

A conformal solution theory for the energy landscape and glass transition of mixtures

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Abstract

We apply conformal solution theory and extend to mixtures a recently derived equation of state for glass-forming liquids. The equation of state is based on the statistical properties of the multidimensional potential energy surface as a function of a macroscopic system's degrees of freedom (energy landscape), and allows the calculation of an ideal glass transition locus, along which the configurational entropy vanishes. The landscape mixing approach yields an expression for the composition dependence of the mixture's glass transition. A non-monotonic composition dependence is predicted by the theory for the glass transition of a binary Lennard–Jones mixture. The composition dependence of species diffusivities obtained by molecular dynamics simulation of this mixture is consistent with the theoretical prediction.

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1. Introduction

Glasses are disordered materials that lack the periodicity of crystals but behave mechanically like solids (e.g., they exhibit proportionality between stress and deformation) [1]. The glassy state is ubiquitous in nature and in technology. It is important in the processing of foods [2], the commercial stabilization of labile biochemicals [3], and the preservation of insect life under extremes of cold or dehydration [4]. Ordinary window glass is probably the best-known example of an engineered amorphous solid. Optical fibers are made of very pure amorphous silica, occasionally carefully doped. Most engineering plastics are amorphous solids, as are some metallic glasses and alloys of interest because of their soft magnetism and corrosion resistance [5]. The silicon used in many photovoltaic cells is amorphous, and it is likely that the most common form of water in the universe is glassy [6].

The most common route to the glassy state is by cooling a liquid fast enough to avoid crystallization (supercooling). The properties of a glass are thus intimately related to those of the liquid from which it is formed by rapid cooling. Understanding quantitatively the extraordinary viscous slowdown that accompanies supercooling and glass formation is a major scientific challenge. What makes the problem difficult is the apparent absence of an obvious structural signature associated with the precipitous sluggishness of structural relaxation (e.g., the viscosity of *o*-terphenyl increases by 11 orders of magnitude across a 50 K range [7]).

An intriguing aspect of supercooled liquid behavior is the apparent connection between dynamics and thermodynamics. This manifests itself in the rapid decrease upon supercooling of the entropy excess that liquids possess over their corresponding crystal phase. This situation was first pointed out by Simon [8] and subsequently documented for several liquids by Kauzmann in his classic review on the glassy state [9]. The consequences of this impending entropy crisis and its potential violation of the Third Law underlie all thermodynamic thinking about the glass transition (e.g., [1]). Experimentally, the coupling between dynamics and thermodynamics is revealed most clearly by the Adam–Gibbs formula [10] (see Section 2), which links the rate

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of structural relaxation to the configurational entropy, and provides a faithful representation of laboratory observations over many decades of structural relaxation time [11].

The interactions operating among the atoms, ions, or molecules of any material system play a dominant role in determining its static and dynamic properties. Dilute gases are easy to analyze, in that interactions occur primarily in isolated small clusters (pairs, triplets, etc.). But the situation is qualitatively different and far more challenging for fluid and solid condensed phases, in which virtually every particle remains in constant contact with many neighbors. In particular, this is true of supercooled liquids and glasses. Under these circumstances it is natural to consider the full N -body potential energy as a function of the degrees of freedom for the system of interest (e.g., $3N$ coordinates for an atomic system), and to seek to describe the manner in which its details generate the wide variety of collective thermodynamic and kinetic phenomena that have been experimentally observed in condensed matter [12]. The statistical mechanical approach based on the properties of the potential energy surface is commonly referred to as the energy landscape formalism [13,14]. It plays a central role in modern theories of glass formation [1].

Although the energy landscape formalism has been widely used in computer simulation studies of single-component glass-formers as well as mixtures (e.g., [15]), we are not aware of any theoretical work aimed at predicting mixture behavior from knowledge of single-component landscape properties. In this work, we develop a theory for the mixing of energy landscapes of two components based on conformal solution theory, and obtain an expression for the glass transition of a mixture based on pure component information. While the application to glasses is new, the idea of developing and using theories based on thermodynamics and statistical mechanics to predict mixture properties from pure component data is an area in which John Prausnitz has made the key contributions that defined much of chemical engineering thermodynamics research over the past 50 years (e.g., Refs. [16–19]).

John Prausnitz has had a lasting impact on the careers of two of us (AZP and PGD). AZP recalls vividly an intense exchange of correspondence between John Prausnitz and his doctoral advisor, Robert Reid at MIT, related to a paper on mixing rules for cubic equations of state [20] that did not conform to the appropriate limiting theoretical expressions and has since been shown to lead to unphysical results for higher order mixtures [21]. John was justly critical of this early work and helped steer the author to other productive directions through highly stimulating discussions and exchanges of letters over the past 20 years. PGD would like to share the words he read on the occasion of John Prausnitz's 70th birthday celebration. Reproduced in Appendix A, these words attempt to convey John's unique role in the chemical engineering thermodynamics community.

This paper is structured as follows. Section 2 reviews the basic elements of the energy landscape formalism, invokes conformal solution theory to derive a landscape-based equation of state for fluid mixtures, and applies these ideas to the problem of calculating a mixture's glass transition locus from pure component information. Section 3 presents computational results for

the glass transition locus of a binary mixture of Lennard–Jones particles, and compares the numerical findings with predictions from the theory presented in Section 2. Conclusions and suggestions for future work are included in Section 4.

2. Theory

The potential energy landscape (PEL) for a molecular system is defined as its potential energy Φ as a function of its degrees of freedom [13,22]. For atomic systems, the PEL depends on the center-of-mass coordinates \mathbf{r}^N and therefore constitutes a hypersurface in $3N + 1$ dimensions. The main focus of energy landscape theory is the elucidation of the constraints, hierarchies, and statistical properties of such surfaces, and the implications of these characteristics on the system's macroscopic behavior [14]. The most prominent features of energy landscapes are their numerous local potential energy minima, whose number scales exponentially with system size [24]. These “inherent structures” correspond to mechanically stable configurations in which the net force on every molecule is zero. A “basin of attraction” surrounding each inherent structure is uniquely defined through a steepest-descent procedure, and the collection of all basins exactly tiles the entire configuration space. Such basins represent local traps to which the system can become confined for appreciable periods of time at low temperatures.

The PEL formalism permits an exact transformation of the canonical partition function in terms of the depth distribution of inherent structures and the free energy associated with vibrations of the system around minima of a given depth. We briefly review this formalism here, but refer the reader to the recent review of Sciortino [23] for further details. For single-component systems, the landscape expression for the Helmholtz free energy A is given by [13]:

$$\frac{A}{N} = \phi^* - T s_{\text{conf}}(\phi^*, \rho) + a_{\text{vib}}(T, \phi^*, \rho) \quad (1)$$

where N is the number of particles, ϕ is the per-particle inherent structure energy, and ρ is the system density. The temperature- and density-dependent parameter ϕ^* is the value of ϕ which minimizes this expression and provides the energy of inherent structures most frequently explored by the system. The special functions s_{conf} and a_{vib} contain statistical measures of the energy landscape, and are termed the configurational entropy and vibrational free energy, respectively. For structureless particles, these two functions are given by the following expressions:

$$\frac{\partial \Omega_{\text{IS}}}{\partial \phi} = C e^{N s_{\text{conf}}/k_{\text{B}}} \quad (2a)$$

$$e^{-\beta N a_{\text{vib}}} = \Lambda^{-3N} \left\langle \int_{\Gamma_k} e^{\beta[\Phi(\mathbf{r}^N) - \Phi_k]} d\mathbf{r}^N \right\rangle_{\phi} \quad (2b)$$

where C is a constant with units of inverse energy whose value has no effect on thermodynamics, $d\Omega_{\text{IS}}$ gives the number of inherent structures residing at the per-particle potential energy $\phi \pm d\phi/2$, Λ is the thermal de Broglie wavelength, Γ_k denotes the configuration space of the basin for minimum k , Φ_k is the potential energy of minimum k , and the average in Eq. (2b) is

performed over all inherent structures (minima) with a specified value of ϕ . In physical terms, s_{conf} measures the number of inherent structures of a given depth in the landscape, while a_{vib} gives the free energy of the system when confined to an average basin of specified depth. For supercooled liquids, it is important to note that the counting embedded in Ω_{IS} in Eq. (2a) and the basin-averaged integral in Eq. (2b) exclude those inherent structures whose associated configurations contain crystalline regions [25].

The usefulness of the energy landscape equations in describing the behavior of supercooled liquids stems from the separation of the inherent structure (configurational) and vibrational contributions to the free energy. At low temperatures, the dynamic trajectory of a supercooled liquid consists of long periods of rattling within local potential energy minima, punctuated by infrequent hops among basins in the landscape. As a result, intrabasin equilibration at the environmental temperature occurs significantly faster than movement among adjacent basins (corresponding to major configurational rearrangements). If the temperature is sufficiently lowered, the latter time scale grows longer than the observation time, and the system remains confined to a single basin from the laboratory perspective. At this point, a glass has formed. Similarly, when Eq. (1) is evaluated for supercooled liquids, decreases in temperature result in lower values of ϕ^* and correspondingly smaller values of $s_{\text{conf}}(\phi^*, \rho)$. That is, the system explores deeper and less numerous potential energy wells as thermal energy is removed.

Although the preceding equations constitute a purely thermodynamic treatment of energy landscapes, an a posteriori connection to macroscopic dynamics can be established through the Adam–Gibbs equation [10]:

$$\tau = \tau_0 \exp\left(\frac{A}{Ts_{\text{conf}}}\right). \quad (3)$$

Here, τ is a characteristic relaxation time (comparable, for example, to a viscosity or inverse diffusivity), τ_0 is a prefactor weakly dependent on temperature, and A is a constant with units of energy. The Adam–Gibbs expression is reminiscent of an Arrhenius law with a variable activation energy given by A/s_{conf} , such that super-Arrhenius behavior occurs as the temperature is lowered since s_{conf} also decreases with T . In their original derivation, Adam and Gibbs did not identify s_{conf} with the landscape statistic given by Eq. (2a), but rather linked it with the broad notion of a “cooperatively rearranging region” of molecules within the supercooled liquid. Though they did not provide a method for identifying such regions within real systems – which precludes a rigorous connection of their work with landscape statistics – Eq. (3) has been remarkably successful in describing the relationship between measured dynamic data and the landscape-defined configurational entropy in detailed computational studies [26–28]. These results therefore suggest that the quantity $s_{\text{conf}}(\phi^*, \rho)$, which measures the degeneracy of inherent structures explored by the system at a given temperature, is a key determinant of liquid-state dynamics.

An interesting possibility afforded by the form of the Adam–Gibbs equation is that of an ideal glass (IG) transition, a finite temperature T_{IG} at which the configurational entropy vanishes

and the relaxation time scale accordingly diverges. Of course, such a transition can never be realized experimentally since it is always preempted by the usual (kinetic) glass transition, but the limiting notion of a thermodynamic ideal glass has provided a useful and fruitful framework for the analysis and interpretation of glass formation phenomena. In terms of landscape properties, the existence of an ideal glass transition hinges on the ϕ -dependence of the configurational entropy. Presuming the existence of a minimum-energy amorphous configuration with energy ϕ_{min} , an IG transition exists if the derivative $\partial s_{\text{conf}}/\partial\phi$ evaluated at ϕ_{min} is finite. Although there has been some argument as to whether such behavior is realistic for liquids [25,29], an apparent IG transition extrapolated from higher temperature data often serves as a useful locus for demarcating the onset of glassy behavior [30,31]. In this sense, the IG transition provides a convenient theoretical tool for locating such conditions. We can therefore make significant progress in theories for T_{G} assuming that the (hypothetical) ideal glass transition is sufficiently similar to the kinetic glass transition of the system at hand. That is, we assume that the IG locus in the (T, P) plane lies sufficiently close to the boundary between the manifest equilibrium liquid and nonequilibrium glassy behavior [30,31].

The power of the PEL formalism is that, when used in conjunction with the Adam–Gibbs equation, it permits the development of statistical-mechanical models which yield thermodynamic properties of the liquid as well as dynamical information (e.g., the glass transition). Our goal here is to use such a model to capture changes in the glass transition temperature with mixture composition, at constant pressure. In the text below, we begin by deriving the equation of state of the ideal glass phase for a simple one-component fluid consisting of soft-sphere repulsions and mean-field attractions. Subsequently, we assume one-fluid mixture behavior and apply conformal relations to map mixture properties onto the single-component theory. Our final step entails a manipulation of the equations to express T_{IG} at constant pressure conditions.

One of the most frequently studied energy landscape models is the soft-sphere/mean-field (SSMF) system, which consists of particles interacting through an inverse-power repulsion and a mean-field, density-dependent attraction [31–37]. This system is the landscape equivalent of the venerable van der Waals model of fluids, and constitutes a minimalist description of supercooled liquids. The SSMF system is particularly convenient to analyze in terms of its energy landscape, since the expressions for s_{conf} and a_{vib} can be evaluated explicitly [31,32]:

$$s_{\text{conf}}(\phi, \rho) = k_{\text{B}}\sigma_{\infty} \left[1 - \left(\frac{\phi - \gamma_{\infty}\rho^{n/3} + a\rho}{\rho^{n/3}\Delta\gamma} \right)^2 \right] \quad (4a)$$

$$a_{\text{vib}}(T, \phi, \rho) = 3k_{\text{B}}T \ln \left(\frac{\Theta_{\text{E}}}{T} \right) \quad (4b)$$

where n is the repulsive exponent, Θ_{E} is an Einstein frequency characteristic of amorphous normal-mode vibrations, and σ_{∞} is such that $\exp(N\sigma_{\infty})$ gives the total number of inherent structures. The parameter γ_{∞} , when multiplied by $\rho^{n/3}$, gives the average energy of inherent structures; similarly, $\rho^{n/3}\Delta\gamma$ gives the difference between the mean and minimum inherent structure

energies. Several assumptions have entered into the derivation of these equations. Specifically, the vibrational contribution is modeled in the harmonic approximation and is assumed to be independent of basin depth, both valid at very low temperatures. More importantly, the functional dependence of s_{conf} on ϕ is assumed to be quadratic, which corresponds to a Gaussian energy distribution of inherent structures. The Gaussian approximation is frequently invoked to describe model energy landscapes, and has been found in computational studies to accurately render the thermodynamics properties of supercooled liquids in the range of temperatures accessible to simulations [38–42]. However, the Gaussian distribution must be truncated artificially at the minimum amorphous energy ϕ_{min} . This has the effect of introducing an ideal glass transition into the thermodynamics of the SSMF model; its locus is given by [32]:

$$T_{\text{IG}}(\rho) = \frac{\rho^{n/3} \Delta\gamma}{2k_{\text{B}}\sigma_{\infty}}. \quad (5)$$

With Eqs. (1), (4a) and (4b), the free energy of the SSMF system is completely defined and all of its thermodynamic properties are readily extracted from free energy derivatives. In a previous study [32], the equation of state predicted by the SSMF model was fitted to results for the equilibrated Lennard–Jones fluid, yielding values for the model parameters, and was found to accurately capture the behavior of the pressure at temperatures ranging from $T = 0.7$ to 1.3 and at densities above 0.90 (units expressed in terms of the Lennard–Jones length and energy parameters, σ and ϵ). The success of the SSMF model for this fit suggests it may also provide an accurate description of pressure effects on the lower-temperature supercooled liquid, and particularly the glass transition locus. Of relevance to the present study, therefore, is the SSMF equation of state for the ideal glass transition locus, given by:

$$P_{\text{IG}}(\rho) = \left(m(\gamma_{\infty} - \Delta\gamma) + (n+2) \frac{\Delta\gamma}{4\sigma_{\infty}} \right) \rho^{m+1} - a\rho^2 \quad (6)$$

where m denotes $n/3$. Alternatively, substitution of Eq. (5) yields the temperature version of the IG pressure:

$$P_{\text{IG}}(T) = bT^{1+1/m} - cT^{2/m},$$

$$b = \left(m(\gamma_{\infty} - \Delta\gamma) + (n+2) \frac{\Delta\gamma}{4\sigma_{\infty}} \right) \left(\frac{2k_{\text{B}}\sigma_{\infty}}{\Delta\gamma} \right)^{1+1/m},$$

$$c = a \left(\frac{2k_{\text{B}}\sigma_{\infty}}{\Delta\gamma} \right)^{2/m} \quad (7)$$

where the constants b and c have been introduced for clarity. It is useful to express b and c in terms of energy (ϵ) and length scales (σ) of the liquid, such that

$$b = \bar{b}\epsilon^{-1/m}\sigma^{-3} \quad (8a)$$

$$c = \bar{c}\epsilon^{-2/m}\sigma^{-3} \quad (8b)$$

where \bar{b} and \bar{c} are pure numbers. Fig. 1 shows the effects of particle size and energy on the predicted ideal glass transition temperature.

Our goal is to understand the dependence of the glass transition temperature on system composition, at constant pressure.

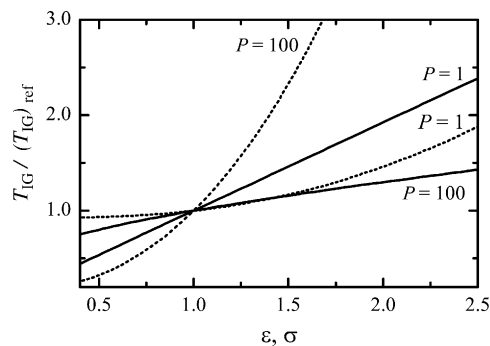


Fig. 1. Effect of particle size (σ) and interaction energy (ϵ) on the ideal glass transition, as given by Eqs. (7) and (8) using values for parameters \bar{b} and \bar{c} determined from previous work [32]. All quantities are expressed in dimensionless units. The dotted lines correspond to varying σ with $\epsilon = 1$ and the solid lines to varying ϵ with $\sigma = 1$. Two pressures for each case are provided for comparison. The reference quantity $(T_{\text{IG}})_{\text{ref}}$ corresponds to the predicted ideal glass transition temperature for $\epsilon = 1$, $\sigma = 1$ at the given pressure.

Focusing on the ideal glass transition specifically, we are faced with a thermodynamic problem to which it becomes possible to apply standard solution theories to the energy landscape equations. In the present investigation, we employ a one fluid-model appropriate to spherically symmetric molecules that treats mixtures as single component systems of effective, composition-dependent energy and length scales. We assume the specific relations:

$$\epsilon_{\text{eff}} = \sum_i \sum_j x_i x_j \epsilon_{ij} \quad (9a)$$

$$\sigma_{\text{eff}}^3 = \sum_i \sum_j x_i x_j \sigma_{ij}^3 \quad (9b)$$

where x denotes mole fraction, the sums extend over all species, and ϵ_{ij} and σ_{ij} are the energy and length scales characterizing the interactions between molecules of species i and j . Our choice of these particular relations is motivated by the desire to include the cross-terms explicitly, which accommodates systems that exhibit significant deviations from standard combining rules (e.g., the system studied in our numerical calculations below). The effective parameters ϵ_{eff} and σ_{eff} , in conjunction with the dimensionless constants \bar{b} and \bar{c} , can be substituted directly into Eqs. (8) and then (7) to yield the pressure along the ideal glass transition locus. For a fixed pressure, the composition dependence of the glass transition can then be extracted by solving this expression for T_{IG} as the x_i (and hence ϵ_{eff} and σ_{eff}) are varied. In general, this necessitates the solution of a nonlinear equation in T_{IG} .

For simplicity, we consider the case of a binary mixture of particles. To find the change in the ideal glass transition temperature at constant pressure for a dilute mixture of component 2 in component 1, we must solve the following equation for T_{IG} :

$$P_{\text{IG}}(T_{\text{IG},1}; \epsilon_{11}, \sigma_{11}) = P_{\text{IG}}(T_{\text{IG}}; \epsilon_{\text{eff}}, \sigma_{\text{eff}}) \quad (10)$$

where $T_{\text{IG},1}$ is the IG transition temperature of pure component 1. An analogous equation exists for the case in which component 2 is the reference pure component, with a dilute amount

of component 1. For both equations, the limiting behavior of T_{IG} at infinite dilution can be extracted through substitution of Eqs. (7)–(9), and series expansion in T_{IG} . The simplest functional form for T_{IG} which matches the values and derivatives with respect to composition at both pure components is a cubic equation:

$$T_{IG}(x_2) = T_{IG,1} + h_1 x_2 + [3(T_{IG,2} - T_{IG,1}) - (2h_1 + h_2)]x_2^2 + [(h_1 + h_2) + 2(T_{IG,1} - T_{IG,2})]x_2^3 \quad (11)$$

where the parameters h_1 and h_2 are given by:

$$h_1 \equiv \frac{\partial T_{IG}}{\partial x_2} \quad (x_2 = 0) \quad (12a)$$

$$h_2 \equiv \frac{\partial T_{IG}}{\partial x_2} \quad (x_2 = 1) \quad (12b)$$

The cubic polynomial can be thought of as a two-point Taylor expansion, such that the values and first derivatives of the $T_{IG}(x_2)$ curve match the first-order expansions at the pure component limits. Higher order expansions are possible, each resulting in odd polynomials for T_{IG} . Our initial work suggests that a third-order polynomial is sufficient to reproduce the full, non-linear solution to good accuracy in most cases. To solve for h_1 and h_2 , we substitute Eqs. (7)–(9) into Eq. (10) and take the derivative with respect to x_2 . The final results are:

$$h_1 = \frac{c_1 T_{IG,1}^{1/m} [(2-m)s_1 + mt_1] - b_1 T_{IG,1} [s_1 + mt_1]}{(m+1)b_1/2 - T_{IG,1}^{1/m-1}} \quad (13a)$$

$$h_2 = -\frac{c_1 T_{IG,2}^{1/m} [(2-m)s_2 + mt_2] - b_2 T_{IG,2} [s_2 + mt_2]}{(m+1)b_2/2 - T_{IG,2}^{1/m-1}} \quad (13b)$$

where b_i and c_i are the values of b and c evaluated using the energy and length scales of pure component i , $s_i = 1 - \epsilon_{12}/\epsilon_{ii}$, and $t_i = 1 - \sigma_{12}^3/\sigma_{ii}^3$. Thus, Eqs. (11) and (13) constitute a prediction for the glass transition temperature in binary mixtures as a function of composition. The prediction takes as input the landscape-defined dimensionless parameters \bar{b} and \bar{c} , the pure-component glass transition temperatures, and the set of interaction parameters ϵ_{ij} and σ_{ij} . Based on a fit of the landscape-derived equation of state to the Lennard Jones fluid [32], appropriate values of the dimensionless parameters are $\bar{b} = 51.3$ and $\bar{c} = 25.0$. In addition, the cross-parameters ϵ_{12} and σ_{12} might be estimated from the pure-component interactions using an appropriate combining rule. We note that, although this expression has been derived at constant pressure, P drops out of the equations entirely, its effect contained in the pure component T_{IG} values.

3. Simulation results

For our numerical calculations, we examine a well-studied glass-forming mixture of Lennard–Jones particles [43], whose mutual interactions roughly mimic the behavior of metal–metalloid alloys [44]. The system consists of two kinds of particles, A and B, with equal masses but asymmetric sizes and interaction energies. At a composition of 80% A particles and 20% B particles, this system possesses a deep eutectic, is readily

supercooled, and has been shown to exhibit pronounced glassy dynamics [43,45–47]; these properties have made the binary mixture a standard model for the study of supercooled liquids. In the present study, all units are expressed in terms of the A–A interaction parameters.

We conduct isobaric molecular dynamics simulations of the mixture over a composition range of 10–90% A particles, in 10% increments. The Martyna, et al. implementation of the Nose–Hoover equations [48] is used to thermostat the system and maintain the pressure at $P = 3.2$. The total number of particles is kept at 250, and the time step employed is $\delta t = 0.003$. For each composition, we initially thermalize the system at the high temperature of $T = 2.0$ and cool it in decrements of 0.02–0.1 towards absolute zero. Data at each temperature is obtained by first equilibrating the system for 2 million time steps and subsequently performing a 5 million step production run for the calculation of dynamic quantities. The self-diffusivities of both species are determined using the Einstein relation with 100 time origins separated by 10.0 time units.

For each simulation run, the trajectory and final configurations are examined for evidence of crystallization. Data taken from temperatures at which the system has crystallized is discarded. The low-temperature diffusivities of both types of particles are fit to Vogel–Tamman–Fulcher (VTF) forms at each composition [49]:

$$D = D_0 \exp\left(\frac{B}{T_0 - T}\right) \quad (14)$$

where D_0 , B , and T_0 are the fitted constants. The fitting procedure consists of minimizing the squared error in predictions for $\ln D$ for all state points for which $\ln D \leq -3$. Since our interest is in the glass transition, we investigate the temperature T_0 as an indicator of glassy behavior. T_0 corresponds to a vanishing diffusivity according to Eq. (14), and is closely related to (but not necessarily identical to) the ideal glass transition. The VTF regression for each species yields an estimate for T_0 . For our analysis, we consider the mole-fraction-weighted average of the two estimates: $T_0 = x_A T_{0,A} + x_B T_{0,B}$, where the subscripts “A” and “B” denote the estimates for T_0 based on diffusivities of that species in the mixture (i.e., they are not pure component values). We also compute isodiffusive loci for the mixture, that is, points in the temperature–composition plane along which the diffusivity of particles is constant. Since many of our compositions crystallize at lower temperatures, the isodiffusive lines are only calculated for $\ln D \geq -4$.

Not all compositions can be supercooled to very low temperatures, owing to crystallization events. This is especially problematic for the pure-component cases (for which T_{IG} is needed as per Eqs. (11) and (13)), as the Lennard–Jones system readily crystallizes in simulation. For the case of pure A, we use results from a previous study by Brakkee and de Leeuw to estimate T_0 [50]. In that work, extensive molecular dynamics trajectories for a Lennard–Jones system at $P = 3.2$ were performed, and runs were carefully monitored for crystallization and pruned accordingly. These authors calculated a mode-coupling temperature – a point where slow activated processes begin to dominate structural relaxation – at $T = 0.27$. The same characteris-

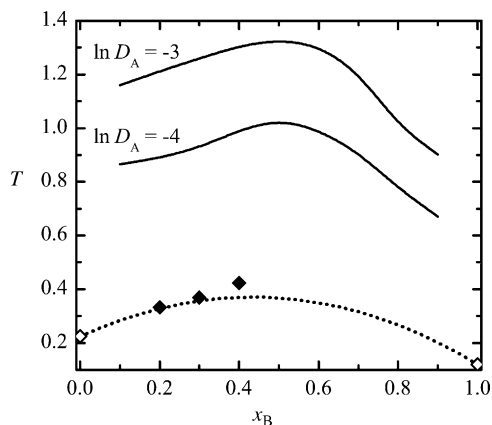


Fig. 2. Diffusive loci in the $T - x$ plane, as measured from simulation and predicted by the landscape-based theory. The upper curves correspond to lines of constant diffusivity of the A particles. The lower curve is the theoretical prediction for the ideal glass transition, given by Eq. (11). The filled diamonds represent T_0 values from the VTF regression for those systems which did not crystallize during simulations at low temperatures. The hollow diamonds represent estimated T_0 values for the pure components.

tic temperature has been found to be $T = 0.435$ in the binary mixture of 80% A particles, although at a slightly lower pressure [45]. We use the ratio of these two temperatures to scale the known T_0 at $x_A = 0.8$ to its corresponding value for pure A. To estimate the same parameter for pure B, we scale T_0 by the ratio of the ideal glass transition temperatures at the two pure component limits (Eq. (5)). These are both coarse approximations of the pure component T_0 values, but they still provide a reasonable basis for assessing the performance of the theory.

Fig. 2 shows the results from our molecular dynamics simulations. Isodiffusive lines for the A particles clearly reach a maximum at roughly equimolar composition, with obvious asymmetry in the trends towards both limits of infinite dilution. Three compositions were able to be supercooled sufficiently to yield an estimate for T_0 : $x_B = 0.2, 0.3,$ and 0.4 . Alongside these numerical results, we have plotted the predictions of the theory for the ideal glass transition developed in Section 2 (Eq. (11)). In this case, we identify T_0 with T_{IG} and let the pure component IG temperatures be equal to the corresponding VTF temperatures. The interaction energies and length scales are taken directly from the Lennard–Jones parameters for the mixture. As Fig. 2 shows, the theory predicts a non-monotonic $T_{IG}(x_B)$ curve with a maximum near $x_B = 0.45$. The theoretical maximum is not as pronounced as those of the measured isodiffusive lines, perhaps indicating a higher-order or synergistic interaction between the diffusive motions of A and B particles which is not captured by the one-fluid conformal theory. Still, the ability of the theory to describe qualitatively the composition dependence of T_{IG} is an important advance, since it might permit “tuning” of glass transition behavior on the basis of mixture components. In particular, the close location of the maxima in the isodiffusive loci and T_{IG} suggests that the theory might be used quite successfully to predict the optimal composition for maximizing (or minimizing) the glass transition of mixtures.

4. Conclusions

In this paper we have proposed a theory for the equation of state of a glass-forming mixture based on the properties of the pure component energy landscapes. We have applied the theory to derive an expression for the composition dependence of a binary mixture’s glass transition temperature.

The key assumption underlying this work is that the form of the mixture equation of state is identical to the single components’ once effective, composition-dependent energy and length scales are introduced. Since the single-component equation of state that we use was derived from the statistical properties of energy landscapes [32], our approach amounts to a conformal solution theory for the mixing of energy landscapes.

Although numerical difficulties (crystallization, glassy dynamics) prevent the direct comparison of theoretical predictions and computer simulations, we note that the non-trivial composition dependence of the glass transition locus predicted by the present theory (i.e., a non-monotonic $T_G(x)$ relation) is, satisfyingly, also present in the isodiffusive lines calculated by simulation.

Under the intellectual leadership of John Prausnitz, molecular thermodynamics has made invaluable contributions to the chemical engineering profession, thanks to its judicious blend of statistical mechanics, physical intuition, and the heuristics of engineering practice. The compositional and structural complexity of the mixtures whose phase behavior has yielded to molecular thermodynamics scrutiny is impressive (e.g., [51]). As chemical engineers become increasingly involved in processes such as the solid-phase stabilization of labile biochemicals [3], the scientifically challenging and technically important case of dynamically complex glass-forming, deeply supercooled liquids will play an ever more important role and move closer to the core of our discipline. This will enrich chemical engineering and should in turn lead to novel insights that will improve our basic understanding of the vitreous state of matter.

In this paper we have addressed the prediction of the composition-dependent mixture glass transition temperature, and more generally the application of standard engineering approximations (such as one-fluid theory) within the framework of energy landscape theory. In spite of the encouraging results (i.e., prediction of non-monotonic $T_G(x)$ locus for the Kob–Andersen mixture [45]), much remains to be done. Deriving landscape-based free energies for complex molecules that are not well-represented by the soft-sphere/mean-field model; providing a rigorous theoretical foundation for the Adam–Gibbs equation [10]; applying the present theory to the study of low-temperature complex mixture phase behavior are examples of future avenues of inquiry that we believe will prove to be, like John Prausnitz’s brainchild, molecular thermodynamics, scientifically rewarding and technically important.

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Appendix A. On the Occasion of John Prausnitz's 70th Birthday¹

I would like to say a few words about John Prausnitz and the civilizing role that he has had in this community, both as a teacher and as a colleague.

I must confess at the outset that I am that rarest of anomalies: a chemical engineering thermodynamicist who is not a member of John's academic tree. And yet, like everyone else in this room, and countless others around the world, I have been profoundly influenced by John. With each of us he has established a dialogue through which he has commented, encouraged, praised, and criticized. The ability to correspond, meaningfully, with so many is, by itself, extraordinary. Yet it is not John's epistolary stamina, but rather the pedagogical and, yes, civilizing role of the dialogue that John has undertaken with each of us and with this community at large that I want to talk about.

The academic profession is a noble calling. Upon entering it, we become part of the never-ending conversation through which knowledge is enriched and renewed. To partake in this conversation is a privilege, for our interlocutors are not only our contemporaries, but also those who came before us, our intellectual ancestors. For us thermodynamicists, this means Gibbs, Helmholtz, Boltzmann, van der Waals. All of us here share the magnificent audacity of wanting to add something worth preserving to the splendid intellectual edifice erected by these giants. John's contribution is, of course, molecular thermodynamics, that is to say the judicious blend of thermodynamics, statistical mechanics, and the heuristics of engineering practice. Some 40 years after its creator left Princeton to conquer the Wild West, molecular thermodynamics has been firmly established as the defiantly Aristotelian addition to Gibbs' magnificent Platonic structure.

But John has never been content with mere technical success. To him, scholarship is not enough. Never the narrow specialist, he has sought to elucidate, not just to describe; he has pursued the profound satisfaction of understanding, instead of the simpler charm of cataloguing. John has channeled this impulse by attempting to reconcile, indeed make one of, chemical engineering and the humanities. Recognizing the dissolution of boundaries that is perhaps the defining feature of our times, he has embraced contingency and context, and refused to retreat to the safety of his own little niche of scholarship. He has, on the contrary, delighted in placing his scholarship firmly in relation to its broader human and societal implications. This has given meaning to his intellectual pursuit.

To him, the ultimate uncompartamentalizer, the perfection of a Mozart quartet, the depth of understanding of human character

of a Titian portrait, or the tension between an appreciation of bourgeois culture and the acute awareness of its precariousness that informs Thomas Mann's works, are sources of inspiration not just for his inner, spiritual life, but also for his scholarly and technical pursuits. This is because, for John, what defines us as humans is our need to understand ourselves and our world, and our striving for a better life. In this context, designing a new drug delivery device, feeding the hungry in Sudan, or listening to an opera, are all closely related activities. Their commonality is their humanity, that is to say their addressing a human need or aspiration, whether this be health or beauty. And so John reminds us, in his favorite example, that ammonia synthesis is about catalysis, reaction equilibria, and about fertilizers. But it is also about explosives. The Haber process helps feed the hungry, but it also kept the German war machine running in World War I. The next time we teach the Haber process, we should also talk about Verdun, and read the poems of Robert Graves. In so doing, we and our students will have become better, more complete human beings, hence better engineers.

This is the message that John has sought to deliver. He has done so publicly, of course, in numerous speeches and writings. But he has also done this individually, with each one of us, both in spoken conversation and through letters. In so doing he has gone beyond intellectual leadership; he has become a pedagogical and civilizing influence, a rabbinical, paternal voice, the conscience of this community.

As we all know, good paternal advice is often listened to, but much less frequently followed. John, I must confess that I do not always agree with your tastes, views, or opinions. But I always respect them, and there are very few people of whom I can say this. In reminding us of the political and societal implications of our discipline, you have made us more alert. In conjuring Freud, Brahms and Wagner to comment on our work, to which I can attest, you have made us more sensitive. In urging us to think about the broader context in which we work, you made our lives fuller, nobler, more human. For this we are all enormously grateful. Thank you John, and may you continue to live a life well lived for many years to come.

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¹ Words delivered by Pablo G. Debenedetti at a gathering of family, friends, students, and colleagues in celebration of John Prausnitz's 70th birthday, at the annual meeting of the American Institute of Chemical Engineers, Miami Beach, November 1998.

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