Entropic barriers, activated hopping, and the glass transition in colloidal suspensions

Kenneth S. Schweizer and Erica J. Saltzman
Departments of Materials Science & Engineering and Chemistry, Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 5 February 2003; accepted 2 April 2003)

A microscopic kinetic description of single-particle transient localization and activated transport in glassy fluids is developed which combines elements of idealized mode-coupling theory, density functional theory, and activated rate theory. Thermal fluctuations are included via a random force which destroys the idealized glass transition and restores ergodicity through activated barrier hopping. The approach is predictive, containing no adjustable parameters or postulated underlying dynamic or thermodynamic divergences. Detailed application to hard-sphere colloidal suspensions reveals good agreement with experiment for the location of the kinetic glass transition volume fraction, the dynamic incoherent scattering relaxation time, apparent localization length, and length scale of maximum nongaussian behavior. Multiple connections are predicted between thermodynamics, short-time dynamics in the nearly localized state, and long-time relaxation by entropic barrier crossing. A critical comparison of the fluid volume fraction dependence of the hopping time with fit formulas which contain ideal divergences has been performed. Application of the derivative Stickel analysis suggests that the fit functions do not provide an accurate description over a wide range of volume fractions. Generalization to treat the kinetic vitrification of more complex colloidal and nanoparticle suspensions, and thermal glass-forming liquids, is possible.


I. INTRODUCTION

Slow dynamics of glass-forming materials is of major scientific and technological importance and has recently been the subject of intense study.1 There are many different theoretical approaches, the validity of which remain strongly debated. The relative importance of thermodynamics (including possible underlying phase transitions) versus kinetics in determining laboratory vitrification is particularly unclear.1,2 The microscopic “idealized” mode-coupling theory (IMCT) of Gotze and co-workers3–6 is a purely kinetic approach which focuses on the self-consistent description of local dynamics due to particle caging. Nonlinear and non-Markovian coupling of collective density fluctuations is proposed as the essential physical process which is treated using projection operator and factorization approximations. A primary result is the prediction of an “ideal” nonergodicity or glass transition. IMCT makes an impressive number of predictions for transport coefficients and wave-vector-dependent collective and single-particle dynamic density fluctuations. These include the bifurcation of correlators into (fast) beta and slow alpha relaxations, critical-like power-law decays at intermediate times, long-time stretched exponential relaxation, anomalous self-diffusion, and critical power-law divergences of all relaxation times.3–5 IMCT is unique in being formulated at the microscopic level of forces. Most explicit IMCT results have been obtained for fluids composed of spherical particles. Recently, extensions to simple molecular models such as diatomics and ellipsoids7,8 and short-chain flexible polymers9 have been performed.

So-called “schematic” formulations of IMCT have been widely applied to interpret experimental measurements on thermal glass-forming molecular, ionic, and polymeric liquids.3,4 A major problem is that the predicted critical power-law divergence of the alpha relaxation time is not observed and is generally agreed to be an unphysical consequence of the inherent approximations of IMCT. Based on fitting two or three parameters, IMCT typically describes (over an intermediate-temperature range) two or three orders of magnitude variation of the alpha relaxation time and fails for thermal glass formers far above the laboratory transition.1,10 Analysis of Potts spin-glass models,11–13 experiments1 and computer simulations,14–18 all suggest that IMCT accurately describes dynamical precursor phenomena in moderately supercooled liquids, but does not account for (free) energy landscapes, barriers, or activated transport. The basic reason for the latter limitations appears to be that IMCT is of a dynamic mean-field (infinite-dimensional) nature, with effective barrier heights that scale with system size and hence are insurmountable in the thermodynamic limit.11,13 The latter aspect is consistent with connections derived between IMCT and static density functional theory.12 In reality, particles reach local minima in an energy landscape in a finite time and long-time motion is controlled by activated dynamics.13 This insight has motivated the development of phenomenological single-particle “trap models” which are fundamentally different than IMCT for the long-time alpha relaxation process.13,19

4Electronic mail: kschweiz@uiuc.edu
It is noteworthy that even above (but near) the apparent mode-coupling temperature $T_c$, computer simulations find evidence of a relatively sharp transition in single-particle transport from smooth, hydrodynamic-type motion to a dynamics characterized by vibration about fixed positions coupled with local activated hopping or jump diffusion events.\textsuperscript{15–18} Failure of the Stokes–Einstein relation, or “translation–rotational decoupling,”\textsuperscript{1,2} is not predicted by IMCT and is often experimentally found to begin close to the estimated IMCT transition. This decoupling effect has been suggested to be correlated with the emergence of activated hopping as the primary mode of transport.\textsuperscript{17,18} Attempts to include activated transport within MCT have mainly involved low-order coupling of density fluctuations to current modes (phonons),\textsuperscript{3,4} which destroys the IMCT nonergodicity transition. This approach is largely phenomenological and nonpredictive. It is important to note that a number of IMCT results (especially in the fast $\beta$ relaxation regime) remain valid even in the presence of hopping processes.

Incorporation of the activated hopping physics within a predictive approach formulated at the level of forces remains a critical unsolved problem. An interesting dynamic density functional theory has been proposed\textsuperscript{20} in an attempt to include activated processes. This approach is numerically complex even for simple fluids, and results are rather limited. Alternative mesoscopic attempts to go beyond IMCT built on concepts from spin-glass theory\textsuperscript{11} appear to have made progress in understanding some aspects of the low-temperature activated regime.\textsuperscript{12} The essential physics is tied to an underlying “random first-order” thermodynamic phase transition\textsuperscript{11} and “entropy catastrophe,” the existence and/or relevance of which is the subject of vigorous debate.\textsuperscript{2,15,21}

The goal of the present work is to propose a theory of slow single-particle dynamics formulated at the level of forces. It is a kinetic approach which combines, and in some aspects extends, elementary ideas of mode-coupling, density functional, and activated rate theory. We are motivated by the desire\textsuperscript{2} to build a bridge between landscape and MCT approaches at the simplest technical level. The theory does not account for the rich consequences of nonlinear and non-Markovian coupling of dynamic density fluctuations described by the full IMCT in the dynamic precursor regime. Rather, building on the “naïve” single-particle version of mode-coupling theory,\textsuperscript{22} a simpler approach is adopted since our primary goal is to go beyond IMCT in the sense of describing free-energy barriers and activated hopping.

Our basic ideas are general and will likely be of most value for thermal glass-forming materials. But for a variety of reasons, we first develop and apply the theory for model hard-sphere colloidal suspensions. Besides their molecular simplicity, the microscopic structural information required as input to the dynamical theory is readily available for hard spheres, and coarse graining of molecular complexities can be avoided. The hard-sphere suspension is also the system for which IMCT has been most successful.\textsuperscript{3–5} IMCT predicts a literal nonergodicity glass transition at a packing fraction of $\phi_{\text{MCT}}\sim 0.52$, which is well below the kinetic experimental value\textsuperscript{23–25} of $\phi_s \sim 0.57–0.58$, which is well below classic random close packing $\phi_{\text{RCP}} \sim 0.64$ or other estimates\textsuperscript{26} of a maximum jamming volume fraction $\phi_{\text{MAX}}$. By empirical rescaling (fitting) of $\phi_{\text{MCT}}$, IMCT agrees nearly quantitatively with a number of dynamic light scattering measurements on hard-sphere suspensions\textsuperscript{3,5,23,24} and also computer simulations for related model fluids which probe the dynamical precursor regime.\textsuperscript{15,16}

A popular argument for the success of IMCT for hard-sphere suspensions is that since colloidal momentum is not conserved, phononlike excitations are absent (strongly overdamped), which renders activated processes irrelevant.\textsuperscript{3,4,23,27} However, intrinsic entropic barriers of a suitably defined free-energy surface must be present. Indeed, dissipative Brownian dynamics simulations have shown that activated hopping motions are present and may be the primary mechanism of the $\alpha$ relaxation even above the apparent IMCT ideal glass transition.\textsuperscript{17} There are quantitative differences in the slow relaxation based on Newtonian and Brownian dynamics, the latter being slower by roughly an order of magnitude.\textsuperscript{16} But the qualitative aspects of the activated hopping processes are the same despite the lack of any collective “phonon assistance.”\textsuperscript{15–17} This strongly suggests that the long-time processes that destroy the IMCT transition are, to a first approximation, independent of the nature of the microscopic dynamics.\textsuperscript{15–17} Brownian dynamics simulations\textsuperscript{17} find that the rather sharp crossover in transport mechanism does not result in any abrupt changes in the intermediate dynamic scattering function, and transient plateaus on the particle-size length scale only clearly emerge below the apparent mode-coupling transition temperature.\textsuperscript{15,17} These observations again suggest the importance of activated hopping processes. Experimentally, transient nonergodicity in hard-sphere suspensions as indicated by well formed plateaus in the collective dynamic structure factor only becomes clearly observable\textsuperscript{23} above $\phi_0 \sim 0.55–0.56$.

From a practical perspective, the experimental study of an activated dynamics regime in colloidal suspensions is severely hindered (relative to thermal glass formers) due to the slow elementary diffusive time scale for Brownian particles. Typically only a factor of $10^3–10^4$ in time is accessible between the freezing and kinetic vitrification volume fractions,\textsuperscript{23–25} thereby restricting experiments to a dynamic precursor regime. The latter is also true of computer simulations, which typically probe $\sim 3$ orders of magnitude of dynamical slowing down.\textsuperscript{15,16} Hence, the existence of a divergent relaxation time can only be inferred via a large extrapolation. The reliability of the latter seems especially uncertain given recent light scattering,\textsuperscript{20} confocal microscopy,\textsuperscript{28–31} and microgravity experiments\textsuperscript{32} using model hard spheres of various sizes and chemical constitutions. All these studies find significant motion exists for $\phi > \phi_s$, which may persist\textsuperscript{32} up to $\phi_{\text{MAX}}$. Whether this motion corresponds to small-scale “aging” phenomena in a globally frozen solid or ultralow structural relaxation and flow is not well understood. Possible long-time diffusion in the “glass” due to activated processes has been suggested.\textsuperscript{23,27–31}

The remainder of the paper is structured as follows: The basic theoretical ideas are developed in Sec. II. Section III presents numerical results for an “effective free energy”
function and characteristic time, energy, and length scales. Comparisons between various features of this free-energy function and dynamic experiments are presented. Activated barrier hopping is the subject of Sec. IV, and quantitative comparisons with incoherent dynamic light scattering measurements are given. Section V presents detailed comparisons of the relaxation time results with various fit functions, all of which invoke a divergence. A summary and discussion is given in Sec. VI.

II. THEORY

We adopt a single-particle dynamical description, partially motivated by the seminal efforts of Wolynes and co-workers\textsuperscript{22,23,33} to connect “naive” IMCT and density functional theory (DFT). We are also motivated by the desire to quantify, and provide a more fundamental basis for, phenomenological “‘trap models.’”\textsuperscript{19} The latter aim to describe single-particle motion in a cage via a static random potential. Although the restriction to single-particle dynamics carries obvious limitations, it is important to note that many colloid experiments\textsuperscript{23,24} and simulations\textsuperscript{15–18} have found a close correlation between local single-particle and collective cage slow dynamics.

A. Naive idealized MCT

The “naive” IMCT (Ref. 22) focuses on calculation of the force–force time correlation, or memory, function:

\[
K(t) = \langle \hat{F}(0) \cdot \hat{F}(t) \rangle = \frac{1}{3} \beta^{-2} \int \frac{d\mathbf{q}}{(2\pi)^3} q^2 C^2(q) \rho S(q) \Gamma_c(q,t) \Gamma_c(q,t).
\]

(1)

\(\hat{F}(t)\) is the total force exerted on a tagged particle by the surrounding fluid at time \(t\), and \(\beta\) is the inverse thermal energy. The second line is a Fourier decomposition which follows from the MCT approximation of projecting forces onto a bilinear product of single-particle and collective density variables, coupled with factorization of four-point correlations into products of pair correlations.\textsuperscript{3,34} The MCT approximations are not correct at early times, but are intended to capture the slow dynamics associated with many particle caging. \(C(q)\) is the direct correlation function, \(S(q)\) the dimensionless collective structure factor, and \(\rho\) the fluid number density.\textsuperscript{34} The product \(q^2 \rho C(q)\) is an effective mean-square force exerted by the surrounding liquid on a tagged particle. The “propagator” \(\Gamma_c(q,t)\) \(= \Gamma_c(q,t)\) is the \(t = 0\) normalized single-particle [collective] dynamic structure factor which decays to zero at long times in the fluid phase.

The propagators do not decay to zero at long times in a glass. The localized state enters Eq. (1) via Debye–Waller factors describing arrested single-particle and collective density fluctuations. Adopting a harmonic model of the amorphous solid state yields\textsuperscript{22}

\[
\Gamma_c(q,t \to \infty) = e^{-q^2/4\alpha},
\]

corresponding to a real-space Einstein oscillator description of the single-particle density:

\[
\rho(\mathbf{r}) = \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha \rho^2}.
\]

The variable \(r\) is the particle displacement from a randomly located position. The Gaussian form is consistent with experiments on colloids,\textsuperscript{24} simulations,\textsuperscript{15–18} and IMCT.\textsuperscript{3–6} The parameter \(\alpha\) is the local order parameter related to a mean-square displacement, or localization length, as

\[
r_\text{LOC}^2 = 3/2\alpha.
\]

(4)

In the naive IMCT analysis\textsuperscript{22} a “Vineyard” approximation\textsuperscript{34} was invoked corresponding to replacing the collective density fluctuation propagator by its single-particle analog. As emphasized by the original workers,\textsuperscript{22} this simplification is rigorously valid for very high wave vectors, but not for dynamic fluctuations on the length scale of the cage or smaller wave vectors.\textsuperscript{34} Use of the Vineyard approximation in Eq. (1) corresponds to neglecting vertex corrections and certain collective dynamical effects present in the full IMCT.\textsuperscript{22} In the hypothetical infinite-dimensional limit, the vertex corrections have been shown\textsuperscript{22} to vanish and naive IMCT is equivalent to IMCT.

We suggest a modest improvement of naive MCT concerning the Vineyard approximation motivated by the fact that on the cage length scale, single-particle dynamics, collective density fluctuations, and stress relaxation are dynamically strongly coupled.\textsuperscript{3,24} However, static collective correlations are always present which we propose to approximately account for in a mean-field fashion as

\[
\Gamma_c(q,t \to \infty) = e^{-q^2/4\alpha},
\]

(5)

This form is motivated by the presence in MCT, and the exact short-time analysis of \(S(q,t)\), of the classic de Gennes narrowing effect which correlates the relaxation rate of density fluctuations of wave vector \(q\) with the inverse of the structure factor.\textsuperscript{3,34,35} For example, in the overdamped Brownian limit at short times, \(\Gamma_c(q,t) = e^{-q^2/6\zeta_S(q)}\), where \(\zeta_S\) is a short-time friction constant.\textsuperscript{35} Within the context of MCT, \(\Gamma_c(q,t \to \infty)\) is the collective “nonergodicity parameter.” Based on both experiment\textsuperscript{23} and many Brownian and Newtonian computer simulations,\textsuperscript{15–18} it is known the wave vector dependence is of a damped oscillatory form which is in phase with the static structure factor. Hence, the adoption of Eq. (5) is expected to result in a quantitatively more realistic description than prior work.\textsuperscript{22} It also correctly suppresses the small wave vector contributions in the integrand of Eq. (1) which are not important at high volume fractions.

The long-time mean-square displacement obeys the self-consistent relation\textsuperscript{22}

\[
\alpha = \frac{1}{2} \beta^2 K(t \to \infty) = \frac{1}{6} \int \frac{d\mathbf{q}}{(2\pi)^3} \rho q^2 C^2(q) S(q) \exp\left(-\frac{q^2}{4\alpha} \left[1 + S^{-1}(q)\right]\right).
\]

(6)

At sufficiently low volume fractions \(\phi = \pi \rho a^3/6\), only the \(\alpha = 0\) fluid solution exists. Based on Percus–Yevick (PY) theory\textsuperscript{34} for the static correlations, Eq. (6) predicts a localization transition at \(\phi_{\text{MCT}} = 0.432\), lower than the full IMCT result\textsuperscript{5} of \(\phi_{\text{MCT}} \approx 0.515\). The localization length is \(r_{\text{LOC}}\).
\[ r_{\text{LOC}} = 0.19 \sigma, \text{ comparable to the classic Lindemann length}^{34} \text{ and in excellent agreement with the full IMCT result}^{5} \text{ of } r_{\text{LOC}} = 0.183 \sigma. \]

If the \( 1/S(k) \) correction in Eq. (5) is ignored, we find \( \phi_{\text{MCT}} = 0.464 \) and \( r_{\text{LOC}} = 0.204 \sigma \). All our results are quantitatively, but not qualitatively, dependent on whether the \( 1/S(k) \) correction is included in Eq. (5). Since we believe there is a good theoretical reason for including it, we shall do so in all the numerical results and figures presented below. Selected results based on ignoring this correction are presented to illustrate the quantitative sensitivities.

### B. Beyond idealized mode-coupling theory

We adopt the common interpretation that the IMCT non-ergodicity transition signals the emergence of finite barriers in a free-energy landscape and strong transient localization and reequilibration in a cage which requires activated dynamics to escape.\(^{11-15}\) To proceed we seek a stochastic equation of motion (EOM) for the single-particle dynamic scalar order parameter \( r(t) \) or \( \alpha(t) = 3/2 r^2(q) \). The purpose of this EOM is restricted to describing the localization process and escape over a barrier, in the spirit of the Langevin approach to chemical reactions,\(^{36,37}\) and some applications of the so-called model B for the slow dynamics of a nonconserved order parameter.\(^{38}\)

The explicit construction of the EOM is guided by three considerations: (i) For Brownian colloids, short-time motion is overdamped Fickian diffusion. (ii) In the absence of thermal fluctuations or noise, IMCT is assumed to correctly predict the tendency to localize in a cage. Hence, in the deterministic limit the EOM description should recover the naive IMCT localization condition. This idea guides construction of an effective force \(-\partial F/\partial r\), which at high density favors localization. We shall refer to \( F \) as an “effective free-energy” function, although it does not have a rigorous equilibrium meaning. (iii) Ergodicity-restoring thermal fluctuations are included which destroy the naive IMCT glass transition and allow for activated hopping when \( \phi > \phi_{\text{MCT}} \).

To address points (i) and (ii) we adopt a scalar, deterministic (no noise or random forces), nonlinear, and Markovian EOM for the order parameter:

\[
\frac{d}{dt} r = -\mu \frac{\partial}{\partial r} F, \tag{7}
\]

with the initial condition \( r(t=0) = 0 \). Here, \( \mu \) is a mobility coefficient that describes short-time frictional processes and sets the time scale for a coarse-grained description of particle trapping and escape dynamics. The form of Eq. (7) corresponds to assuming that the rate of change of particle displacement is linearly proportional to a driving force. It is the simplest dynamical model that reduces at “equilibrium” (long-time steady-state limit, \( dr/dt \to 0 \)) to the condition of vanishing effective force in the spirit of a steepest-descent trajectory. Equation (7) can also be written as a simple force balance

\[
-\zeta_r \frac{d}{dt} r - \frac{\partial}{\partial r} F = 0. \tag{8}
\]

This emphasizes its Brownian character and the description of short-time motion by a dissipative drag term or corresponding short-time diffusion constant \( D_r = k_B T / \zeta_r \). In colloidal suspensions\(^{35,39,40}\) \( \zeta_r = \zeta_0 G \), where the single-particle Stokes–Einstein \( \zeta_0 = 3 \pi \sigma \eta_0 \) with solvent viscosity \( \eta_0 \) and factor \( G > 1 \) is discussed in Sec. IV.

The effective free-energy function should describe the difference between localized (nonzero \( \alpha \)) and delocalized (\( \alpha = 0 \)) states in the spirit of DFT.\(^{32,33,38}\) This motivates the following explicit form for \( F \) (in units of thermal energy):

\[
F(\alpha) = \frac{3}{2} \ln(\alpha) - \int \frac{d\mathbf{q}}{(2\pi)^3} \rho C^2(q) S(q) \left[ 1 + S^{-1}(q) \right]^{-1} \times \exp \left[ -\frac{q^2}{4 \alpha} \left[ 1 + S^{-1}(q) \right] \right] = F_0 + F_I, \tag{9}
\]

where irrelevant additive constants have been omitted. The first “ideal” term favors the fluid state and is identical to what is employed in DFT for a harmonic solid.\(^{32,38}\) Since our interest is restricted to motions on the particle size and smaller scale, the strong localization form of \( F_0 \) is a reasonable approximation. The second “interaction” contribution corresponds to an entropic trapping potential favoring localization. Minimization of Eq. (9) with respect to the order parameter, or solution of Eq. (8), yields the naive IMCT localization condition of Eq. (6). This is the physically motivated constraint which guided construction of Eq. (9). For \( \phi > \phi_{\text{MCT}} \), a barrier and local minimum appear in \( F(r) \).

We emphasize that Eq. (9) is not an equilibrium or extensive free-energy functional as employed in the thermodynamic DFT of the glass transition\(^{32,33}\) and recent dynamic DFT.\(^{19}\) These approaches adopt a conventional equilibrium form for the interaction free energy. The thermodynamic theory\(^{22,33}\) predicts a fluid–glass phase transition and implicitly corresponds to effective free-energy barriers of macroscopic magnitude.\(^{13,22}\) In reality, a “mosaic” structure is believed to emerge below the IMCT transition corresponding to finite clusters of particles existing as local minimum free-energy configurations which are separated by finite barriers.\(^{11-13}\) Our approach adopts a simple single-particle description of intensive free-energy barriers.\(^{41}\)

In general, white noise (thermal fluctuations) due to rapid processes and, possibly, inertial effects (particle mass \( M \)) are important [point (iii)]. These are accounted for by a standard fluctuating random force resulting in an EOM of the Langevin form:\(^{36,37}\)

\[
-\zeta_r \frac{d}{dt} r - \frac{\partial}{\partial r} F + \delta f = M \frac{d^2}{dt^2} r, \tag{10}
\]

\[
\left\{ \delta f(0) \delta f(t) \right\} = 6 \beta^{-1} \zeta_r \delta(t). \]

The fluctuating force is statistically uncorrelated with the tagged particle position and velocity. Equations (9) and (10) define the EOM description and are reminiscent of Kramers’ approach\(^{36}\) for chemical reactions and activated processes. However, \( F(r) \) is not an equilibrium potential-of-mean force, but rather is “self-generated” via collective liquid structure. The Markovian form implies that a literal solution
of Eq. (10) does not automatically recover the long-time diffusion constant since the forces which define the cage constraints in $F(r)$ ultimately transform to an additional viscous friction. Description of the latter process requires a self-consistent, non-Markovian formulation which is beyond the scope of this initial study. This problem is the analog of constructing a time-dependent random potential in the phenomenological trap models.$^{13,19}$

C. Limiting behaviors and diffusion length

At early times or small displacements the interaction contribution in Eq. (9) is irrelevant, and solving Eq. (10) correctly yields Fickian diffusion in the overdamped limit of interest. This follows explicitly from Eq. (9) by noting that for small displacements (large $\alpha$) the ideal contribution to the effective force is dominant since

$$\frac{\partial F_0}{\partial r} = -3\dot{r}, \quad \frac{\partial F_I}{\partial r} \approx r.$$  \hspace{1cm} (11)

Equation (10) then simplifies to

$$\zeta_s \frac{d}{dt} r = -r + \delta f,$$  \hspace{1cm} (12)

the solution of which is $\langle r^2(t) \rangle = 6\zeta_s t$.

A “diffusion length” $R_D$, is defined as the displacement beyond which Fickian motion applies. Without explicitly solving the EOM, the latter displacement is not unambiguously defined. We consider two ideas, which are shown below to result in nearly identical results. One natural condition is irrelevance of the interaction component of the effective force, which is equivalent to

$$-\frac{r}{3} \frac{\partial}{\partial r} F \rightarrow 1, \quad \text{at } r \rightarrow R_D.$$  \hspace{1cm} (13a)

This condition is attained at “large enough” displacements since the interaction force $\partial F_I/\partial r \rightarrow 0$ exponentially fast at a displacement $\sim \sigma$. Equation (13a) is precisely quantified by requiring the ratio $T = |\partial F_I/\partial r|/|\partial F_0/\partial r| \leq 0.01$. Calculated displacements are weakly sensitive to the chosen tolerance; for example, if a threshold of $T \leq 0.001$ is used, we find that $R_D$ changes by only $\sim 5\%$–$20\%$ over a wide range of volume fractions.

As a second estimate, we consider the displacement where the “rate of change of the work,” $|(d/dr)(r dF/dr)|$, has decayed to a fraction $Q$ of its maximum value:

$$\left| \frac{d}{dr} \frac{dF}{dr} \right| = Q \left| \frac{d}{dr} \frac{dF}{dr} \right|_{\text{MAX}}.$$  \hspace{1cm} (13b)

As true for calculations based on Eq. (13a), we find that reduction of the tolerance from $Q = 0.01$ to 0.001 results in only $\sim 15\%$–$20\%$ changes in $R_D$, regardless of whether the total free energy or just its interaction part is employed in Eq. (13b).

III. EFFECTIVE FREE ENERGY

Examples of the effective free-energy function based on PY static input are shown in Fig. 1. There are three basic forms:42 (a) At relatively low packing fractions and/or small displacements, $F(r)$ decays monotonically with particle dis-

![FIG. 1. Effective “free energy” (units of thermal energy) as a function of dimensionless displacement for (from top to bottom) $\phi=0.3$, 0.432, 0.50, 0.57, and 0.6. Five characteristic lengths, the barrier height, and four regimes of dynamical behavior (1)–(4) are defined in the inset for the case of $\phi=0.55$.](image-url)
non-Gaussian process. We expect that the strongest deviation from a diffusive or Gaussian process will be correlated with the location of the maximum restoring force defined to occur at \( R^* \). Another length scale of possible interest is the displacement of maximum work, \( R_{\text{mw}} \), defined by maximizing the product \( r_d F(r_d) \).

(4) Activated hopping over an entropic barrier of magnitude \( F_B \) located at the “transition state” displacement \( r_B \). The characteristic hopping time \( \tau \) is influenced by the local friction constant, barrier height, and attempt frequency and driving force for barrier crossing via the well and barrier harmonic (positive) curvature constants \( K_0 \) and \( -K_B \), respectively. The elastic or spring constants enter the determination of the “attempt frequency” \( \omega_0 \) and the dynamical driving force near the top of the barrier via \( \omega_B = \sqrt{(-K_B/M)} \). A hopping diffusion constant follows from dimensional analysis:

\[
\begin{align*}
D_{\text{HO}} &= \frac{L_D^2}{6\tau}, \\
L_D &= R_D - r_{\text{LOC}},
\end{align*}
\]

where a mean “jump length” \( L_D \) is estimated as the difference between the displacement beyond which no interaction effects are present [computed from Eq. (13)] and \( r_{\text{LOC}} \).

Throughout Secs. III–V, the discussion of numerical results and figures is based on calculations employing the de Gennes narrowing factor in Eq. (5) unless explicitly stated otherwise.

A. Characteristic length scales

Figure 2 shows the five characteristic length scales (in units of the particle diameter) as a function of colloid volume fraction. The solid curves include the \( 1/S(\mathbf{q}) \) correction in Eq. (5). The location of the minimum of \( F(r) \) decreases strongly with packing fraction and is well described by an exponential law \( r_{\text{LOC}} \approx 30e^{-1.2\phi} \). The displacement of maximum restoring force decreases exponentially as \( R^* \approx 3.3e^{-0.6\phi} \), more weakly than the localization length. The displacement of maximum work also follows an exponential law \( R_{\text{mw}} \approx 0.92e^{-3.65\phi} \) and is larger, and more weakly varying, than \( R^* \). The barrier location (“transition state”) increases weakly with volume fraction and approaches \( \sigma/2 \) at large \( \phi \). The latter value is intuitively reasonable since it corresponds to a displacement distance which maximally disrupts the strong local cage order. The mean diffusive jump length is almost independent of volume fraction with \( L_D \approx 0.8\phi \), independent of which version of Eq. (13) is employed. Thus, the displacement beyond which Fickian diffusion applies is nearly constant and less than a particle diameter, as typically found in computer simulations. This value is also consistent with both our restricted interest in small-length-scale dynamics and the idea that Fickian diffusion commences once a particle escapes from its local cage.

Also shown in Fig. 2 as dashed curves are the corresponding results based on assuming the collective nonergodicity factor equals its incoherent single-particle analog, \( \Gamma_c(q) = \Gamma_s(q) \). Neglect of the de Gennes narrowing factor results in systematically larger values for all length scales, as might be expected given the larger value of \( \phi_M \). However, the qualitative behavior is identical. The modest quantitative differences depend on property and vary from \( \sim 3\% \) to \( 35\% \). Except for \( R_{\text{mw}} \), the differences decrease with increasing volume fraction.

B. Experimental measurements of length scales

Incoherent scattering experiments and confocal microscopy analyses of colloid trajectories have attempted to identify important lengths in the transient localization and early stage cage escape processes. We do not expect a quantitative correspondence between the lengths deduced from dynamic experiments and the characteristic length scales of \( F(r) \). However, it is of interest to explore possible qualitative or semiquantitative correlations.

The dynamic mean-square displacement (MSD) in several different model hard-sphere suspensions has been measured. The confocal microscopy experiments clearly find the apparent (transient) localization length is a decreasing function of volume fraction over the range \( \phi \approx 0.52 - 0.64 \). To be more specific, we first consider the experiments of Weeks and Weitz on solid (WW) on \( \sigma \approx 2.36 \mu m \) colloids. Perfectly horizontal (transient) plateaus in the MSD are never seen. Thus, we deduce a mean localization length as the displacement where the time dependence of the MSD passes through an inflection point as quantified by when the non-Fickian anomalous diffusion exponent attains a minimum. Experimental results are shown in Fig. 2 for two fluid states, and rather good agreement is found with the calculated \( r_{\text{LOC}} \). An important caveat is that the "hard
spheres” studied in Ref. 28 carry a small amount of charge. This feature modifies the equilibrium fluid–crystal transition and also introduces uncertainty in the precise determination of suspension volume fraction.

The WW experiments\textsuperscript{28} have also measured a “cage rearrangement time,” and corresponding displacement (“cage size”), deduced from the location of a maximum non-Gaussian parameter. Results are shown in Fig. 2 for two fluid samples, and surprisingly good agreement with the calculated $R^{*}$ is found. The experimental ratio $R^{*}/r_{\text{LOC}} \approx 1.8 \pm 0.2$, compared with the theoretical result of $2.3 \pm 0.2$. An alternative measure of “cage size” $r_{\text{cage}}$ has also been deduced from single-particle trajectories as the displacement beyond which a linear restoring force behavior fails.\textsuperscript{28} This length is shown in Fig. 2 for two fluid samples and is larger than $R^{*}$. Curiously, the experimental values of $r_{\text{cage}}$ are close to the calculated “displacement of maximum work,” $R_{\text{raw}}$, although a fundamental theoretical reason for this is not obvious.

The incoherent scattering measurements of van Megen and co-workers\textsuperscript{24} (VM) probe single-particle motion of a colloidal system very close to the hard-sphere model ($\sigma \approx 400$ nm). The time-dependent MSD was extracted. Since measurements of the non-Gaussian parameter were not reported, extraction of a localization length as described for the WW experiments\textsuperscript{28,29} cannot be done. However, at a glassy volume fraction of $\phi = 0.583$ the plateau in the MSD is sufficiently flat to allow a direct estimate. The result is shown in Fig. 2 and differs from the value of WW (Refs. 28 and 29) and the calculated $r_{\text{LOC}}$.

Another set of confocal microscopy experiments involves $\sigma \approx 900$ nm cross-linked microgel fluids.\textsuperscript{27,31} These model hard spheres do not undergo a fluid–crystal transition, and calibration of the absolute magnitude of $\phi$ is more uncertain. As in the WW study,\textsuperscript{28} a mean localization length and displacement of maximum non-Gaussian behavior can be determined (see Fig. 2). The localization length is roughly consistent with the VM experiments, while the experimental $R^{*}$ is significantly larger than measured by WW. The experimental ratio $R^{*}/r_{\text{LOC}} \approx 1.8$ in agreement with WW.

### C. Vibrational features

The “vibrational” features of $F(r)$ are summarized in the inset of Fig. 3. The harmonic well curvature (in units of $k_{B}T/\sigma^{2}$) increases rapidly with packing fraction and is well fit by an exponential law $K_{0} \sim 10^{-3} e^{25.3\phi}$. A strong correlation with the “localization length” is found. The product $K_{0}r_{\text{LOC}}^{2}$ is nearly constant, and roughly equal to 1.4. Calculations which ignore the de Gennes narrowing factor are shown as dashed curves. The elastic constant $K_{0}$ is smaller, by a factor of $\sim 1.2$–2 over the range $\phi = 0.52$–0.62, with deviations that decrease with volume fraction.

The harmonic well curvature also enters in the determination of a characteristic oscillation frequency $\omega_{0} = (K_{0}/M)^{1/2}$. For typical colloids such as polymethylmethacrylate or silica the density $\sim 1$–2 grams/cm$^{3}$, and at $\phi = 0.58$ a frequency in the range $\omega_{0} \sim 10^{3}$–$10^{4}$ Hz is predicted for diameters varying from 1 $\mu$m to 10 nm, respectively. For a sphere of diameter $\sim 1$ nm, a value relevant to small molecule glass formers, a frequency of $\omega_{0}/2\pi \sim 6 \times 10^{11}$ Hz $\sim 20$ cm$^{-1}$ is obtained. Interestingly, this value falls in the typical frequency range of the so-called boson peak observed in the glassy state of small-molecule systems\textsuperscript{43} such as orthoterphenyl and propylene. The possible significance of this result is enhanced by the observation\textsuperscript{44} for small-molecule organic glasses that the characteristic boson frequency scales as $M^{-1/2}$, as in our single-particle description.

The mean-square fluctuation about the minimum, $\langle u^{2} \rangle$, has been computed using standard Boltzmann statistics. Results are shown in Fig. 3 and are compared with the harmonic analog $\langle u^{2} \rangle_{0} = 3/K_{0}$. Harmonic behavior is well obeyed at very high $\phi$, but below $\phi \sim 0.61$–0.62 increasingly strong anharmonic effects are present resulting in larger fluctuations (“softer vibrations”). We find that the deviation is empirically well described by a critical power law

$$\langle u^{2} \rangle - \langle u^{2} \rangle_{0} = 225(0.64 - \phi)^{3.7}.$$\textsuperscript{27}

The trend of increasing anharmonicity as the glass transition is approached from the solid state has been observed in quasielastic neutron scattering experiments on thermal glasses.\textsuperscript{1} Large deviations from harmonic behavior emerge as a precursor of glass melting, which (surprisingly) appear to be closely related to long-time transport concepts such as kinetic fragility.\textsuperscript{1} We are not aware of such measurements being performed on hard-sphere colloidal suspensions.

The absolute magnitude of the barrier curvature is much smaller than its well analog (Fig. 3). It is also weakly dependent on volume fraction, changing by only a factor of $\sim 2$ over the entire range studied. Calculations which ignore the
de Gennes narrowing factor \([\Gamma_{sc}(q) = \Gamma_{s}(q)]\) are shown as the dashed curves, and again differences of only a factor of 2 or smaller are found.

Figure 4 shows calculations of a probability distribution of displacements based on Boltzmann statistics, \(P(r) \propto \exp[F(r_{\text{LOC}}) - F(r)]\), as a function of displacement. Normalization to the localization length \(r_{\text{LOC}}\) (well minimum) is adopted. Only displacements below the barrier location are of interest, and the curves in Fig. 4 are terminated at this point. Our motivation for computing this quantity is twofold. First, for the quasilocalized dynamical regime \(P(r)\) may be closely related to a "distribution of localization lengths." Second, confocal microscopy experiments have measured\(^{27-30}\) the probability distribution of particle displacements in time windows where the colloids are nearly localized in a cage or in the early stages of escape. The experiments find non-Gaussian distributions, with long tails in the large displacement direction which roughly follow an exponential (not Gaussian) law.

We do not expect a rigorous correspondence between our calculations and the dynamic measurements. However, we speculate that qualitative agreement can occur if the dynamics are largely controlled by a suitably defined effective free-energy function. The results in Fig. 4 are very similar to the experimental findings reported in Fig. 3 of Ref. 28, especially for \(\phi = 0.56\). For example, (i) the strong asymmetry towards the large displacement direction roughly follows an exponential law, (ii) the distribution functions for different volume fractions nearly collapse down to the \(\sim 1\% - 10\%\) relative probability level, and (iii) the relatively large 1% probability of a particle displacement \(\sim 5\) times the most probable value.

**D. Elastic shear modulus**

Rigorous calculation of the elastic shear stress modulus \(G_0\) is not possible based on our single-particle approach. However, it can be estimated using simple ideas as recently applied to interpret diffusing wave spectroscopy experiments on colloidal suspensions.\(^{35}\) Within a homogeneous continuum elasticity description, which is consistent with the Einstein oscillator picture of the amorphous solid state, one has\(^{45}\)

\[
G_0 = \frac{2k_BT}{\pi r_{\text{LOC}}} \approx \frac{K_0}{\sigma}\,.
\]

The second equality is often employed in the analysis of fractal networks.\(^{46}\) For the present problem, it is nearly an identity since Fig. 3 shows \(K_0 r_{\text{LOC}}^2 \sim k_BT\sigma^{-1}\), corresponding to the very close connection between a mean localization length and the (harmonic) distribution of localization lengths discussed in Sec. III A. For a 1 \(\mu\)m diameter colloid at room temperature one obtains \(G_0 \sim 4 \times 10^{-6} \text{e}^{55,36} \text{Pa}\). This corresponds to a modulus of \(\sim 10~(1.5)\text{ Pa}\) at \(\phi = 0.58\) (0.51). Experimental measurements of the elastic shear modulus of well-characterized, nearly monodisperse glassy hard-sphere suspensions where \(\phi\) has been accurately determined by calibration with the fluid-crystal transition do not seem to exist. However, the predicted order of magnitude is reasonable compared with the little data that are available.\(^{47,48}\) For a 1 nm diameter sphere, crudely representative of molecular liquids, a shear modulus of \(\sim 10^{-9} - 10^{-10} \text{ Pa}\) is predicted, which is in agreement with the typical experimental range.\(^{34}\)

**E. Entropic barrier**

Calculations of the entropic barrier (in units of \(k_BT\)) are presented in Fig. 5. The barriers are low \((F_B < 1)\) up to \(\phi = 0.49\), followed by a rapid increase reaching a value of \(\sim 8\) at \(\phi = 0.58\). The analogous results based on ignoring the de Gennes narrowing factor are shown in the inset and are qualitatively identical. Quantitative differences of \(\sim 2\%-30\%\) are found for \(\phi > 0.52\), which become monotonically smaller with increasing volume fraction. At the maximum packing fraction is approached, we expect the barrier height diverges. Of course, based on PY theory input this does not happen. Thus as \(\phi \to \phi_{\text{MAX}}\) our calculations may increasingly underestimate the barrier height. Lack of knowledge of the required correlation functions precludes quantitative assessment.

Two interesting connections between the entropic barrier height and other properties have been discovered. First, \(F_B\) is linearly correlated with a thermodynamic property: the inverse dimensionless isothermal compressibility,\(^{34}\)

\[
S(q = 0) = (1 - \phi)^q/(1 + 2\phi)^2\,.
\]

which quantifies the amplitude of static density fluctuations. This is a somewhat surprising and nontrivial result since the theoretical input involves strongly wave-vector-dependent correlation functions with local structural information on the \(q^* - 7\sigma\) cage scale making the dominant contribution to the integrals in Eq. (9). Hence, some type of "self-averaging" of the local cage structure is suggested.
The barrier height is also strongly correlated with two features of the effective free-energy minimum: \( F_B \sim K^{1/2} \sim 1/r_{LOC} \). Since (as discussed below) \( \tau \sim \exp(F_B) \), the first relation connects the long-time barrier hopping process and the localized-state oscillation (attempt) frequency as is explicitly demonstrated in Fig. 5. This is reminiscent of the recent connections found experimentally in thermal glass formers between short-time vibration dynamics (boson peak) and the \( \alpha \) relaxation flow process. \(^1\) The relation \( F_B \sim 1/r_{LOC} \sim 1/\sqrt{\langle u^2 \rangle} \) also follows from Figs. 3 and 4. Neutron scattering measurements \(^49\) on thermal glass formers have found an empirical correlation between the viscosity or \( \alpha \) relaxation time and the inverse of the mean-square vibration amplitude \( \tau \sim \exp(b/u^2) \). An analogous relation has been theoretically suggested \(^50\) and observed in molecular dynamics simulations for a specific model system. \(^51\) A similar relation is found from our approach although the power to which \( \langle u^2 \rangle \) is raised differs.

**IV. BARRIER HOPPING TIME**

The mean barrier hopping time \( \tau \) is expected to be closely correlated with the \( \alpha \) relaxation time. In this section we present model calculations for \( \tau \) and a comparison with experimental measurements of a single-particle relaxation time.

**A. Model calculations**

The conditions for validity of the Kramers first-passage time analysis are \( F_B \gg 1 \) and Markovian local friction \(^36,37\) for which

\[
\tau^{-1} = \frac{\omega_0}{2\pi} \left[ -\frac{\xi_s}{2M\omega_B} + \sqrt{\left(\frac{\xi_s}{2M\omega_B}\right)^2 + 1} \right] e^{-F_B}. \tag{16}
\]

Kramers theory ignores the possible importance of correlated thermal force fluctuations and lack of a time-scale separation between single-particle displacements and collective cage dynamics (non-Markovian effect). However, within this simplified picture Eq. (16) does apply for general degrees of the relative importance of diffusive versus inertial motion near the barrier top. For a concentrated colloidal suspension with the broad barriers found in Sec. III B, the high friction limit is expected to apply corresponding to diffusive motion over the barrier. Formally, this requires the inequality

\[
\xi_s / 2\sqrt{MK_B} \gg 1. \tag{17}
\]

In this limit, Eq. (16) simplifies to

\[
\tau^{-1} = \frac{\sqrt{K_0K_B}}{2\pi \xi_s} e^{-F_B}. \tag{18}
\]

Note that the particle mass drops out. To explicitly evaluate the applicability of Eq. (17), it is rewritten using \( \xi_0 = 3\pi\sigma\eta_0 \) (solvent viscosity \( \eta_0 \)), \( \xi_s = \xi_0G \) with \( G > 1 \), \( K_B = K_Bk_BT\sigma^{-2}, M = \rho_M\pi\sigma^3/6 \), where \( \rho_M \) is the colloid mass density. The result is

\[
\xi_s / 2\sqrt{MK_B} = \frac{3G\sigma\eta_0}{2\sqrt{K_Bk_BT\rho_M\sigma^6}} \gg 1. \tag{19}
\]

Using the numerical results for \( K_B \) from Sec. II B, \( \sigma = 1 \mu m \), a typical solvent viscosity of \( 10^{-2} \) Pa s, \( T = 300 \) K, a typical colloid mass density of \( 1 \sim 2 \) g/cm\(^3\), and \( G \sim 5 \sim 10 \) at high volume fractions (see below), yields a value for this ratio of \( \sim 10^2 \). Even for particles of diameter \( 1 \sim 10 \) nm the ratio is large.

The hopping time of Eq. (18), nondimensionalized by the elementary Brownian diffusion time \( \tau_0 = \sigma^2\xi_0/k_BT \), is thus given by

\[
\frac{\tau}{\tau_0} = \frac{2\pi G}{\sqrt{K_0K_B}} e^{F_B}. \tag{20}
\]

The quantity \( G \) represents the short-time dynamical correction to the single-sphere Stokes–Einstein friction factor. There are alternative theories which ascribe the primary origin of this correction as either independent binary collisions \(^39\) (IBCs) or solvent-mediated high-frequency hydrodynamic interactions associated with two-particle lubrication forces. \(25,40\) In practice, the different approaches yield nearly identical results. For the IBC or Enskog approach, \( G \) is the contact value of the hard-sphere radial distribution function. \(34,39\) An accurate analytic expression for \( g(\sigma) \) is given by the Carnahan–Starling formula \(34\) below \( \phi = 0.5 \) and smoothly crosses over to a different form at higher packing fractions which diverges at random close packing. \(52\)

\[
g(\sigma) = \frac{1 - \phi/2}{(1 - \phi)^2}, \quad \phi > 0.5. \tag{21}
\]
In the hydrodynamic approach, $G$ is the ratio of the high-frequency viscosity to the solvent viscosity. An accurate interpolation formula for this ratio is given by

$$\frac{\eta_\infty}{\eta_0} = \frac{1 + 1.5\phi(1 + \phi(1 + \phi - 2.3\phi^2))}{1 - \phi(1 + \phi(1 + \phi - 2.3\phi^2))}, \quad (\phi < 0.56)$$

$$= -15.78 \ln(1 - 1.16\phi^{1.3}) - 42.47, \quad (\phi > 0.6). \quad (22)$$

To within a factor of less than 2, $G$ is insensitive to which of these expressions are used for all volume fractions up to $\phi \approx 0.62$. Equation (21) is employed in our calculations.

Results for the dimensionless barrier hopping time are presented in Fig. 6. Interestingly, the prefactor of the exponential term in Eq. (20) is found to change by only a factor of $\sim 2$ over the range of $\phi$ ($\sim 0.5 - 0.62$) where $\tau$ increases by $\sim 1.5 \times 10^6$. This is a nontrivial result since the well and barrier curvatures and local friction constant in Eq. (20) vary significantly with $\phi$. Apparently, for hard-sphere suspensions the increase of friction with $\phi$ is nearly perfectly compensated by the increase in attempt frequency. Calculations which ignore the de Gennes narrowing factor $[\Gamma_s(q) = \Gamma_s(q)]$ are also shown and differ by only $\sim 3\% - 35\%$ over the entire range of volume fractions of interest.

**B. Comparison with experiment**

The mean barrier hopping time is of fundamental interest, but its quantitative relation to experiment is property specific.$^1$ For example, an $\alpha$ relaxation time can be deduced from macroscopic $(q = 0)$ stress or dielectric relaxation measurements. Alternatively, length-scale-dependent probes of single-particle, $F(q,t)$, or collective, $S(q,t)$, density fluctuations can be employed to extract a wave-vector-dependent relaxation time.

The kinetic glass transition depends on experimental method. Typically $\tau_{\text{exp}} \approx 10^2 - 10^4$ s is the operational definition.$^1$ Nonuniversal short-time dynamics enters via $\tau_0$ which for colloidal suspensions can vary significantly depending on particle diameter and solvent viscosity. This variability implies a kinetically defined glass transition volume fraction $\phi$ depend on particle size and other factors which influence short-time dynamics. Reduction of particle size and/or solvent viscosity results in an increase in the predicted volume fraction of the hard-sphere kinetic glass transition. This aspect is in contrast with the IMCT scenario$^3$ based on interpretation that $\phi_s = \phi_{\text{IMCT}}$, but is in accordance with the experimental behavior of thermal glass formers where it influences the dynamic “fragility.”$^1$ We are unaware of experiments or simulations for colloidal suspensions which adequately address this point. Uncharged hard-sphere experiments$^{23-25}$ where the volume fraction has been quantitatively calibrated against the fluid–crystal transition have employed colloids of nearly identical diameters of $\sigma \approx 350 - 400$ nm.

To make quantitative comparisons with experiment we consider the incoherent scattering measurements of Ref. 24 where $\sigma = 400$ nm, $\tau_0 = 0.5$ s, and the maximum observation time $\sim 10^4$ s. The most extensive results were obtained for a wave vector of $q\sigma = 2.6$, corresponding to a length scale $2\pi/q = 2.42\sigma$. Since the latter is significantly larger than the particle diameter, nearly pure Fickian diffusion is expected. This is consistent with the observations of a Gaussian wave vector dependence and nearly single-exponential decay of $F(q,t)$ at this wave vector. A slow, single-particle relaxation time $\tau_{\text{inc}}$ was measured. The product of the self-diffusion constant and relaxation time, $D\tau_{\text{inc}}$, was found to be nearly constant over the range $\phi = 0.47 - 0.58$, with the dimensionless ratio $D\tau_{\text{inc}}/(D\tau_0) = 0.38 \pm 0.05$. Interestingly, the measured single-particle relaxation time and the wave-vector-independent collective density fluctuation relaxation time on the cage length scales $q\sigma = 4.5 - 9$ are numerically very close, over $\sim 3$ orders of magnitude in time variation.$^{23,24}$ This again suggests the central role played by single-particle motion on the cage scale.

The kinetic glass transition defined as when $\tau_{\text{inc}} \approx 10^4$ s was experimentally determined$^{24}$ to occur at $\phi_s \approx 0.573$ (or $\sim 0.59$; see footnote 22 in Ref. 24). However, motion was still detected beyond this volume fraction, as indicated by upturns (downturns) in the dynamic mean-square displacement (incoherent structure factor). Hence, the reported value of $\phi_s$ does not appear to represent a literal nonergodicity or localization transition. Rather, in analogy with the behavior of thermal glass formers, it may indicate when the system “falls out of equilibrium” in the sense that the characteristic dynamic time scale exceeds the experimental time scale.$^1$

To make contact with this experiment we employ Fick’s law and Eq. (14) to compute the relevant relaxation time.
with \(2\pi/q = 2.42\sigma\). Adopting the experimental definition of the
glass transition of \(\tau_{\text{inc}} = 10^4\) s, the results in Fig. 6 predict
\(\phi_c \approx 0.579\). For multiple reasons the very good agreement
with experiment may be fortuitous. However, we do believe
the agreement is significant since all prior attempts (e.g.,
IMCT, free-volume model) to confront experiment require an
empirical rescaling of \(\phi\) and/or fitting of a hypothetical
maximum volume fraction where there is a dynamical
singularity.\(^1\),\(^3\)\(^-\)\(^5\)\(^3\) Calculations which ignore the de
Gennes
narrowing factor yield \(\phi_c \approx 0.582\).

The experimental relaxation times\(^2\)\(^4\) as a function of \(\phi\)
are also shown in Fig. 6. Good agreement with the calculations
is found, although some tendency for the theory to vary
more slowly with volume fraction than experiment seems
apparent at the highest colloid concentrations studied.
The horizontal error bars are due to the mixture nature of the
sample which is required to perform the incoherent scattering
measurement. This aspect introduces uncertainties in the
determination of the absolute magnitude of \(\phi\) using the
fluid–crystal phase transition as an internal calibration (see
footnote 22 in Ref. 24). Beyond the kinetic glass transition,
particle motion has been detected experimentally,\(^2\)\(^4\),\(^28\),\(^31\) and
the higher-\(\phi\) theoretical results serve as testable predictions.

Other experiments on weakly charged \(\sigma \sim 2\) \(\mu\)m suspensions\(^2\)\(^8\),\(^29\) and \(\sigma \sim 900\) nm cross-linked microgel fluids\(^2\)\(^7\),\(^31\) have reported kinetic glass transitions in the range
\(\phi_c \sim 0.56–0.6\). As discussed in Sec. III B, calibration of the
absolute magnitude of \(\phi\) is more uncertain for these systems.
Moreover, the kinetic \(\phi_c\) is determined in Refs. 28 and 29 by
when the time-dependent non-Gaussian parameter undergoes
a dramatic change, while the experiments of Refs. 27 and 31
employ a different kinetic glass transition criterion, and both
differ from the \(\tau_{\text{inc}} = 10^4\) s definition of van Megen \textit{et al.}\(^24\)
These differences render impossible any definitive evaluation
of the existence of a nonuniversal dependence of the kinetic
\(\phi_c\) on colloid size. Variation of the colloid diameter by a
factor of \(\sim 5\) results in changes in the elementary Brownian
time of \(\sim 10^2\). From Fig. 6 this implies a variability of
\(\sim 0.02–0.03\) in the predicted kinetic \(\phi_c\).

All three experimental studies\(^2\)\(^4\),\(^27\),\(^28\),\(^31\) detect significant
motion, and perhaps long-time diffusion, beyond the esti-
mated kinetic glass transition volume fraction. This feature
is consistent with the absence of any zero-mobility solid state
in our approach.

V. COMPARISON WITH CRITICAL SCALING,
FREE VOLUME, AND ADAMS–GIBBS APPROACHES

In this section we treat our theoretical results as “data”
and explore the fitting accuracy of both classic empirical
and, more recently proposed, functional forms. Historically,
the search for an understanding of glassy dynamics has been
intimately connected with the ability of empirical functions
to fit relaxation time or viscosity data.\(^1\) The fit functions
generally involve at least three adjustable parameters, often
of unclear physical meaning. They almost all invoke under-
lying divergences, which greatly increases their flexibility in

\[
\tau_{\text{inc}} = \frac{(2\pi/q)^2}{6D_{\text{Hop}}} ,
\]

providing adequate fits over limited ranges of control
variables.\(^1\) The plotting format adopted for making compari-
sions with experiment can significantly change the relative
weight of different dynamical regimes and can strongly in-
fluence the conclusions drawn. The recent analyses of Stickel
and co-workers of relaxation in thermal glass-forming liq-
uids clearly documents such vagaries.\(^10\) We employ their
“derivative analysis” to more critically test the adequacy of
model fit functions. The lack of “noise” in the theoretical
results enhances the usefulness of this procedure. The results
given in this section employ the de Gennes narrowing

correction in Eq. (5); all conclusions and results are virtually
identical if this correction is ignored.

A. Critical power laws

Critical power-law behavior of the relaxation time has
been proposed in various very different contexts. These
include the microscopic IMCT (Refs. 3–5) and phenomeno-
logical approaches such as the critical slowing down ideas of
Souletie\(^2\)\(^4\) and a cluster percolation model of Colby.\(^5\) For
a colloidal suspension, all these approaches would claim that
“close enough” to the glass transition the dimensionless
relaxation time scales as

\[
\frac{\tau}{\tau_0} = A(\phi_c - \phi)^{-\nu},
\]

where \(A\) is a numerical factor, \(\nu\) is a critical exponent, and
\(\phi_c\) is a critical volume fraction.

For hard spheres IMCT predicts\(^5\) \(\nu \sim 2.6\) and \(\phi_c \sim 0.52\).
The accuracy of this critical power law can be tested in sev-
eral ways. In Fig. 7 the relaxation time raised to the 1/2.6
power is plotted. This is a format for which linear behavior is expected, which is accurately found in the interval \( \phi = 0.5 - 0.56 \). The apparent ideal glass volume fraction deduced by linear extrapolation is \( \phi_r \approx 0.57 \), very close to the experimental analysis.\(^{24}\) At higher volume fractions the theoretical results strongly deviate from linearity, which is interpreted within the IMCT scenario as signaling the emergence of activated processes. Of course, the present calculations are based on a theory where transport is controlled by activated processes for all the volume fractions shown. The apparent linear regime is associated with hopping over modest barriers (roughly \(< 6k_BT\)), and deviations from linearity continuously emerge with increasing barrier heights. Thus, the physical interpretation of the shape of the relaxation plot in Fig. 7 is fundamentally different than offered by IMCT. Experiments on suspensions composed of cross-linked network particles find a plot of the same shape as Fig. 7, including significant long-time diffusion beyond \( \phi_{\text{IMCT}} \) which does not follow a critical power law.\(^{27}\) However, the deformability of these model hard spheres may introduce complications.

One can adopt a more empirical approach and treat \( \nu \) as an adjustable parameter to optimize the fit. An example of this procedure is shown in Fig. 7. The choice of a larger critical exponent of \( \nu = 5.46 \) (and corresponding larger apparent \( \phi_c \approx 0.616 \)) results in a quite accurate fit up to volume fractions of \( \approx 0.60 \).

An unbiased test of the appropriateness of a critical power law follows from the Stickel derivative analysis.\(^{10}\) The proper logarithmic derivative of the relaxation time should result in a constant equal to the inverse apparent scaling exponent:

\[
- \frac{d}{d \phi} \left( \frac{d}{d \phi} \ln(\tau/\tau_0) \right)^{-1} = \nu^{-1}.
\]  
(25)

The inset in Fig. 7 shows the effective critical exponent obtained from applying Eq. (25) is not constant and increases monotonically with volume fraction. One could argue the lack of accuracy of a fit which employs the IMCT critical exponent is not unexpected since it describes precursor dynamical phenomena and our calculations involve activated hopping. But we do find the apparent exponent equals the IMCT value of \( \nu = 2.6 \) at \( \phi = 0.51 \), which, remarkably, is very close to the a priori IMCT prediction\(^5\) of \( \phi_c \approx 0.515 \) based on PY input.

We have also considered Eq. (24) with a critical volume fraction being the random close packing (RCP-) like value of 0.64 as suggested by others.\(^{26,32,40}\) Figure 8 shows the optimized fit occurs for a critical exponent of \( \nu = 8.2 \). Curiously this much higher exponent is close to what has been found \( (\nu \approx 9) \) from analyzing polymer melt relaxation data.\(^{55}\) Globally, a better representation of the theoretical results is obtained with the literal hard sphere IMCT form, although the inset of Fig. 7 shows no critical power law is truly an accurate representation. This conclusion is inevitable since our theoretical results do not contain a critical divergence. Minor variation of the assumed \( \phi_c \) (e.g., 0.62, 0.63) does not change our conclusions although the best-fit exponent can change by 10%–20%.

![Figure 8. Log-linear plot of the dimensionless relaxation time (solid circles) as a function of volume fraction. The two fits of Fig. 7 are reproduced in this format as the dashed \((\nu = 2.6)\) and dash-dotted \((\nu = 5.46)\) curves. The solid curve is the best critical power law fit based on a critical volume fraction of 0.64; the corresponding exponent is \( \nu = 8.23 \).](image)

**B. Free-volume forms**

The classic free-volume theory, or Williams–Landel–Ferry (WLF) expression, for the relaxation time also involves three adjustable parameters and is of an essential singularity form\(^1,40\)

\[
\frac{\tau}{\tau_0} = A \exp \left( \frac{B}{\phi_c \phi - \phi} \right), \quad x = 0, 1,
\]  
(26)

where \( A \) and \( B \) are constants. The common choice is \( x = 0 \), although some authors employ \( x = 1 \). The value of \( x \) makes little difference due to the dominance of the essential singularity. Figure 9 shows the best fit to our results with \( x = 0 \) and \( \phi_c = 0.64 \). Rather good agreement is found over roughly four orders of magnitude variation in time which is comparable to, or exceeds, the entire range of volume fractions typically probed experimentally.\(^{19,24,32,40}\) Our results remain virtually unchanged if \( x = 1 \) is employed in Eq. (26).

Systematic deviations between our calculations and the WLF formula are present in Fig. 9. The differences are quantified in the inset by applying the Stickel derivative method\(^{40}\) appropriate for Eq. (26) which states the following quantity is a linear function of volume fraction if the WLF expression is exact:

\[
\left( \sqrt{\frac{d}{d \phi} \ln(\tau/\tau_0)} \right)^{-1} \rightarrow (\phi_c - \phi) B^{-1/2}.
\]  
(27)

Significant deviations are present at low and high volume fractions. The deviations are in the direction of weaker than WLF dependence. The latter trend is qualitatively identical to that found in recent studies of polymer melts\(^56\) where the tendency at high and low (below \( T_s \), but in equilibrium) temperatures is towards an Arrenius law. For colloids, the ana-
log of inverse temperature is volume fraction. The calculations in Fig. 9 show that above the kinetic glass transition volume fraction the logarithm of the predicted relaxation time is reasonably linear over roughly three orders of magnitude in time, which is the hard-sphere suspension analog of an Arrhenius dependence.

### C. Adams–Gibbs forms

The classic Adams–Gibbs (AG) approach\(^1\) argues the relaxation time is exponentially related to a barrier which varies inversely with a “configurational entropy,”

\[
\frac{\tau}{\tau_0} = A \exp\left(\frac{C}{T\Delta S_c}\right),
\]

where \(A\) and \(C\) are numerical factors. Considerable disagreement surrounds how the “configurational entropy” \(\Delta S_c\) should be defined.\(^1\) We consider two different choices employed in the literature. For hard spheres, the free energy is of a purely entropic origin.

The classic idea of Kauzmann is that the configurational entropy is the difference between the fluid and crystal entropies.\(^1\) Following Ref. 2, this is given in units of \(k_B\) by

\[
\Delta S_c \equiv S_{\text{fluid}} - S_{\text{crystal}} = \ln(\pi \sigma^3 / 6) - \ln(\phi) - 2(1 - \phi)^{-1} - (1 - \phi)^{-2} + 2.8776 + 2.3033 \ln(z) - 3 \ln(1 - z) + 0.10463 \ln(z - 0.601),
\]

where \(z\) is a volume-fraction-dependent function chosen such that the crystal is at the same pressure as the fluid. Analytic equations for the fluid and crystal pressures required to enforce this constraint are given in Ref. 2. Note that \(\Delta S_c \to 0\) at \(\phi \sim 0.635\).

An alternative approach is to assume that \(\Delta S_c\) is the difference in entropy between the fluid and some ultrahigh-volume-fraction fluid reference state.\(^7\) For hard-sphere suspensions, one “natural” choice is the maximally jammed state. Without judging its correctness, we adopt a RCP-like value of \(\phi_{\text{MAX}} \sim 0.64\) as the reference state. The relevant entropy is chosen to follow from Eq. (9) which controls the “localization driving force” in our kinetic description. Hence,

\[
T\Delta S_c \equiv F_m(\phi) - F_m(\phi_{\text{MAX}}),
\]

where \(F_m\) is the minimum value of the “effective” (nonequilibrium) free energy of Eq. (9).

The results of fitting Eq. (28) with Eq. (29) or (30) to our theoretical data are shown in Fig. 10, and the entropy differences are plotted in the inset. The volume fraction dependence of the latter are surprisingly similar. Adjustment of the constant \(C\) in Eq. (28) has been performed to optimize the fit in the experimentally relevant range of \(\phi \sim 0.50–0.58\). Reasonably good fits are obtained over this range where the relaxation time increases by \(\sim 3\) orders of magnitude. The fit based on Eq. (30) performs slightly better, but only at lower values of \(\phi\) where the appropriateness of Eq. (28) (and our calculation of the hopping time) is most questionable. Both fits fail badly as volume fraction increases above \(\sim 0.58\),
even though the divergences of both expressions are at $\phi > 0.63$. The quality of the AG fits are nearly identical to that of the WLF results of Fig. 9.

VI. SUMMARY AND DISCUSSION

We have presented a simple kinetic approach for elementary aspects of slow single-particle dynamics which combines elements of naive idealized mode-coupling theory,22 density functional theory, and activated rate theory. The primary new idea is that the slow dynamics are strongly influenced by an underlying “effective (nonequilibrium) free energy” which is determined by the dynamical consequences of structural cage correlations. Quantification of this idea employs the naive version of IMCT to construct the effective free energy which describes, within a Langevin equation-of-motion framework, both the driving force favoring particle localization and entropic barriers. Thermal fluctuations are included via a random force which destroys the (naive) IMCT glass transition and restores ergodicity via barrier hopping. We do not claim any rigorous derivation, but the theory is predictive and contains no adjustable parameters or postulating dynamical or thermodynamic divergences. The basic spirit of our approach might also be viewed as a microscopic quantification of “trap models”13,19 which describe the caging process in a highly coarse-grained fashion via a static random potential which is modeled in various phenomenological manners.

Good agreement of our theory with the experimental kinetic glass transition volume fraction of hard-sphere suspensions is found. Within the uncertainties of the various experiments,24,27-31 reasonable agreement is found for the magnitude and volume fraction dependences of the single-particle relaxation time, apparent localization length, and length scale of maximum non-Gaussian behavior. The basic physical picture differs from IMCT since the slow dynamics and transient localization arise from the emergence of entropic barriers and activated transport. Experiments which measure the relaxation time and other transport properties at higher volume fractions, and possible dependences on nonuniversal system parameters such as hard-sphere diameter and solvent viscosity, will provide further tests of the theory. Further experiments are also required to clearly distinguish the predictions of our theory from fits of IMCT to hard-sphere suspension experiments. Multiple connections are also predicted between thermodynamics, short-time dynamics in the temporarily localized state, and long-time barrier crossing. Many of these connections seem qualitatively similar to puzzling observations made for thermal glass-forming polymer and molecular liquids.1

It is worth noting that the present approach does not invoke concepts such as an underlying thermodynamic phase transition, entropy catastrophe, kinetic singularities, free volume, percolation, frustration, dynamic heterogeneity, cooperatively rearranging regions, or other special collective motions.1 Of course, we are not claiming that these concepts are irrelevant since the single-particle nature and restricted focus of our theory precludes rigorously drawing such a conclusion. But the importance of such “highly many-body” aspects on the observables we have studied is not obvious.

We are also not suggesting our naive IMCT based approach is generically “better” than the full idealized mode-coupling theory. Indeed it is not, and IMCT appears to be a powerful tool for understanding precursor dynamical phenomena which our approach is not meant to accurately address.

Quantitative comparisons of our theoretical results for the relaxation time with vastly different fit formulas have been carried out. We find that the $\phi$ dependence of $\tau$ can be fit rather well over limited ranges by many theoretically motivated functions which all have “idealized divergences” and three adjustable parameters. For hard-sphere colloids, where dynamic light scattering and shear viscosity measurements are limited to rather modest volume fractions of $\sim 0.57$ or less, there is not much to choose among the various functions. Based on fit quality, the empirical critical power law with a hypothetical divergence at (or near) random close packing and a large critical exponent appears to provide the best global description of our theoretical results. However, the derivative Stickel analysis shows that all the considered forms are not fundamental over a wide range in $\phi$, an unavoidable conclusion since our results do not contain any singular features. On the other hand, the ability of the fit functions to reproduce the theoretical trends is strongly contingent on building in an apparent singular state. As emphasized by Stillinger and co-workers2 and others,36,58 this raises questions about the existence and/or practical relevance of true divergences (equilibrium or dynamic) in the glass transition problem.

By design the theory has invoked multiple simplifications. For colloidal suspensions many-body hydrodynamic interactions remain poorly understood and have not been explicitly taken into account. However, it is widely believed that at high volume fractions the direct interparticle forces are dominant.59,60 Non-Markovian effects on rate processes can be important37 and deserve further study. However, these generally result in corrections only to the prefactor in Eq. (16) and, hence, are likely of minor significance. In a one-component fluid the physical origin of a non-Markovian aspect is the lack of a clear time-scale separation between collective cage and single-particle dynamics. For such a correction to be large would seem to require the confining degrees of freedom to relax much more rapidly than the tagged particle. This is generally not the case since collective density fluctuations and stress relaxation are tightly coupled to single-particle motion,3-6,15,17,24 although dynamic heterogeneity61 close to the glass transition might introduce complications.

Our focus on single-particle dynamics on relatively short length scales implies additional limitations. In contrast to the full IMCT, collective wave-vector-dependent quantities such as $S(q,t)$ cannot be rigorously addressed. However, the prime importance at high densities of single-particle motion15-18,24 suggests that progress may be possible using the present theory combined with general MCT and statistical dynamical expressions. This aspect is addressed for the shear viscosity and long-time self-diffusion constant in the following companion paper.62 There is also a need for generalization to treat the smooth dynamical crossover from an activated hopping regime, to the precursor mode-coupling
regime, to the lower-density normal-fluid regime. This is a difficult and largely unsolved task within IMCT and all other theoretical approaches.

The present work provides a foundation to treat the elementary trapping and activated hopping aspects of more complex charged or sticky colloidal and nanoparticle suspensions. Building on recent progress of IMCT,\textsuperscript{63,64} the influence of thermally activated hopping on gelation should be amenable to study. Most excitingly, molecular and polymeric thermal glass-forming liquids can be treated where activated processes can control ten or more orders of magnitude variation of the $\alpha$ relaxation time. Work is in progress in all these directions and will be reported in future publications.

Finally, after this paper was submitted we became aware of two very recent simulation studies,\textsuperscript{65,66} of activated dynamics and potential energy landscapes for a model binary mixture of Lennard-Jones particles (BMLJ). Both studies conclude that the long-time dynamical behavior is controlled by activated barrier hopping processes even \textit{well above} the \textit{empirically deduced} critical temperature $T_c$. IMCT was argued to still be relevant for the short-time (in cage) dynamics, but long-time motion and transport is controlled by rare activated escape from deep traps.\textsuperscript{65} The analysis of Ref. 66 suggests that activated processes determine the diffusion constant up to temperatures far above the \textit{apparent} critical temperature, perhaps up to $\sim T_c$, which curiously is close to the \textit{a priori} calculated $T_c$ of mode-coupling theory for the BMLJ system. Also, there is no indication of a change in diffusion mechanism around the MCT temperature.\textsuperscript{66} Hence, these authors question the commonly cited idea that barriers and activated hopping become important only as $T \rightarrow T_c$. These simulation results seem consistent with our theory in the sense that when we empirically analyze our relaxation time predictions based on the MCT scenario (Fig. 7) an apparent critical volume fraction is identified which is in agreement with the experimental kinetic value of $\phi_0 \sim 0.57$. However, at this volume fraction the entropic barrier is large ($\sim 7k_B T$ from Fig. 5), implying relaxation is controlled by activated hopping over barriers of significant height.

\textbf{ACKNOWLEDGMENTS}

Helpful conversations and correspondence with M. D. Ediger are gratefully acknowledged. We thank V. Ganesan for making us aware of the work of Bouchard and collaborators, D. R. Reichman for informing us of Ref. 65, and S. Granick for encouragement and valuable comments on the manuscript. This work was supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Grant No. DMR-0117792.

perspective, this does not cause problems in our analysis, which is restricted to describing localization and escape over the barrier, and involves displacements of order the particle diameter and much less. A more accurate treatment of the ideal free energy might be achieved based on recent work within a thermodynamic DFT framework [see, for example, C. Kaur and S. P. Das, Phys. Rev. Lett. 86, 2062 (2001)]. However, this involves system-specific technical complexities including the need for an explicit description of the glass structure at the pair correlation level. Such an elaboration also does not seem warranted at present since our Langevin EOM approach has not been generalized to account for non-Markovian friction and explicit prediction of the long-time diffusion constant.


