In a given liquid, the two kinetic processes often obey the Stokes–Einstein relation \[ D = \frac{kT}{C \eta} \] (1), where \( D \) is a constant independent of temperature. In his original paper [5], Einstein did not analyze self-diffusion; rather, he analyzed a macroscopic particle diffusing in a liquid using the continuum theory of Stokes flow. Nonetheless the Stokes–Einstein relation holds for particles down to the molecular scale [6]. In particular, the relation holds for self-diffusion for many liquids over wide ranges of temperature [7].

The Stokes–Einstein relation even holds for some supercooled liquids, substances that remain in the liquid state and do not crystallize when the temperature drops below their melting points [8]. For instance, water has a melting point of 0 °C, but can remain in the liquid state down to \(-37.5 \) °C [9]. As the temperature drops, a supercooled liquid like silica increases its viscosity steeply (Fig. 1(a)), but does not reduce its self-diffusivity as steeply (Fig. 1(b)), such that the ratio \( D / kT \) increases often by orders of magnitude (Fig. 1(c)).

For a liquid that obeys the Stokes–Einstein relation, viscous flow and self-diffusion proceed through a single rate-limiting process: molecules change neighbors. By contrast, for a liquid that violates the Stokes–Einstein relation, viscous flow and self-diffusion proceed by distinct rate-limiting processes. In many cases, a supercooled liquid forms a dynamic structure that consists of regions larger than individual molecules [17–30]. Molecular rearrangement is much slower in some regions than others (Fig. 2). Viscous flow proceeds by disrupting the dynamic structure, but self-diffusion proceeds by the migration of individual molecules through the fast regions. Consequently, as the temperature drops, the dynamic structure increasingly jams viscous flow, but does not retard self-diffusion as much.

As molecular dynamic simulations and microscopic experiments continue to shed light on the physics and chemistry of supercooled...
liquids, it is timely to formulate a continuum theory of supercooled liquids to describe macroscopic phenomena, and to motivate new experiments. Here we formulate a continuum theory by regarding viscous flow and self-diffusion as distinct, concurrent processes. We generalize Newton’s law of viscosity to relate stress, rate of deformation, and chemical potential (Sec. 2). We assume that the self-diffusion flux is proportional to the gradient of chemical potential (Sec. 3). The relative rate of viscous flow and self-diffusion results in a characteristic length (Sec. 4). We apply the theory to a cavity in a supercooled liquid, shrinking under the influence of the surface energy (Sec. 5). The characteristic length demarcates two types of behavior: a large cavity shrinks by the viscous flow, and a small cavity shrinks by the self-diffusion. We place the theory in the context of several other theories (Sec. 6).

2 Homogeneous State

This section generalizes Newton’s law of viscosity to describe a supercooled liquid of a single species of molecules, subject to external forces, and connected to a reservoir of the same species of molecules (Fig. 3). The piece of liquid contains a large number of molecules, but is still small enough to serve as a representative elementary volume. In this continuum picture, the piece evolves through a sequence of homogeneous states, represented by a parallelepiped that changes its shape and volume. Let \( d_{ij} \) be the rate of deformation—for example, \( d_{11} \) is the rate of extension of the piece of liquid in direction 1, and \( d_{12} \) is the rate of shear of the piece of liquid between directions 1 and 2. Let \( R \) be the rate of injection—that is, the number of molecules transferred from the reservoir to the piece per unit volume per unit time. The external forces apply to the piece a state of stress \( r_{ij} \), and the molecules in the reservoir have the chemical potential \( \mu \).

Molecules in a liquid are often nearly incompressible. As an idealization, we assume that the volume per molecule in the liquid, \( \Omega \), remains constant, independent of the stress and the chemical potential of the molecules in the reservoir. At a given time, the volume of the piece is \( V \), the trace of the rate of deformation is \( d_{ii} \), and the piece changes its volume at the rate \( \Omega V \). The idealization of molecular incompressibility, along with the conservation of the number of molecules, requires that

\[
d_{ii} = \Omega R \tag{2}
\]

That is, the increase of the volume of the piece equals the volume transferred from the reservoir.
When the inequality in Eq. (4) holds for arbitrary rate of deformation \(d_{ij}\), the composite system is not in thermodynamic equilibrium. We satisfy this inequality by prescribing a kinetic model that linearly relates two symmetric tensors, \(\sigma_{ij} + (\mu/\Omega)\delta_{ij}\) and \(d_{ij}\). For an isotropic liquid, the linear relation between two symmetric tensors takes the general form [34]

\[
\sigma_{ij} + \frac{\mu}{\Omega} \delta_{ij} = 2\eta \left( d_{ij} - \frac{1}{3} d_{kl} \delta_{kl} \right) + \beta d_{kl} \delta_{ij}
\]

(6)

where \(\eta\) and \(\beta\) are constants. The thermodynamic inequality (4) holds when both \(\eta\) and \(\beta\) are non-negative. Given the material constants \(\Omega, \eta\) and \(\beta\), this kinetic model and the constraint (2) together provide a total of seven independent equations among the 14 variables \(d_{ij}, R, \sigma_{ij}\), and \(\mu\).

The kinetic model (6) can also be motivated in a different way. The trace of the rate of deformation, \(d_{kk}\), describes the rate at which the piece of liquid changes its volume. The deviatoric part of the rate of deformation, \(s_{ij} = d_{ij} - d_{kl} \delta_{ij}/3\), describes the rate at which the piece of liquid changes its shape. The mean stress is \(\sigma_{nn} = \sigma_{kl}/3\), and the deviatoric stress is \(s_{ij} = \sigma_{ij} - \sigma_{ij} \delta_{ij}\). Note the identity \(s_{nn} = \sigma_{nn} + (\mu/\Omega) d_{kk}\), and write Eq. (4) as \(s_{nn} \eta + (\sigma_{nn} + \mu/\Omega) d_{kk} \geq 0\). This inequality suggests a kinetic model: \(s_{nn} = 2\eta\sigma_{nn}\) and \(\sigma_{nn} + \mu/\Omega = \beta d_{kk}\). The thermodynamic inequality holds when both \(\eta\) and \(\beta\) are non-negative. This kinetic model is equivalent to Eq. (6).

The constant \(\eta\) represents the shear viscosity that resists the change in shape, and the constant \(\beta\) represents the bulk viscosity that resists the change in volume. In the limit \(\beta/\eta \to 0\), the change in volume is much faster than change in shape, so that we may assume that \(\sigma_{nn} + \mu/\Omega \to 0\), and the composite system is in partial thermodynamic equilibrium with respect to the exchange of molecules between the piece and the reservoir. In the limit \(\eta/\beta \to 0\), the change in shape is much faster than change in volume, so that we may assume that \(d_{kk} = 0\), and the piece changes shape without changing volume.

The kinetic model (6) generalizes Newton’s law of linear, isotropic, viscous flow. Our model differs from the model of compressible viscosity. We have assumed that molecules in the liquid are incompressible, so that an increase in volume of the liquid is entirely due the injection of molecules from the reservoir to the piece. By contrast, for compressible viscosity, the number of molecules in an element of liquid is fixed, and an increase in the volume of the element is entirely due to the reduction in density.

### 3 Inhomogeneous State

We now consider a body of liquid evolving through a sequence of inhomogeneous states. A continuum theory regards the body as a collection of small pieces. As the body evolves, each piece evolves through a sequence of homogeneous states, as described in Sec. 2. Different pieces communicate through the balance of forces, compatibility of geometry, and transfer of molecules. In classical hydrodynamics, each small piece (commonly called a material particle, a material point, or a material element) is identified by a set of molecules, which do not change identity as the body of liquid evolves. This practice, however, is inapplicable here. As a small piece of liquid transfers molecules to surrounding small pieces by the self-diffusion of molecules, the small piece does not consist of the same molecules and may even disappear after some time.

Here we break away from this practice in classical hydrodynamics and describe the kinematics of the body not by tracking pieces of the liquid, but by tracking markers dispersed in the liquid. Indeed, markers are commonly used in experiments. Examples include precipitates that visualize the creep of a solid solution, and particles that visualize the flow of a fluid. The markers should be small compared to the length characteristic of the inhomogeneous field, so that the markers are carried by the
flow without affecting it. The markers should be large compared to the size of the individual molecules, so that the markers themselves diffuse negligibly. As common with many basic concepts, the relation between markers in experiments and markers in the continuum theory deserves careful examination. This paper proceeds by describing the idealized behavior of the markers within the continuum theory.

We relate the velocity field of markers and the rate of deformation. When two nearby markers drift apart, the piece of the liquid between the markers elongates, and the relative velocity between the two markers defines the rate of extension. At a given time, consider three nearby markers P, A, and B, with the line PA normal to the line PB. When the line PA rotates relative to the line PB, the piece of liquid shears, and the rate of the change in the angle between the two lines defines the rate of shear. Denote the velocity of the markers by a field \( v \). In general, the rate of deformation relates to the gradient of the marker velocity as \( \frac{d}{dt} \left( \frac{\partial v}{\partial n} \right) \). Here, \( d_{ij} = (v_{ij} + v_{ji})/2 \). The two quantities, however, are unequal when pieces of the liquid exchange molecules. The difference between the net flux and the convective flux defines the self-diffusion flux of molecules

\[
J = N - \frac{v}{\Omega} \quad (7)
\]

That is, the net flux of molecules is the sum of the self-diffusion flux and the convective flux.

Due to molecular incompressibility, the number of molecules in any fixed volume is constant. The conservation of the number of molecules requires that

\[
d_{ik} + \Omega J_{ik} = 0 \quad (8)
\]

Even in the absence of injection, \( R = 0 \), the divergence of the velocity field does not necessarily vanish. This behavior differs from that of hydrodynamics of incompressible fluids. Equation (8) is applicable to an inhomogeneous field, whereas Eq. (2) is applicable to a homogeneous field.

The body is subject to loads of several kinds (Fig. 5). Let \( \gamma \) be the surface energy of the liquid per unit area. Associated with the change in the area \( A \) of the surface of the body, the surface energy of the body changes at the rate \( \gamma dA/dt \). The body is subject to external forces. Let \( b \) be the external force per unit volume in the body, and \( f \) be the external force per unit area on the surface of the body. Associated with the velocity of the markers, the

![Image](image-url)
potential energy of the external forces changes at the rate \(- \int b_j v_j dV - \int f_j v_j dA\). Upon diffusing from the bulk to the surface, molecules are assumed to plate out on the surface, but do not leave the body. Associated with the molecules plated out, the surface of the body advances at velocity \(\Omega_j n_j\), the traction normal to the surface \(t_j n_j\) does work, and the potential energy of the external forces changes at the rate \(- \int t_j n_j \Omega_j dA\). Each small piece of the body may be in contact with a reservoir of the same species of molecules. Let \(\mu\) be the chemical potential of molecules in the reservoir, and \(R\) be the rate at which the reservoir injects molecules into the piece. The whole body can be connected with a field of reservoirs, so that both \(\mu\) and \(R\) are fields. Associated with the transfer of molecules from the reservoirs to the body, the Helmholtz free energy of the reservoirs changes at a rate \(- \int \mu dV\). The surface, the body, the external forces, and the reservoirs together constitute a composite thermodynamic system. Thermodynamics requires that the Helmholtz free energy of the composite system should never increase.

\[
\frac{dA}{dt} - \int b_j v_j dV - \int t_j n_j \Omega_j dA - \int \mu dV \leq 0 \quad (9)
\]

Recall that we have set the Helmholtz free energy per molecule inside the liquid to be zero. The thermodynamic condition \(9\) holds for an inhomogeneous field, which should be compared to the thermodynamic condition for a homogeneous field \(3\).

Let \(\kappa\) be the mean curvature of an element of the surface of the body. For example, the mean curvature of a spherical particle of radius \(a\) is \(\kappa = 1/2a\), and the mean curvature of spherical cavity of radius \(a\) is \(\kappa = -1/2a\). Recall an identity in differential geometry: as the surface moves at velocity \((v_j + \Omega_j n_j)\), the area of the surface changes at the rate \(dA/dt = \int k(v_j + \Omega_j n_j) n_j dA\). Pieces in the body communicate through the balance forces, \(\sigma_{ij} + b_i = 0\), giving \(\int b_j v_j dV = \int \sigma_{ij} n_j v_j dA = \int \mu_j dV\). Also note an identity \(\int \mu_j dV = \int \mu_j n_j dA - \int \mu dV\).

The above relations allow us to rewrite the thermodynamic condition \(9\) as

\[
\left( t_j - \sigma_{ij} n_j - \gamma \kappa n_i \right) v_j dA + \left( \mu + \Omega_j n_j - \Omega_j \gamma \kappa \right) n_i dA
+ \left( \sigma_{ij} + \frac{\mu_j}{\Omega_j} \right) v_j dV + \left( -\mu_j \right) J dV \geq 0 \quad (10)
\]

The inequality holds when the composite system is not in thermodynamic equilibrium, whereas the equality holds when the composite system is in thermodynamic equilibrium. The thermodynamic condition \(10\) holds for two independent and arbitrary fields: the velocity of markers, \(v\), and the self-diffusion flux of molecules, \(J\). Consequently, the integrand of each of the four integrals must be non-negative.

We satisfy the four distinct conditions as follows. We assume local thermodynamic equilibrium at the surface of the body, so that the first two integrands vanish, namely,

\[
\sigma_{ij} n_j = t_j - \gamma \kappa n_i \quad (11)
\]

\[
\mu = -\Omega_j n_j + \Omega_j \gamma \kappa \quad (12)
\]

These equations represent four distinct boundary conditions. Whereas Eq. \(11\) expresses the balance of forces acting on the markers in the liquid near the surface, Eq. \(12\) expresses the condition of equilibrium as molecules in the interior of the liquid diffuse out and plate onto the surface, when no molecules leave the body or are added to the body from external reservoirs. In the absence of the surface energy, Eq. \(11\) recovers the familiar balance of forces on the surface, and Eq. \(12\) relates the chemical potential on the surface to the normal traction. In the absence of the traction due to external forces, Eqs. \(11\) and \(12\) reduce to the expressions for the Laplace pressure and the Thompson effect [38]. The third integrand in Eq. \(10\) is non-negative once we adopt the generalized model of viscous flow (Sec. 2). The fourth integrand in Eq. \(10\) is non-negative once we adopt a model of self-diffusion, \(J_i = -(D/\Omega k T) \mu_j\), where \(D\) is the self-diffusivity [39].

4 Governing Equations and Characteristic Length and Time

We now summarize the governing equations. Using the relation \(d_j = (v_{ij} + v_{ij})/2\), we write the generalized model of viscosity as

\[
\sigma_{ij} + \frac{\mu}{\Omega} \delta_{ij} = \eta \left( v_{ij} + v_{ij} \right) + \left( \beta - \frac{2\eta}{3} \right) v_{ik} \delta_{ij} \quad (13)
\]

The balance of forces gives

\[
\sigma_{ij} + b_i = 0 \quad (14)
\]

The model of self-diffusion connects the self-diffusion flux to the gradient of the chemical potential

\[
J_i = -\frac{D}{\Omega k T} \mu_j \quad (15)
\]

The molecular incompressibility, the conservation of the number of molecules, and the relation \(d_{kk} = v_{kk}\) together give that

\[
v_{kk} + \Omega J_k = \Omega R \quad (16)
\]

Equations \(13\)–\(16\) represent 13 independent partial differential equations for the 13 fields \(v_i, \sigma_{ij}, J_i, \mu\).

Inserting Eqs. \(13\) into \(14\), we obtain that

\[
\eta \nu_{kk} + \left( \frac{\eta}{3} + \beta \right) v_{kk} - \frac{\mu_j}{\Omega} + b_i = 0 \quad (17)
\]

Inserting Eq. \(15\) into Eq. \(16\), we obtain that

\[
v_{kk} - \frac{D}{k T} \mu_{kk} = \Omega R \quad (18)
\]

Equations \(17\) and \(18\) represent four distinct partial differential equations for the four fields, \(v_i, \mu\). These four differential equations are solved along with the four independent boundary conditions \(11\) and \(12\).

We will be usually interested in problems with vanishing body force \(b\) and vanishing rate of injection \(R\). In the latter case, the body is disconnected from reservoirs of molecules. The value of \(\mu\) at a particular piece in the body can be interpreted by the following operation. When we connect the piece in the body to a reservoir, \(\mu\) is the chemical potential of the molecules in the reservoir needed to equilibrate with the piece. Thus, the reservoir serves as an instrument that measures chemical potential, analogous to a thermometer that measures temperature.

A comparison of Eqs. \(17\) and \(18\) gives a length [37]

\[
\Lambda = \sqrt{\frac{\eta D \Omega}{k T}} \quad (19)
\]

The length characterizes the relative rate of viscous flow and self-diffusion. For any given boundary-value problem, the geometry of the body specifies additional lengths. Let \(a\) be a length representative of the geometry of the body. In the limit \(a \geq \Lambda\), self-diffusion is negligible, Eq. \(18\) reduces to \(v_{kk} = 0\), and Eq. \(17\) recovers the Stokes equations for viscous flow [34]. In the limit \(a \ll \Lambda\), viscous flow is negligible, Eq. \(18\) reduces to the equation for self-diffusion [39].

The characteristic length \(\Lambda\) is material-specific (Fig. 6(a)). Note that the quantity \(\eta D/k T\) appears both in the equation defining the
characteristic length (19) and in the Stokes–Einstein relation (1). For a liquid obeying the Stokes–Einstein relation, such as silica, viscous flow, and self-diffusion result from the single rate-limiting process—molecules change neighbors, so that the length $\Lambda$ is of molecular size and is independent of temperature. For a liquid violating the Stokes–Einstein relation, however, viscous flow and self-diffusion result from different rate-limiting processes, so that the length $\Lambda$ can be much larger than the molecular size and increases as temperature drops.

We also identify a characteristic time

$$\Gamma = \eta \Lambda / \gamma$$

This time is also material-specific and temperature-dependent (Fig. 6(b)). The surface energy $\gamma$ typically depends on temperature weakly. For a liquid obeying the Stokes–Einstein relation, the length $\Lambda$ is independent of temperature, and the time $\Gamma$ follows the Arrhenius behavior of viscosity. By contrast, for a liquid violating the Stokes–Einstein relation, the length $\Lambda$ may be much larger than the size of molecules, and the viscosity exhibits non-Arrhenius behavior. Consequently, the plot of the time $\log \Gamma$ as a function of $1/T$ curves up significantly.

5 Shrinking of a Cavity in a Supercooled Liquid

We apply our theory to a cavity in an infinite body of supercooled liquid (Fig. 7). Under the influence of the surface energy, the cavity shrinks by concurrent viscous flow and self-diffusion. The cavity is spherical, so that the nonvanishing fields are the radial component of stress $\sigma_r$, circumferential component of stress $\sigma_\theta$, and radial component of stress $\sigma_z$. The molecular incompressibility takes a simple form under the spherical symmetry. Here we assume that the liquid is disconnected from any reservoir of molecules. Denote the radius of cavity at time $t$ by $a(t)$. At a given time, the net flow of molecules crossing the surface of the cavity is $4\pi r^2 (da/\Omega) / \gamma$, and the net flow of molecules across the spherical surface of radius $r$ is $4\pi r^2 J(r) = \gamma (a^2 da / \Omega) dt$. The molecular incompressibility requires that the two flows should be equal, giving that

$$\gamma (a^2 da / \Omega) dt = 4\pi r^2 J(r)$$

We use this equation to express $\gamma (a^2 da / \Omega) dt$ in terms of $J(r)$.

Equations (21)–(23) are three first-order ordinary differential equations for the three functions $\sigma_r(r)$, $\mu(r)$, $J(r)$, in the interval $r \in (a, \infty)$, subject to the following boundary conditions. The surface of the cavity is concaved and has a negative mean curvature, $\kappa = -1/2a$. No external traction is applied on the surface of the cavity, so that the boundary conditions (11) and (12) become

$$\sigma_r(a) = \gamma / 2a$$

Far from the cavity, the radial stress and the chemical potential vanish:

$$\sigma_r(\infty) = 0$$

$$\mu(\infty) = 0$$

The molecular incompressibility takes a simple form under the spherical symmetry. Here we assume that the liquid is disconnected from any reservoir of molecules. Denote the radius of cavity at time $t$ by $a(t)$. Under the influence of the surface energy, the cavity shrinks by concurrent viscous flow and self-diffusion. The cavity is spherical, so that the nonvanishing fields are the radial component of stress $\sigma_r$, circumferential component of stress $\sigma_\theta$, and radial component of stress $\sigma_z$. The surface energy $\gamma$ typically depends on temperature weakly. For a liquid obeying the Stokes–Einstein relation, the length $\Lambda$ is independent of temperature, and the time $\Gamma$ follows the Arrhenius behavior of viscosity. By contrast, for a liquid violating the Stokes–Einstein relation, the length $\Lambda$ may be much larger than the size of molecules, and the viscosity exhibits non-Arrhenius behavior. Consequently, the plot of the time $\log \Gamma$ as a function of $1/T$ curves up significantly.

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For a given radius $a$, we solve the three coupled ordinary-differential equations numerically using the shooting method. Specifically, we assume some values of $J(a)$ and $da/da$, use the two boundary conditions $\sigma_1(\alpha) = \gamma/2a$ and $\mu(\alpha) = -\Omega/2a$, and numerically integrate the three ordinary differential Eqs. (21)–(23). We adjust the values of $J(a)$ and $da/da$ to satisfy the boundary conditions $\sigma_1(\alpha) = 0$ and $\mu(\alpha) = 0$. We plot the shrinking rate of the cavity as a function of the radius of the cavity (Fig. 7).

In the large-cavity limit, $a \gg \Lambda$, the cavity shrinks by viscous flow, and molecular incompressibility (24) reduces to $v(r) = (a/r)^2 da/da$. Newton's law of viscoelasticity applies $\sigma_1 - \sigma_0 = 2\eta_d(\alpha - \alpha_0) = -6\alpha a^2 r^{-3} da/da$. Inserting this expression into the equation of the balance of forces $\partial \sigma_1/\partial r + 2(\sigma_1 - \sigma_0)/r = 0$, integrating over the interval $r \in (\alpha, \infty)$, and using the boundary conditions $\sigma_1(\alpha) = \gamma/2a$ and $\sigma_1(\infty) = 0$, we obtain

$$\frac{da}{dt} = \frac{\gamma}{8\eta}$$

(25)

This expression agrees with the numerical solution of concurrent viscous flow and self-diffusion in the limit of large cavities (Fig. 7).

In the small-cavity limit, $a \ll \Lambda$, the cavity shrinks by self-diffusion, and molecular incompressibility (24) reduces to $\Omega(r) = (a/r)^2 da/da$. Inserting this expression into the model of self-diffusion $J = -(D/\Omega K) da/da$, integrating over the interval $r \in (a, \infty)$, and using the boundary conditions $\mu(a) = -\Omega/2a$ and $\mu(\infty) = 0$, we obtain

$$\frac{da}{dt} = \frac{-D_2 \Omega}{2K a^2}$$

(26)

This expression agrees with the numerical solution of concurrent viscous flow and self-diffusion in the limit of small cavities (Fig. 7).

The transition from shrinking mediated by self-diffusion to that mediated by viscous flow takes place when the radius of the cavity is comparable to the length $\Lambda$, and when the time of observation is on the scale of $\Gamma$ (Fig. 7). For a liquid that obeys the Stokes–Einstein relation, such as silica, the length $\Lambda$ is of molecular dimension (Fig. 6(a)), so that a cavity of any size larger than individual molecules shrinks by viscous flow. For a liquid that violates the Stokes–Einstein relation, the length $\Lambda$ can be much larger than molecular dimension as the temperature drops (Fig. 6(a)), so that a small enough cavity shrinks by self-diffusion.

6 Discussion

At a given temperature, a supercooled liquid forms dynamic structure of some length scale $\tilde{\xi}$ [27]. The dynamic structure has a lifetime $\tau$, after which the correlation within the structure disappears [41–43]. Any continuum theory should be interpreted with care when the geometric length and the time scale is close to, or smaller than, $\tilde{\xi}$ and $\tau$. The exact connection between this molecular picture and our continuum theory remains open.

We can compare our theory with the classical hydrodynamics. Our theory regards viscous flow and self-diffusion as concurrent, but distinct, kinetic processes. We describe the kinematics of a liquid by two independent fields: the velocity of markers, $v$, and the net flux of molecules, $N$. Both fields can be determined in macroscopic experiments. We define the self-diffusion flux by $J = -N \nabla \mu$. We describe kinetic models for viscous flow and self-diffusion separately. By contrast, in the classical hydrodynamics, the Navier–Stokes equations govern the velocity of the center of mass $v_m$, which relates to the net flux of molecules by $v_m = \Omega N$, leaving no room for self-diffusion to contribute to the governing equations [34].

The Navier–Stokes equations use Newton's law of viscous flow, and the Stokes–Einstein relation links the viscosity and self-diffusivity. As we have noted, experiments in recent decades have shown that the Stokes–Einstein relation is invalid for many supercooled liquids (Sec. 1).

For a body in three dimensions, our theory requires four independent boundary conditions. We have so far given boundary conditions that describe a surface under the influence of traction and surface tension, Eqs. (11) and (12). We can also apply boundary conditions of other types. For example, for a rigid, impermeable wall, we may prescribe the boundary conditions $v = 0$ and $J_n = 0$. The former is the same as the no-slip, no-penetration boundary conditions in classical hydrodynamics. The latter represents the condition that molecules in the interior of the liquid cannot plate out onto the surface, or vice versa. This boundary condition has been used to analyze concurrent electromigration and creep in solders [44].

The kinetic model (6) is reminiscent of Biot's model of poroelasticity [45]. In recent years, Biot's model has been adapted to analyze gels, where molecules are assumed to be incompressible [46–48]. The kinetic model is analogous to the model of poroelasticity once we replace the rate of deformation with strain, and replace the two viscosities with the two elastic moduli. In particular, when molecules are assumed to be incompressible, the bulk modulus in poroelasticity has nothing to do with elastic compressibility, but represents the ability of the material to absorb additional solvent under hydrostatic tensile stress [48]. In analogy with Biot’s model of poroviscosity, we may call the kinetic model (6) a model of poroviscosity.

Our continuum theory of supercooled liquids is closely related to concurrent creep and self-diffusion in solids [37,45]. We have neglected elasticity and adopted the simplest kinetic models. However, supercooled liquids may exhibit viscoelasticity. Our theory can be extended to describe concurrent self-diffusion and viscoelastic flow, similar to previous theories for amorphous systems [49,50]. One could, for instance, adopt a Maxwell-type viscoelasticity model with multiple relaxation times. We have also adopted a linear relation between the self-diffusion flux and the gradient of chemical potential, with a constant self-diffusivity. However, several authors reported the existence of crossover length (which scales with $\tilde{\xi}$) and time below which the self-diffusivity varying with the length of the observation [27,29,51]. As previously mentioned, our theory is not intended to analyze phenomena at a length below the size of the dynamic heterogeneity and a time shorter than the lifetime of the dynamic heterogeneity.

7 Conclusion

As the temperature drops, a supercooled liquid may be partially jammed: viscous flow slows down greatly, but self-diffusion does not slow down as much. We regard viscous flow and self-diffusion as distinct processes, and formulate a continuum theory to evolve a body of such a liquid under the influence of external forces, surface tension, and reservoirs of molecules. Because small pieces of the liquid exchange molecules and do not retain identities, we describe kinematics not by tracking the small pieces of the liquid, but by tracking the velocity of markers and the net flux of molecules. We describe viscous flow and self-diffusion using two independent kinetic models. The relative rate of the two kinetic processes defines a characteristic length that demarcates two types of behavior. Large objects evolve by viscous flow, and small objects evolve by self-diffusion. It is hoped that an experimental system will soon be identified to demonstrate this transition. Concurrent diffusion and viscous flow should also be important in other partially jammed systems, such as gels consisting of macromolecules and small-molecule solvents, and glasses consisting of dissimilar atoms.

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