NVU perspective on simple liquids' quasiuniversality

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The last half-century of research into the structure, dynamics, and thermodynamics of simple liquids has revealed a number of approximate universalities. This paper argues that simple liquids' reduced-coordinate constant-potential-energy hypersurfaces constitute a quasiuniversal family of compact Riemannian manifolds parametrized by a single number; from this follows the quasiuniversalities.

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I. INTRODUCTION

Simple liquids are traditionally defined as systems of spherically symmetric particles interacting via pairwise additive forces [1–16]. It is now known, however, that a number of such systems like the Gaussian core model [17–20], the Lennard-Jones Gaussian model [21], the Jagla and related discontinuous-force models [22–25], and other models [25–29] exhibit quite complex behavior. On the other hand, van der Waals *molecular* liquids are generally regular and "simple" in their properties [10,11]. In view of these facts we recently with Ingebrigtsen and Schrøder suggested [30] defining instead liquid simplicity from the property of strong correlations between equilibrium virial and potential energy fluctuations in the *NVT* ensemble [31–35]. This is how the term "simple liquid" is used below. In practice there is considerable overlap between the two definitions, for instance the Lennard-Jones liquid and related systems are simple in both senses. One notable difference is that realistic systems are only simple in the present meaning of the term in part of their phase diagram—simplicity does not apply near the critical point or at gas states (where different kinds of simplicity apply, of course). With regard to real liquids, it appears that most or all van der Waals bonded and metallic liquids are simple, whereas covalently bonded, hydrogen-bonded, and strongly ionic liquids are generally not simple because directional and competing interactions tend to weaken the virial potential-energy correlations [30].

Simple liquids are characterized by having isomorphs in their thermodynamic phase diagram [34]. An isomorph is an equivalence class of the following equivalence relation: two state points are isomorphic if all pairs of physically relevant microconfigurations of the state points, which trivially scale into one another, have the same configuration-space canonical probability. Among pair-potential liquids only inverse-power-law (IPL) systems have exact isomorphs, but all "strongly correlating" liquids have isomorphs to a good approximation [34].

Simple liquids' simple properties derive from the fact that the existence of isomorphs implies that their thermodynamic phase diagram is effectively one-dimensional instead of two-dimensional for all properties that are isomorph invariant. Examples of such properties are [34]: Newtonian and Brownian reduced-unit dynamics, reduced-unit static structure factors of any order, the excess entropy, the isochoric heat capacity. For any simple liquid solidification defines an isomorph in the phase diagram; this implies invariance along the melting

curve of, e.g., excess entropy, reduced viscosity, reduced heat conductivity, reduced diffusion constant, etc., as well as invariance of the Lindemann melting criterion [34,35].

The isomorph theory explains a number of previously noted regularities relating to a given simple liquid [34]. The theory cannot explain, however, the intriguing similarities between *different* simple liquids known for a long time. This is the focus of the present paper that views simple-liquid quasiuniversality from an *NVU* perspective.

NVU dynamics [36], which is inspired by earlier approaches to dynamics conserving [37–39] or limiting [40] the potential energy, is defined as geodesic motion on the constant-potential-energy hypersurface. If $\mathbf{R} \equiv (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is the $3N$-dimensional position vector describing a system of N identical particles, $\mathbf{R}_i$ the position vector at time step i, and $\mathbf{F}_i$ the corresponding $3N$-dimensional force vector, the *NVU* algorithm for tracing out a geodesic in simulation [36] is $\mathbf{R}_{i+1} = 2\mathbf{R}_i - \mathbf{R}_{i-1} - 2[\mathbf{F}_i \cdot (\mathbf{R}_i - \mathbf{R}_{i-1})]\mathbf{F}_i/\mathbf{F}_i^2$. As shown in Ref. [41], if m is the particle mass and Δt the time step of the Verlet algorithm $\mathbf{R}_{i+1} = 2\mathbf{R}_i - \mathbf{R}_{i-1} + \mathbf{F}_i(\Delta t)^2/m$, the *NVU* and Verlet algorithms are equivalent in the thermodynamic limit because the fluctuations of the *NVU*-force prefactor become insignificant as $N \to \infty$. Consequently, the radial distribution function, diffusion constant, coherent and incoherent intermediate scattering functions, etc., are identical in the thermodynamic limits of *NVU* dynamics and standard *NVE* or *NVT* Newtonian dynamics. This has been confirmed in computer simulations of both atomic and molecular models [36,41,42].

NVU dynamics provides an alternative view of a liquid's molecular dynamics. At any given state point all information about the liquid's structure and dynamics is encoded in its constant-potential-energy hypersurface Ω. If $\langle U \rangle$ is the average potential energy at the state point in question, this compact Riemannian differentiable manifold is defined by

$$\Omega \equiv \{\mathbf{R} \mid U(\mathbf{R}) = \langle U \rangle\}. \tag{1}$$

Ω is a so-called level set of the function $U(\mathbf{R})$. If standard periodic boundary conditions are employed, Ω is embedded as a $(3N-1)$-dimensional hypersurface in the $3N$-dimensional torus. The manifold Ω is not only defined for simple liquids, of course, but for all liquids, solids, and gasses.

The present paper considers systems of N identical particles in volume V. For simplicity we focus on systems interacting via pairwise additive forces. Thermodynamic quantities are excess quantities, i.e., in excess of the corresponding ideal gas quantities at the same density and temperature. Thus S is the excess extensive entropy ($S < 0$) and C_V the excess extensive

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isochoric specific heat, which we for simplicity refer to as just "entropy" and "specific heat". The corresponding intensive quantities are denoted by lower-case letters, i.e., $s \equiv S/N$ and $c_V \equiv C_V/N$. Reduced quantities are marked by a tilde.

It is clear from the results of many years of research into the liquid state that there is no such thing as exact universality, even among narrowly restricted classes like the IPL liquids. Thus any theory predicting liquid-state universality is too simple. The philosophy of this paper is that *approximate* universalities may provide useful insights. In this connection it is an obvious conjecture that genuine simple-liquid universality is approached as the spatial dimension increases towards infinity—if this is the case, we have for liquids a situation reminiscent to that of critical phenomena.

Section II argues for the existence of a quasiuniversal family of constant-potential-energy hypersurfaces for simple liquids, parametrized by just one parameter. The argument presented is not rigorous, but suggests one route for justifying quasiuniversality. The reader may choose to accept quasiuniversality in its *NVU* formulation, skip most of Sec. II, and proceed to the central part of the paper, Sec. III, which derives and discusses a number of consequences of the *NVU* formulation of simple liquids' quasiuniversality. Section IV returns briefly to what causes quasiuniversality. Finally, Sec. V gives a few concluding remarks.

II. A SINGLE-PARAMETER FAMILY OF HYPERSURFACES $\tilde{\Omega}(\lambda)$ COMMON TO ALL SIMPLE LIQUIDS

Any state point in the thermodynamic phase diagram of a liquid gives rise to a constant-potential-energy hypersurface Ω as defined in Eq. (1). At first sight these manifolds may appear to be completely characterized by the number $\langle U \rangle$, but actually the system volume V is a second parameter implicit in the definition of $U(\mathbf{R})$. Thus for liquids in general, Ω is described by two parameters, corresponding to the two independent thermodynamic variables.

Using reduced units means measuring length in units of $\rho^{-1/3}$, where $\rho \equiv N/V$ is the density, time in units of $\rho^{-1/3}\sqrt{m/k_BT}$, and energy in units of k_BT. The reduced $3N$-dimensional position vector is thus defined by $\tilde{\mathbf{R}} \equiv \rho^{1/3}\mathbf{R}$. Appendix A of Ref. [34] showed that a liquid has strong virial potential-energy correlations, i.e., is simple, if and only if the liquid has isomorphs to a good approximation, and that this happens if and only if the liquid's reduced constant-potential-energy hypersurfaces are (almost) invariant along certain curves in the phase diagram, the liquid's isomorphs. Thus for any given simple liquid a single number, λ, parameterizes the reduced constant-potential-energy hypersurfaces. We indicate this by writing

$$\tilde{\Omega} = \tilde{\Omega}(\lambda), \qquad (2)$$

where

$$\tilde{\Omega} \equiv \{\tilde{\mathbf{R}} \mid U(\rho^{-1/3}\tilde{\mathbf{R}}) = \langle U \rangle\}. \qquad (3)$$

The isomorph theory says nothing about how these hypersurfaces compare between different simple liquids. We now argue that the family $\tilde{\Omega}(\lambda)$ is quasiuniversal, i.e., approximately the same for all simple liquids.

The only systems with 100% correlation between *NVT* equilibrium fluctuations of potential energy and virial $(W(\mathbf{R}) \equiv -1/3 \sum_i \mathbf{r}_i \cdot \nabla_i U)$ are the inverse-power-law (IPL) systems, for which the potential energy scales with interparticle distance as r^{-n}. For these systems the 100% correlation follows from the identity $U(\lambda\mathbf{R}) = \lambda^{-n}U(\mathbf{R})$ and Euler's theorem for homogeneous functions. The last decade has given rise to a number of studies of how well experimental systems may be understood by reference to an IPL system (see, e.g., Refs. [43–47]). In these works the value of the IPL exponent n plays a central role because n determines how the system reacts to volume changes.

A simple liquid by definition has strong correlations between the *NVT* equilibrium fluctuations of W and U at its condensed-phase state points. Consequently, at each of it's strongly correlating state points the liquid behaves much like an IPL system. The value of the effective IPL exponent n generally varies with state point. For Lennard-Jones (LJ) liquids n is fairly constant, between 5 and 6 at typical liquid state points. For the 99.9% correlating "repulsive LJ liquid" defined by the pair potential $\epsilon[(r/\sigma)^{-12} + (r/\sigma)^{-6}]/2$ [48], the exponent varies from $n \cong 12$ at high densities to $n \cong 6$ at low densities. How much the effective IPL exponent varies throughout the phase diagram is of no importance for the arguments given below for $\tilde{\Omega}(\lambda)$ quasiuniversality, however.

In many respects IPL systems with different exponents have similar ("quasiuniversal") behavior. This was noted long time ago in relation to these systems' structure and DC dynamic properties expressed, e.g., via the diffusion constant [49–57]. During the last decade IPL quasiuniversality has come into focus again [58–60] and been extended to include general dynamic properties, termed "dynamic equivalence" by Medina-Noyola and coworkers. Dynamic equivalence has been established for Brownian [61,62] as well as Newtonian [63–66] dynamics.

Because structure and dynamics are both encoded in $\tilde{\Omega}$, IPL quasiuniversality follows if IPL systems have almost identical constant-potential-energy hypersurfaces. But why should this be the case? To understand this, we consider two infinitesimally close configurations with same n-IPL potential energy and argue that they for all m to a good approximation have the same m-IPL potential energy.

The m-IPL potential energy is given by $U_m = \epsilon_m \sum_{ij}(r_{ij}/\sigma)^{-m}$, in which r_{ij} is the distance between particles i and j. The change in U_m between two nearby configurations is given by

$$\delta U_m = -m\,\epsilon_m \sum_{ij}\left(\frac{r_{ij}}{\sigma}\right)^{-m-1}\frac{\delta r_{ij}}{\sigma}. \qquad (4)$$

By assumption $\delta U_n = 0$. Equation (4) implies

$$\frac{d}{dm}\left(\frac{\delta U_m}{m\,\epsilon_m}\right) = \sum_{ij}\left(\frac{r_{ij}}{\sigma}\right)^{-m-1}\ln\left(\frac{r_{ij}}{\sigma}\right)\frac{\delta r_{ij}}{\sigma}. \qquad (5)$$

The factor $\ln(r_{ij}/\sigma)$ in Eq. (5) does not vary dramatically because it is a logarithm. This factor is multiplied by $(r_{ij}/\sigma)^{-m-1}$ that varies a lot. Their product is dominated by a rather narrow range of interparticle distances, the most important of which is denoted by $\langle r \rangle_m$. This quantity depends on both m and the

state point. As a good approximation one can replace $\ln(r_{ij}/\sigma)$ by $\ln(\langle r\rangle_m/\sigma)$, and Eq. (5) now becomes, via Eq. (4),

$$\frac{d}{dm}\left(\frac{\delta U_m}{m\,\varepsilon_m}\right) = -\ln\left(\frac{\langle r\rangle_m}{\sigma}\right)\left(\frac{\delta U_m}{m\,\varepsilon_m}\right). \qquad (6)$$

Recall that $\delta U_n = 0$. Since $\delta U_m/(m\varepsilon_m) \equiv 0$ is the unique solution to this first-order differential equation that obeys $\delta U_n/(n\varepsilon_n) = 0$, it follows that $\delta U_m = 0$ for all m. Note that the approximation made by replacing $\ln(r_{ij}/\sigma)$ by a constant is questionable when $m \leqslant 2$, in which case no narrow range of interparticle distances dominates Eq. (5) because $\sum_j r_{ij}^{-m-1}$ diverges. Note also that, since the approximation relies on fluctuations in r_{ij} being small in the region where force is greatest, the argument can be expected to work better in higher dimensions. This supports the conjecture that genuine simple-liquid universality is approached as the spatial dimension increases towards infinity (Sec. I).

Within the above approximation the potential-energy functions $U_n(\mathbf{R})$ have the same constant-potential-energy hypersurfaces for all $n \geqslant 2$. Possibly, this applies for all n. Since a simple liquid at a given state point may be approximated by an IPL system, this means that all simple liquids have approximately the same constant-potential-energy hypersurfaces. In other words, to a good approximation one family of manifolds parametrized by a single parameter, $\tilde{\Omega}(\lambda)$, is common to all simple liquids. Each isomorph of a simple liquid corresponds to a particular value of λ, i.e., to one specific manifold $\tilde{\Omega}$.

III. CONSEQUENCES OF $\tilde{\Omega}(\lambda)$ QUASIUNIVERSALITY

This section derives consequences of the above justified central idea that the family of reduced constant-potential-energy hypersurfaces to a good approximation is common to all simple liquids.

A. Different IPL systems exhibit close similarities with respect to structure and dynamics, similarities that extend to all other simple liquids [49–76]

Because reduced-unit structure and dynamics are both encoded in $\tilde{\Omega}$, any two state points of two different IPL systems with same $\tilde{\Omega}$ have the same structure and dynamics. The extension of similarities to all simple liquids follows from $\tilde{\Omega}(\lambda)$ quasiuniversality. Note that the hard-sphere (HS) system also exhibits these quasiuniversalities because it is the $n \to \infty$ limit of n-IPL systems.

B. The Young-Andersen approximate scaling principle [63,64]

This principle states that if two liquids at two state points have approximately the same reduced radial distribution function $g(\tilde{r})$, they have approximately the same reduced dynamics. $g(\tilde{r})$ is determined from $\tilde{\Omega}$, so having the same $g(\tilde{r})$ implies having the same $\tilde{\Omega}$. This implies the same dynamics if the two liquids are simple.

C. Quasiuniversality of the order-parameter maps of Debenedetti and coworkers [77–79]

Plotting a translational order parameter versus an orientational order parameter for various state points leads to a one-dimensional curve for any simple liquid, because both order parameters are isomorph invariant [34]. The approximate identity between the order-parameter curves of different simple liquids follows from $\tilde{\Omega}(\lambda)$ quasiuniversality, because $\tilde{\Omega}$ determines both order parameters.

D. Excess entropy scaling [80–83]

Rosenfeld noted in 1977 that the reduced diffusion constants $\tilde{D}$ of different simple liquids have an approximately universal dependence on the (excess) entropy per particle, s [80]. This quasiuniversality applies also, e.g., for the reduced heat conductivity as a function of excess entropy [84]. For any simple liquid, since $\tilde{D}$ and s are both isomorph invariant, one quantity is a function of the other. Quasiuniversality of the function $\tilde{D}(s)$ is a consequence of the fact that $\tilde{D}$ and s are both encoded in $\tilde{\Omega}$ (the entropy $S = Ns$ is the logarithm of the area of $\tilde{\Omega}$).

E. The Lindemann melting criterion [85–87]

According to the Lindemann criterion a crystal melts when the vibrational mean-square displacement obeys $\sqrt{\langle \tilde{x}^2\rangle} \simeq 0.1$, where $\tilde{x} \equiv x\rho^{1/3}$ in which x is the atomic vibrational displacement from equilibrium in a fixed direction. The melting curve in the phase diagram is an isomorph [34,35], so melting takes place for a particular manifold $\tilde{\Omega}_c$ of the crystalline state. This manifold determines $\langle \tilde{x}^2\rangle$. Thus any simple crystal melts when $\langle \tilde{x}^2\rangle$ reaches a certain, quasiuniversal value. The Lindemann criterion and its generalizations [85,87,88] have been questioned on the grounds that they are single-phase criteria, whereas melting occurs when the crystal and liquid free energies are the same, so any melting criterion should refer to properties of both phases. One possible resolution of this paradox is that the Lindemann criterion does not, in fact, determine the melting line, but a spinodal at a slightly higher temperature where the crystal becomes mechanically unstable [89,90]. Alternatively, for the class of simple liquids $\tilde{\Omega}$ quasiuniversality implies that there is basically just one melting process, which takes place at state points where the crystalline manifold is $\tilde{\Omega}_c$. Any single-phase melting criterion referring to this manifold applies for all simple solids.

F. Freezing rules referring to the liquid

Quasiuniversality of such rules follows from the fact that $\tilde{\Omega}$ is quasiuniversal also on the liquid side of melting. For instance, this implies the Hansen-Verlet rule that a liquid crystallizes when the maximum value of the static structure factor upon cooling reaches 2.85 [50]. Likewise, any simple liquid's c_V is close to $3k_B$ at freezing [91,92] (it is shown below that c_V is encoded in $\tilde{\Omega}$). Other quasiuniversal melting rules similarly follow from $\tilde{\Omega}(\lambda)$ quasiuniversality [88]. Examples are the Andrade equation from 1934 implying a quasiuniversal value of the reduced melting point viscosity [93,94], the Raveche-Mountain-Streett criterion [95] of a quasiuniversal ratio between maximum and minimum of the radial distribution function at freezing, Lyapunov-exponent based criteria [89], or the criterion of zero higher-than-second-order liquid configurational entropy at crystallization [96]. Note that the theory also predicts a quasiuniversal constant-volume melting

entropy for simple liquids, which is consistent with experiment [91,97].

G. Algebraic closedness of the class of simple potentials

If $U_1(\mathbf{R})$ and $U_2(\mathbf{R})$ are both potentials of simple liquids, i.e., strongly correlating liquids, their sum and product are also simple: since at any density the functions $U_1(\tilde{\mathbf{R}})$ and $U_2(\tilde{\mathbf{R}})$ are both constant on the manifolds $\tilde{\Omega}(\lambda)$, this applies also for their sum and product. In particular, note the following property. Writing a simple pair potentials as $v(r) = \varepsilon\phi(r/\sigma)$, the derivative with respect to σ, $\partial v(r)/\partial\sigma$, is also a simple pair potential. Less trivial is the property that the product of two simple pair potentials defines the pair potential of another simple liquid (see Sec. IV).

H. Additivity of thermodynamic quantities

Suppose $U(\mathbf{R}) = U_1(\mathbf{R}) \pm U_2(\mathbf{R})$ in which $U_1(\mathbf{R})$ and $U_2(\mathbf{R})$ each define a simple liquid (the symbol $\pm$ signals that the below arguments apply for both signs). An example is when $U(\mathbf{R})$ is the LJ potential, $U_1(\mathbf{R})$ is an $n = 12$ IPL potential, and $U_2(\mathbf{R})$ is an $n = 6$ IPL potential. Then $U(\mathbf{R})$ defines a simple liquid, and as functions of density and entropy the corresponding temperatures obey $T(\rho,S) = T_1(\rho,S) \pm T_2(\rho,S)$ [98]. To show this, note that since the entropy determines $\tilde{\Omega}$, at given values of ρ and S the three constant-potential-energy manifolds are identical: $\Omega = \Omega_1 = \Omega_2$. This implies that $U(\rho,S) = U_1(\rho,S) \pm U_2(\rho,S)$, from which $T(\rho,S) = T_1(\rho,S) \pm T_2(\rho,S)$ follows via the definition of temperature $T \equiv (\partial U/\partial S)_\rho$. The thermodynamic relation $W = (\partial U/\partial\ln\rho)_S$ similarly implies additivity of virials: $W(\rho,S) = W_1(\rho,S) \pm W_2(\rho,S)$. The (excess) Helmholtz free energy F, (excess) Gibbs free energy G, and (excess) enthalpy H are likewise additive: $F(\rho,S) = F_1(\rho,S) \pm F_2(\rho,S)$, $G(\rho,S) = G_1(\rho,S) \pm G_2(\rho,S)$, $H(\rho,S) = H_1(\rho,S) \pm H_2(\rho,S)$.

As an application we note the intriguing "additivity of melting temperatures" first discussed by Rosenfeld [55]: Since crystallization for all simple liquids takes place at a certain value of the liquid entropy, at any given density one has $T_m = T_{m,1} \pm T_{m,2}$. An IPL liquid's melting temperature scales with density as $T_m \propto \rho^{n/3}$, so for the LJ liquid this implies an expression of the form $T_m = A\rho^4 - B\rho^2$ [48,55,99].

I. A partly quasiuniversal equation of state

It was recently shown that simple liquids have simple thermodynamics in the sense that temperature factorizes into a product of a function of entropy and a function of density, $T = f(s)h(\rho)$ [48]. We now show that the function $f(s)$ is quasiuniversal, i.e., all specific system dependence is in the function $h(\rho)$. This justifies writing the equation of state as

$$T = f_0(s)h(\rho). \qquad (7)$$

The point is that the specific heat, like the entropy, depends only on $\tilde{\Omega}$. This can be shown by first writing c_V in terms of fluctuations of canonical ensemble probabilities, and then relating the latter to microcanonical (NVU) probabilities, arguing as follows. According to Einstein $C_V = \langle(\Delta U)^2\rangle/k_B T^2$ in which the average refers to the canonical ensemble. In terms of the configuration-space probability $p \propto \exp(-U/k_B T)$

this implies $C_V = k_B\langle(\Delta\ln p)^2\rangle$. The canonical ensemble is realized from the microcanonical NVU ensemble in the standard textbook way by considering a small subvolume V_m of the total volume V. On average V_m contains m particles where $m/N = V_m/V$. Each configuration of m particles in V_m, $(\mathbf{r}_1,\ldots,\mathbf{r}_m)$, has a probability $p(\mathbf{r}_1,\ldots,\mathbf{r}_m)$ that can be calculated from the manifold Ω (or $\tilde{\Omega}$) by integrating out the remaining degrees of freedom. The set of configurations in Ω with precisely m particles in volume V_m is denoted by Ω_m. Integrating out the remaining degrees of freedom from the configurations in Ω_m determines $p(\mathbf{r}_1,\ldots,\mathbf{r}_m)$, so this function is given by Ω (or $\tilde{\Omega}$). From $c_V = k_B\langle(\Delta\ln p)^2\rangle/m$ it now follows that $c_V = c_V(\lambda)$. Since $c_V = (\partial s/\partial\ln T)_\rho$ and $s = s(\lambda)$, this implies that at fixed density $d\ln T = \phi_0(\lambda)d\lambda$ for some quasiuniversal function $\phi_0(\lambda)$. Thus, while for two simple liquids the temperatures corresponding to the same manifold $\tilde{\Omega}$ may well differ, the relative temperature changes (at fixed density) between different $\tilde{\Omega}$s are the same. By integration this implies that for each simple liquid one can write $T = \Phi(\lambda)T_*(\rho)$. Combining this with the equation of state $T = f(s)h(\rho)$ shows that the function $f(s)$ is determined by λ, i.e., by the manifold $\tilde{\Omega}$. In summary, $\tilde{\Omega}(\lambda)$ quasiuniversality implies that $f(s)$ is quasiuniversal, $f(s) = f_0(s)$. The function $T_*(\rho) = h(\rho)$ is not quasiuniversal; it reflects how the liquid's characteristic energy scale varies with density [100].

J. Quasiuniversality of simple liquids' specific-heat temperature dependence

Eliminating λ between $c_V(\lambda)$ and $T = f_0(s)h(\rho)$ where $s = s(\lambda)$ leads to $c_V = F_0(T/h(\rho))$ for some quasiuniversal function F_0. This is consistent with the Rosenfeld-Tarazona expression $c_V \propto T^{-2/5}$ [81], which as shown by computer simulations applies to a good approximation not just for all IPL systems, but also for LJ-type liquids and other simple liquids [101–106]. Note that $c_V \propto T^{-2/5}$ implies $s \propto -T^{-2/5}$ since $c_V = (\partial s/\partial\ln T)_\rho$ and $s \to 0$ for $T \to \infty$. This means that

$$f_0(s) \propto (-s)^{-5/2}. \qquad (8)$$

K. Quasiuniversal isochoric fragility of simple liquids

NVU dynamics give the same relaxation times as NVE or NVT dynamics, and thus the reduced relaxation time $\tilde{\tau}$ is determined by $\tilde{\Omega}$. This not only means that $\tilde{\tau}$ is a unique function of the excess entropy ("excess entropy scaling"), it also implies a quasiuniversal temperature dependence of $\tilde{\tau}$ at constant density: The quasiuniversal equation of state Eq. (7) implies that at any given density, entropy is a quasiuniversal function of temperature in the following sense: $s = s_0(T/h(\rho))$. This implies quasiuniversality of the form $\tilde{\tau} = \tilde{\tau}_0(T/h(\rho))$ [100]. In particular, at constant density Angell's fragility, $-d\log_{10}(\tilde{\tau})/d\ln T|_{T=T_g}$ [107], is a quasiuniversal number for any given cooling rate defining the glass transition temperature T_g [107–109]. This is reminiscent of the universal temperature dependence of viscosity discussed in 1996 by Kivelson *et al.* [110], although these authors subtracted the high-temperature activation energy before demonstrating data collapse. A quasiuniversal isochoric

fragility is consistent with simulations of De Michele *et al.*, who found that different IPL systems have the same fragility [111] (see, however, also Ref. [112]). The prediction is not entirely consistent with available experimental data, although there does seem to be a tendency that van der Waals liquids have isochoric fragilities not far from 50 [113]. In this connection it should be pointed out that it is an experimental challenge to determine the isochoric fragility accurately.

L. The hard-sphere system

Temperature plays no role for the configurational degrees of freedom of the hard-sphere (HS) liquid. Since only density is important, the HS thermodynamic phase diagram is effectively one-dimensional. This brings to mind isomorphs, the existence of which implies that a simple liquid's phase diagram is also effectively one-dimensional. Is the HS liquid simple? Since its potential energy is zero whereas the virial is not, the HS liquid is not simple in the sense of the term used here. In our opinion, the HS liquid should be thought of more as the $n \to \infty$ limit of an n-IPL system than as a physical system of its own right. When a simple liquid is modeled by a HS system, each of the liquid's isomorphs correspond to a specific value of the HS packing fraction η. This establishes a one-to-one correspondence $\lambda \leftrightarrow \eta$, which explains why simple liquids' entropy, reduced relaxation time, reduced viscosity, etc, have all been found to be quasiuniversal functions of the η parameter of the HS reference system.

Arguments for quasiuniversality were traditionally based on the fact that any simple liquid is well represented by the HS reference system [2,71,114–118]. In this view, the HS system is useful because it captures the essence of liquids' harsh repulsive forces [116,117,119]. This picture is intuitively appealing, but runs into problems when confronted with known facts. On the one hand, IPL quasiuniversality extends down to $n = 3$ or $n = 4$, in fact for some quantities down to $n = 1$ [80,120] where repulsions are quite smooth. On the other hand, there are several systems with harsh repulsive forces that exhibit anomalous behavior which is not captured by the HS system [21–29]. From the *NVU* perspective, the HS system's usefulness is not the *explanation* of simple liquids' quasiuniversality, but a *consequence* of it: since all n-IPL systems are quasiuniversal, the HS system inherits this property because it is the $n \to \infty$ limit of n-IPL systems.

M. Role of entropy

Theories relating a liquid's relaxation time to its entropy go back in time at least to Bestul and Chang, who in 1964 noted that the glass transitions of different glass-forming liquids occur at virtually the same value of the (excess) entropy [121]. Since the glass transition for a given cooling rate takes place when the liquid's relaxation time reaches a certain value, by generalization to other cooling rates this result implies that the relaxation time is a quasiuniversal function of entropy. Independently, based on computer simulations and approximate analytical arguments, Rosenfeld in 1977 proposed excess entropy scaling [80]. These two results, as well as the Adam-Gibbs model from 1965 in which entropy is also crucial [122–124], may appear counterintuitive since

entropy is global property: How can a global property control the relaxation time, which is determined as an average of (fairly) local properties? For simple liquids $\tilde{\Omega}(\lambda)$ quasiuniversality provides the following answer. Entropy *identifies* the relevant manifold $\tilde{\Omega}$, and $\tilde{\Omega}$ *determines* the relaxation time. Accordingly, other markers of $\tilde{\Omega}$ should be equally useful for determining the relaxation time, for instance the two-particle entropy that Dzugutov in 1996 suggested controls the relaxation time [88,125].

N. Characterizing $\tilde{\Omega}$ via the mean curvature

It is difficult to visualize a high-dimensional differentiable manifold. A primitive analog is a two-dimensional closed surface in ordinary three-dimensional space. Such a surface has two obvious geometric characteristics, its area and its mean curvature. The latter is conveniently quantified in terms of the average radius of curvature $\mathfrak{R}$, defined as the average inverse curvature. Both the area and the curvature concepts generalize to multidimensional Riemannian surfaces [126–128] (good introductions to this branch of mathematics are available, for instance Refs. [129–131]). The entropy is the logarithm of the manifold's area, but what is the physical interpretation of the average radius of curvature? To answer this we start from the configuration-space canonical ensemble expression [132–134],

$$k_B T = \frac{\langle (\nabla U)^2 \rangle}{\langle \nabla^2 U \rangle}, \tag{9}$$

which is derived by partial integration of $\int d\mathbf{R}\nabla \cdot \nabla U(\mathbf{R}) \exp[-U(\mathbf{R})/k_B T]$. Because of ensemble equivalence, the *NVU* configuration-space microcanonical ensemble may be used to calculate the averages in Eq. (9) as integrals over Ω. The inverse radius of curvature at a point on a d-dimensional hypersurface Ω is $\nabla \cdot \mathbf{n}/d$ [130,131] where $\mathbf{n}$ is the normal vector to Ω at the point in question, which is in our case given by $\mathbf{n} = \nabla U/|\nabla U|$. To leading order in $1/\sqrt{N}$ fluctuations of the denominator are insignificant. This implies for the inverse average radius of curvature $1/\mathfrak{R}$ (replacing $3N - 1$ by $3N$)

$$\frac{1}{\mathfrak{R}} = \frac{1}{3N} \frac{\langle \nabla^2 U \rangle}{\langle |\nabla U| \rangle}. \tag{10}$$

If the average length of the $3N$-dimensional force vector $\mathbf{F} = -\nabla U$ is denoted by F, because fluctuations are insignificant as $N \to \infty$, one has $\mathrm{F}^2 = \langle (\nabla U)^2 \rangle$ and Eqs. (9) and (10) imply

$$\mathfrak{R}\mathrm{F} = 3Nk_B T. \tag{11}$$

We see that a small radius of curvature corresponds physically to a large average force. As $N \to \infty$, $\langle \nabla^2 U \rangle \sim N$ and $\langle |\nabla U| \rangle \sim \sqrt{N}$ which implies $\mathfrak{R} \sim \sqrt{N}$. Likewise, $\mathrm{F} \sim \sqrt{N}$ as $N \to \infty$. If one defines $\tilde{\mathfrak{R}} \equiv \rho^{1/3}\mathfrak{R}/\sqrt{3N}$ and $\tilde{\mathrm{F}} \equiv \rho^{-1/3}\mathrm{F}/(\sqrt{3N}k_B T)$, these quantities are dimensionless, independent of N in the thermodynamic limit, and related by

$$\tilde{\mathfrak{R}}\tilde{\mathrm{F}} = 1. \tag{12}$$

Thus $\tilde{\Omega}$'s curvature is basically $\tilde{\mathrm{F}}$. This quantity provides an alternative to the entropy for characterizing $\tilde{\Omega}$.

Entropy and $\tilde{\mathrm{F}}$ both have simple geometric interpretations, but the curvature $\tilde{\mathrm{F}}$ has the advantage of being the average of a locally defined quantity. This implies that, since fluctuations

are unimportant in the thermodynamic limit, $\tilde{F}$ may be calculated from a short-time simulation. Note also that $\tilde{F}$ may be calculated from standard *NVE* or *NVT* simulations.

The quasiuniversal entropy dependencies observed for simple liquids' structure and dynamics may equally well be interpreted as quasiuniversal dependencies on $\tilde{F}$, the curvature of $\tilde{\Omega}$. Interestingly, this is the quantity that controls the relaxation time in the entropic barrier hopping theory of Schweizer and co-workers [135–137]—except for the fact that here the real forces are replaced by effective forces defined by the direct correlation function.

The connection between curvature and force is not surprising since motion on a flat manifold requires no force. Indeed, this point was made by one of the pioneers in connecting mechanics and differential geometry, Lipschitz, who wrote in 1873 [138]: "When a material particle, which is not influenced by any accelerating force, is bound to move on a given surface, the pressure exerted in each point of the trajectory is inversely proportional to the radius of curvature of this trajectory" (quoted from Ref. [139]). What happens is the following. When a particle (i.e., the system) moves on a perfectly smooth surface like $\tilde{\Omega}$, since no work is performed, the kinetic energy is conserved and thus the particle's velocity v is constant. This implies that the centripetal force keeping the particle on the surface, $\propto v^2/r$, is inversely proportional to the local curvature radius r.

For viscous liquids most motion is vibrational and one can estimate $\tilde{F}$ by adopting a harmonic approximation. Writing for the force on a particle $-Cx$, where x is the displacement away from its short-time average, implies $\langle F^2 \rangle \propto C^2 \langle x^2 \rangle$. Since $C\langle x^2 \rangle/2 = k_B T/2$ by equipartition, this means that if $a \equiv \rho^{-1/3}$ is the average interatomic spacing, $\langle \tilde{F}^2 \rangle \equiv \rho^{-2/3}\langle F^2 \rangle/[3N(k_B T)^2] \propto a^2/\langle x^2 \rangle \equiv 1/\langle \tilde{x}^2 \rangle$. Thus for viscous simple liquids the quantity $1/\langle \tilde{x}^2 \rangle$ identifies $\tilde{\Omega}$ and "controls" the relaxation time in the same sense as entropy does. This is an old idea [140–147], which is closely related to the shoving model and other elastic models for the temperature dependence of viscous liquids' relaxation time [109,148–150]. Note also that, since $1/\langle \tilde{x}^2 \rangle$ identifies $\tilde{\Omega}$, for simple liquids the crossover to activated transitions takes place at a quasiuniversal value of the reduced vibrational displacement $\langle \tilde{x}^2 \rangle$, as recently predicted by Lubchenko and coworkers from the random first-order transition theory [151,152].

O. Quasiuniversal interdependence of isomorph invariants

We showed above that the isomorph invariant c_V is encoded in $\tilde{\Omega}$. Generally, any isomorph invariant is encoded in $\tilde{\Omega}$. As a consequence, $\tilde{\Omega}(\lambda)$ quasiuniversality implies the following principle:

The relation between any two isomorph invariants is quasiuniversal.

From the $\tilde{\Omega}(\lambda)$ quasiuniversality perspective, excess entropy scaling is thus a special case of a much more general principle.

P. A single microconfiguration is enough to identify $\tilde{\Omega}$

Given an equilibrium configuration $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$ of a simple liquid the corresponding reduced vector $\tilde{\mathbf{R}}$ identifies the relevant manifold $\tilde{\Omega}$. From $\tilde{\Omega}$ all the system's isomorph invariants like entropy, specific heat, reduced relaxation time, reduced diffusion constant, reduced heat conductivity, reduced incoherent scattering function, etc, can be calculated. The reduced radial distribution function $g(\tilde{r})$ is also included, of course, being trivially given by $\tilde{\mathbf{R}}$. This illustrates again the Young-Andersen approximate scaling principle that for simple liquids knowing $g(\tilde{r})$ determines many other quantities.

IV. TOWARDS A THEORY OF SIMPLE LIQUIDS

Rosenfeld in 1977 justified IPL quasiuniversality by assuming that any n-IPL system is well represented by a HS reference system [80]. Since the HS system has just one parameter, this implies IPL quasiuniversality. Given the fact that the HS system is the $n \to \infty$ limit of n-IPL systems, this reasoning may be regarded as somewhat circular by assuming part of what is to be arrived at. Section II gave a non-circular argument for quasiuniversality, but we wish here to supplement it by another argument, suggesting a deeper reason for quasiuniversality.

We take as starting point that the pair potential defined by a simple exponentially decaying function of r is strongly correlating, i.e., defines a simple liquid. This remains to be thoroughly investigated and documented, but the recent simulations by Veldhorst *et al.* [153] of the Buckingham potential, which has a harsh exponentially repulsive term, certainly indicates that this is the case. Thus we assume that systems with pair potentials of the form $v(r) = \varepsilon \exp(-r/\sigma)$ are strongly correlating, at least in the part of the $(\sigma^3 \rho, k_B T/\varepsilon)$ parameter space defining dense fluid states. This means that the reduced constant-potential-energy hypersurfaces $\tilde{\Omega}$, which are *a priori* parametrized by the two dimensionless numbers $\sigma^3 \rho$ and $k_B T/\varepsilon$, constitute a single-parameter family $\tilde{\Omega}(\lambda)$, where $\lambda = \lambda(\sigma^3 \rho, k_B T/\varepsilon)$.

We proceed to argue that this one-parameter family characterizes all simple liquids. It is enough to show that all IPL pair potentials have in common these "exponential" reduced constant-potential-energy hypersurfaces. Now, following the reasoning of Sec. III G any linear combination of exponential pair potentials, $C_1 \varepsilon_1 \exp(-r/\sigma_1) + C_2 \varepsilon_2 \exp(-r/\sigma_2)$, has the same family of reduced constant-potential-energy hypersurfaces as a single exponential. By generalization, this implies via the mathematical identity

$$r^{-n} = \frac{1}{(n-1)!} \int_0^\infty x^{n-1} e^{-xr} dx \tag{13}$$

that the family $\tilde{\Omega}(\lambda)$ is common to all IPL potentials and, by implication, to all simple liquids. Thus, while the IPL functions constitute a convenient "basis set" for simple-liquid pair potentials, an even simpler basis set is provided by the exponential pair potentials. Interestingly, such potentials come out naturally from quantum mechanics; in fact, these were the first pair potentials discussed in the literature [154] (by Born, Born-Meyer, Morse, etc.).

The above implies that the pair potential of any simple liquid is equivalent to a sum of exponentials. Consequently, the product of any two simple pair potentials defines a simple pair potential.

V. CONCLUDING REMARKS

We have shown that the several quasiuniversalities found for simple liquids' structure, dynamics, and thermodynamics follow from one fundamental quasiuniversality, namely the existence of a common single-parameter family of reduced constant-potential-energy hypersurfaces $\tilde{\Omega}(\lambda)$. This "$\tilde{\Omega}(\lambda)$ quasiuniversality" was justified for IPL systems in Sec. II by a nonrigorous argument, but it can also be arrived at from the fact that the exponentially repulsive pair potential is simple in a large part of its parameter space (Sec. IV). IPL quasiuniversality generalizes to all simple liquids by virtue of their property of having strong correlations between *NVT* equilibrium virial and potential-energy fluctuations.

It is important to emphasize again that there is no exact universality among simple liquids, only *approximate* universality. A demonstration of this is provided by the well-known fact that the crystalline state is only face-centered cubic for IPL exponents larger than seven (below which it is body-centered cubic). Another point to be emphasized is that, in contrast to mode-coupling theory and other fully renormalized theories of liquid dynamics, the present approach does not distinguish between short and long time scales—quasiuniversality applies on vibrational time scales and longer.

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