffusivity with size ratio over an intermediate range, in contrast to the much steeper, non-exponential variation previously obtained from the SCNLE. For sticky penetrants, the relative and absolute influence of steric caging versus physical bond formation was studied, and a rich behavior was predicted, including the possible speeding up of transport at very high attraction strengths. The conditions for a dynamic crossover from a time scale separation between the penetrant and matrix activated hopping to a “slaved” or “constraint release” regime were determined.

The sphere mixture model can be mapped to treat experimental thermal systems composed of penetrants in atomic, molecular, and polymer liquids and glasses. Application of SCCHT to water, toluene, methanol, and oxygen diffusion in PVAC liquids and glasses was performed. Encouragingly, the new theory agrees with the experiment better than the prior SCNLE approach and with values of the penetrant-matrix size ratio much closer to their chemically intuitive values. Testable predictions were made for these systems in the rubbery, deeply supercooled, and glass states. Extension of the theory to treat penetrant diffusion in systems of interest in the oil and gas industry, such as gas diffusion in semicrystalline polyethylenes of variable degrees of side chain branching and crystalline fraction,⁴⁷ is in progress.

The theoretical frontier is now to extend the SCCHT ideas to treat penetrant-matrix mixtures of arbitrary composition under diverse thermodynamic state conditions. This is a rich problem in the thermal liquid and colloidal suspension areas. Adding penetrants can speed up (plasticize) or slow down (anti-plasticize) dynamics. Moreover, they will modify the dynamic shear and Young's moduli, which can be determined using our force-level theoretical tools. Efforts in these directions are ongoing. In the longer run, extension of the approach to treat transport in ionic systems and membrane-based phenomena seems possible.

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- ¹J. S. Vrentas and C. M. Vrentas, *Diffusion and Mass Transfer* (CRC Press, Boca Raton, 2013).
- ²S. C. George and S. Thomas, *Prog. Polym. Sci.* **26**, 985 (2001).
- ³J. Guan, B. Wang, and S. Granick, *ACS Nano* **8**, 3331 (2014).
- ⁴M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, *J. Chem. Phys.* **102**, 471 (1995).
- ⁵K. Paeng, H. Park, D. T. Hoang, and L. J. Kaufman, *Proc. Natl. Acad. Sci. U. S. A.* **112**, 4952 (2015).
- ⁶D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul, and B. D. Freeman, *Polymer* **54**, 4729 (2013).
- ⁷G. M. Geise, H.-S. Lee, D. J. Miller, B. D. Freeman, J. E. McGrath, and D. R. Paul, *J. Polym. Sci., Part B: Polym. Phys.* **48**, 1685 (2010).
- ⁸B. J. Blaiszik, S. L. B. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White, *Annu. Rev. Mater. Res.* **40**, 179 (2010).
- ⁹C. E. Diesendruck, N. R. Sottos, J. S. Moore, and S. R. White, *Angew. Chem., Int. Ed.* **54**, 10428 (2015).
- ¹⁰J. F. Patrick, M. J. Robb, N. R. Sottos, J. S. Moore, and S. R. White, *Nature* **540**, 363 (2016).
- ¹¹G. M. Geise, D. R. Paul, and B. D. Freeman, *Prog. Polym. Sci.* **39**, 1 (2014).
- ¹²J. N. Ryan and M. Elimelech, *Colloids Surf., A* **107**, 1 (1996).
- ¹³P. R. Johnson, N. Sun, and M. Elimelech, *Environ. Sci. Technol.* **30**, 3284 (1996).
- ¹⁴E. Zaccarelli, *J. Phys.: Condens. Matter* **19**, 323101 (2007).
- ¹⁵E. Zaccarelli and W. C. K. Poon, *Proc. Natl. Acad. Sci. U. S. A.* **106**, 15203 (2009).
- ¹⁶C. R. Wilke and P. Chang, *AIChE J.* **1**, 264 (1955).
- ¹⁷J. C. Bosma and J. A. Wesselingh, *Chem. Eng. Res. Des.* **77**, 325 (1999).
- ¹⁸S. Bhattacharyya and B. Bagchi, *J. Chem. Phys.* **106**, 1757 (1997).
- ¹⁹J. Budzien, J. D. McCoy, D. Rottach, and J. G. Curro, *Polymer* **45**, 3923 (2004).
- ²⁰D. N. Theodorou, “Principles of molecular simulation of gas transport in polymers,” in *Materials Science of Membranes for Gas and Vapor Separation*, edited by Yu. Yampolskii, I. Pinnau, and B. D. Freeman (Wiley, Hoboken, NJ, 2006), pp. 49–94.
- ²¹L. Xi, M. Shah, and B. L. Trout, *J. Phys. Chem. B* **117**, 3634 (2013).
- ²²J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Part B: Polym. Phys.* **15**, 403 (1977).
- ²³J. S. Vrentas and J. L. Duda, *J. Polym. Sci., Part B: Polym. Phys.* **15**, 417 (1977).
- ²⁴N. Ramesh, P. K. Davis, J. M. Zielinski, R. P. Danner, and J. L. Duda, *J. Polym. Sci., Part B: Polym. Phys.* **49**, 1629 (2011).
- ²⁵R. Zhang and K. S. Schweizer, *J. Chem. Phys.* **143**, 144906 (2015).
- ²⁶R. Zhang and K. S. Schweizer, *Macromolecules* **49**, 5727 (2016).
- ²⁷S. Mirigian and K. S. Schweizer, *J. Phys. Chem. Lett.* **4**, 3648 (2013).
- ²⁸S. Mirigian and K. S. Schweizer, *J. Chem. Phys.* **140**, 194506 (2014).
- ²⁹D. Emin, *Polarons* (Cambridge University Press, Cambridge, 2013).
- ³⁰T. R. Kirkpatrick and P. G. Wolynes, *Phys. Rev. A* **35**, 3072 (1987).
- ³¹J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986).
- ³²K. S. Schweizer and E. J. Saltzman, *J. Chem. Phys.* **119**, 1181 (2003).
- ³³K. S. Schweizer, *J. Chem. Phys.* **123**, 244501 (2005); K. S. Schweizer and G. Yatsenko, *ibid.* **127**, 164505 (2007).
- ³⁴R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, Oxford, 2001).
- ³⁵V. N. Novikov, K. S. Schweizer, and A. P. Sokolov, *J. Chem. Phys.* **138**, 164508 (2013).
- ³⁶J. Colmenero, F. Alvarez, Y. Khairy, and A. Arbe, *J. Chem. Phys.* **139**, 044906 (2013).
- ³⁷D. C. Viehman and K. S. Schweizer, *J. Chem. Phys.* **128**, 084509 (2008).
- ³⁸D. C. Viehman and K. S. Schweizer, *Phys. Rev. E* **78**, 051404 (2008).

- ³⁹D. M. Sussman and K. S. Schweizer, *J. Chem. Phys.* **134**, 064516 (2011).
- ⁴⁰D. Chandler and J. P. Garrahan, *Annu. Rev. Phys. Chem.* **61**, 191 (2010).
- ⁴¹S. Mirigian and K. S. Schweizer, *J. Chem. Phys.* **140**, 194507 (2014).
- ⁴²S. Mirigian and K. S. Schweizer, *Macromolecules* **48**, 1901 (2015).
- ⁴³G. L. Hunter and E. R. Weeks, *Rep. Prog. Phys.* **75**, 066501 (2012).
- ⁴⁴D. Meng and S. K. Kumar, "Simulation of spherical penetrant diffusion in bead-spring polymer model glasses" (unpublished).
- ⁴⁵S.-J. Xie and K. S. Schweizer, *Macromolecules* **49**, 9655 (2016).
- ⁴⁶R. P. Danner, *Fluid Phase Equilib.* **362**, 19 (2014).
- ⁴⁷B. Flaconnèche, J. Martin, and M. H. Klopffer, *Oil Gas Sci. Technol.* **56**, 261 (2001).