Glass Transition "Issues"


The objective of this presentation is to provide some basic examination and analysis of glass transition phenomena that are observed for atomic and molecular glass formers.

---

View1. Title, topics, objectives

----

The intended scope of the remarks includes both the interpretation of laboratory measurements, as well as the relevance of mathematical models intended to describe those measurements. Although quantum phenomena certainly could be incorporated in the relevant statistical mechanical theory, they are not a central issue. Classical statistical mechanics should suffice for present purposes.

The glass-forming substances of interest are chemically very diverse. Some specific classes of these substances with representative examples are presented in the following View2. These range from pure elements to high-molecular-weight polymers, and include

---

View2. Glass-forming substances

----

important examples of both inorganic and organic materials. Some colloidal suspensions are useful for experimental study because they also can exhibit glass transitions. An important distinction needs to be stressed here at the outset. By "glass-forming" one refers to creation of amorphous solids under continuous (and essentially reproducible) pathways from the stable liquid into deep metastable states by temperature reduction and/or compression. For the glass-formers of interest this treatment bypasses nucleation and growth of the thermodynamically stable crystal phase below its melting temperature \( T_m \), taking advantage of marked increase in structural relaxation (i.e., reorganization) times as cooling proceeds in the liquid medium of interest. This excludes from the discussion other amorphous solids such as those prepared by vapor phase deposition, or by disrupting a crystal phase due to severe mechanical deformation or radiation damage.

The long history of scientific and technological interest in glasses has generated an enormous phenomenology presented in a vast array of scientific/technical publications. For present purposes only a few of the primary concepts will be examined. These are basic inferences from the fitting and extrapolation of laboratory data. Extrapolation is necessary to pass downward in temperature through the experimental glass transition temperature \( T_g \) at which relaxation times have grown to impractical magnitudes \(( \geq 10^2 \text{ sec})\). Keep in mind that \( T_g \) tends to be slightly cooling-rate dependent -- slower cooling produces a lower observed \( T_g \).

An historic paper written over 60 years ago by Princeton's Professor Walter
Kauzmann, now deceased, considers implications of simple extrapolation for $T < T_m$ of the difference $\Delta S$ in entropies between the crystal phase (presumed to persist thermodynamically to $T = 0$), and the supercooled liquid. For most (if not all) glass formers, this extrapolation apparently indicates that this entropy difference vanishes at a positive temperature $T_K$, nowadays called the "Kauzmann temperature". This situation arises because the heat capacity of the supercooled liquid tends to exceed that of the crystal. Further extension of the extrapolation below $T_K$ would at first sight seem to imply that $\Delta S < 0$. On account of the fact that the crystal is essentially fully ordered (possessing a vanishing configurational entropy) at such a $T_K$, the argument has been advanced that because the metastable liquid could not in fact attain a lower (negative) configurational entropy, an "ideal glass transition" evidently would have to intervene.

Kinetic slowdown in supercooled liquids as $T$ declines toward $T_g$ has long been known to display substantial deviations from a simple Arrhenius temperature dependence for a variety of kinetic properties. One popular curve-fitting choice for measurements of these properties is the Vogel-Tammann-Fulcher (VTF) function, a temperature-shifted version of the Arrhenius function. Its fitting parameters have been used to classify glass formers on a "strong" vs. "fragile" scale, with the extremes illustrated respectively by $SiO_2$ and by ortho-terphenyl. The significance of these VTF fits is that they imply divergence of shear viscosity $\eta(T)$, self-diffusion constant $D(T)$, or mean stress and dielectric relaxation times $\tau_{stress}(T), \tau_{die}(T)$ at a positive temperature $T_0$ that in many cases is close to the Kauzmann temperature $T_K$ for the same substance. This approximate coincidence would seem to support the notion of an ideal glass transition at positive temperature. However it must be kept in mind that VTF fitting parameters often depend non-trivially on the temperature range of the data being fitted. In any case questionable extrapolation is invoked for both the $T_K$ and the VTF applications.
The metastable-phase thermodynamic argument for an ideal glass transition, built upon Kauzmann's observations, and the qualitative kinetic VTF analysis suggesting the existence of the same qualitative phenomenon, have been connected by the Adam-Gibbs relation. The underlying concept is that relaxation and flow processes in the deeply supercooled regime proceed via local structural excitations that occur within essentially independent cooperatively rearranging regions (CRRs) of the supercooled medium. The number of CRRs is presumed to be roughly proportional to the inverse of their average size over $0 < T < T_m$. Furthermore, the size of these CRRs, as well as their excitation free energies, is postulated to be inversely proportional to the configurational entropy at the prevailing temperature. This was an early prelude to the now-popular concept of dynamic heterogeneity. Most significantly, the Adam-Gibbs relation clearly presumes that there exists a basic connection between the metastable-phase thermodynamics of a supercooled liquid on the one hand, and that liquid's various kinetic phenomena on the other hand.

In order to evaluate these two basic hypotheses for glass-forming substances (existence of ideal glass transitions, and a fundamental thermodynamics-kinetics connection), it is useful to migrate thinking from three dimensions to the high-dimensional configuration space for the $N$-particle system, and to consider details of the multidimensional topography of the potential energy function $\Phi(X_1...X_N)$ that incorporates all interactions present. This function can be identified as the electronic ground-state Born-Oppenheimer energy plus nuclear Coulomb repulsions. It is dependent of course on the spatial positions of all nuclei present, where those contained in molecule $j$ are represented by the vector $X_j$ of cartesian coordinates. This Born-Oppenheimer presumption nominally excludes metallic systems from the analysis, but it certainly applies to many insulating materials as illustrated earlier in View2. The $\Phi$ topography in general will contain interparticle interactions, which may involve significant non-pairwise-additive aspects. It will also contain any intramolecular force-field information (chemical bond stretching, bending, and other conformational deformations). If real container walls (as opposed to periodic boundary conditions) are present, it will specify those as well.

A useful way to analyze that $\Phi$ landscape is to divide the configuration space into steepest-descent basins. Each basin represents the locus of all points in the configuration space that are connected to an interior relative $\Phi$ minimum (an "inherent structure") by a steepest-descent path. An inherent structure is a mechanically stable particle arrangement, and intrabasin displacements are vibrations away from that minimum. Anharmonicity increases with displacement magnitude, eventually creating negative curvature directions. By construction every basin contains a single inherent structure and is connected, but not necessarily singly connected. The inherent structures include
periodic and defective crystal structures, as well as amorphous structures that underlie the stable and metastable liquids.

Shared boundaries between neighboring basins contain $\Phi$ landscape saddle points, \emph{i.e.}, transition states for elementary interbasin readjustments within the system. It is also possible in principle for basins to contain interior saddle points that obviously do not involve interbasin transitions. But for transition states in atomic and molecular glass formers, only local rearrangements of molecular dimensions are involved, owing to the relatively short range of interactions. Thus such local rearrangements in separate macroscopic sub-volumes are essentially independent, a basic feature that underlies enumeration of basins and their inherent structures.

Inherent structures and their basins fall into equivalence classes, owing to permutational and other symmetry operations that apply to the constituent particles. A system containing $N$ identical structureless particles that are confined by impenetrable walls has $N!$ replicas of each basin within the landscape, due to the possibilities for permuting particle positions. If each of the $N$ identical particles has an internal structure leading to $\gamma$ equivalent intramolecular rotational or deformational configurations, the basin equivalence number must include an additional factor $\gamma^N$. These numbers have straightforward generalizations for multicomponent systems.

The full $\Phi$ landscape includes regions (sets of basins) that are occupied respectively when liquid or crystal phases are present, or even when phase coexistence is present. The equilibrium occupancies of those regions can be represented by the canonical ensemble and its partition function $Q_N(T)$ at a given temperature and density. This statistical-mechanical description assumes that the Newtonian dynamics represented by the full --

\textbf{View8. Canonical ensemble partition function $Q_N(T)$} --

ensemble, for the given particle masses and $\Phi$, samples different regions of configuration space in a "complete" fashion with Boltzmann weighting for the given temperature. In the large-$N$ limit quantitative details of the first-order melting/freezing transition are contained in $Q_N(T)$. It should be realized though that since the number of distinct basin types rises exponentially with $N$, having any one ensemble member dynamically visit all of them would require an exponentially long time. However thermal equilibration for a single ensemble member really requires only visiting a very small "representative" basin subset during the time of observation.

Note that in addition to the canonical partition function an analogous constant pressure ("isobaric") partition function could also be exhibited, for which the Born-Oppenheimer potential $\Phi$ would be augmented by adding $pV$ to it. Then the volume $V$ is treated as an additional configurational variable that can be interpreted as a piston position applying a fixed force per unit area to the system. Both of these ensembles and their partition functions can be modified to describe at least some features of metastable states (specifically, of supercooled liquids), the technical details of which will be examined after covering some general observations about the $\Phi$ (equivalently $\Phi + pV$) landscape.
The kind of natural tiling analysis of the potential energy landscape generated by steepest descent mapping leads to a conceptually simple way of representing the canonical partition function to describe strict thermodynamic equilibrium. This is a necessary first step before modifying that partition function to describe metastability, especially for supercooled glass formers. Specifically this approach involves classifying

\[ Q_N(T) \text{ reduction to a } \varphi \text{ integral} \]

the landscape basins by \( \varphi \), their inherent structure depths (potential energies) on a per-particle basis, and identifying the mean intrabasin vibrational free energy to be assigned to those basins at depth \( \varphi \). Along with a generic enumeration function for the distinguishable basin types that is exponential in system size \( N \), this reduces \( Q_N(T) \) to a simple \( \varphi \) quadrature.

In the large-system (macroscopic) regime, the \( Q_N(T) \) quadrature will be dominated by the immediate neighborhood of the integrand maximum. At a given temperature \( T = (k_B \beta)^{-1} \) the position of this maximum, to be denoted by \( \varphi^*(\beta) \), is determined by

\[ \text{Definition of } \varphi^*(\beta); \text{ graphical construction to identify equilibrium state} \]

slopes equality of \( \sigma \) and of \( \beta(\varphi + f_{vib}) \) when plotted vs. \( \varphi \). This dominating integrand maximum gives rise to a simple expression for the Helmholtz free energy. A similar result applies for the Gibbs free energy in the case of the isobaric (constant pressure) ensemble.

At this stage it is appropriate to point out that large families of distinct potential

\[ \text{Different } \Phi \text{ s can produce same } Q_N(\beta); \text{ "stirred } \Phi \text{" example} \]

energy functions can give rise to identically the same \( Q_N(T) \), and therefore can produce identical thermodynamic functions at all temperatures \( T \). One hypothetical family of possibilities rests upon a transformation of configurational variables that involves a multidimensional divergence-free "stirring" operation. Under this displacement operation, all differential elements of the configuration space retain their hypervolumes while generally being shape-distorted, and their corresponding pieces of landscape retain their respective landscape altitudes. Although the thermodynamics remains invariant under this transformation by construction, the Newtonian dynamics on the respective landscapes will differ, leading to distinct kinetic properties. Furthermore, one should realize that the \( N \)-particle geometric structures involved will have shifted probabilities, and thus the corresponding atomic and/or molecular distribution functions will be changed.

Perhaps a more physically relevant, or at least visually more appealing, version of thermodynamic degeneracy for distinct landscapes can be illustrated with another type of example, again within the classical statistical mechanical regime. Such examples can be
created by fusing together elementary one-dimensional modular units, each with its own internal minimum, and rising or falling by one energy unit from end to end. Details of
-----
**View12. Rearrangeable modules that can be fused end-to-end to form one-dimensional landscapes.**
-----
this "cut-and-paste" approach are presented in View12. The single internal minimum contained within each module lies 17/27 below the lower endpoint. By way of illustration, View13 shows a distinct pair of constructed landscapes consisting of eight modular units arranged in two different ways, but each case satisfying periodic boundary
-----
**View13. Eight-module cut-and-paste landscapes**
-----
boundary conditions. The key degeneracy stems from the fact that for both examples shown the count of modules as a function of their altitude is the same: 4 and 4. The landscapes are continuous and twice differentiable. Needless to say the respective Newtonian dynamics for the two cases will differ.

A second more complicated but more striking example pair, using the same underlying idea, is presented in View14. These involve 60 modules of the same kind, again combined to produce a continuous and twice differentiable pair of landscapes.
-----
**View14. More complicated landscape examples, 60 rearranged modules**
-----
Once again they satisfy periodic boundary conditions. With this many modules a large number of distinct arrangements are possible, even when subject to a fixed vertical distribution. From bottom to top, the common altitude count for the 60 modules in the two examples shown is 2, 4, 6, 8, 8, 8, 6, 6, 6, 6. Because one of these landscapes presents a single "metabasin", while the other presents four, it is obvious that the respective Newtonian dynamics and consequent relaxation behaviors would be drastically different, while by construction the thermodynamics remains identical.

Although these examples are merely one dimensional, the basic idea of fusing together modular landscape units can and has been be extended to higher dimensions. Quantum corrections (at least in low order) could have been included, but at some cost in technical complication. Such examples call into question the basis of the Adam-Gibbs relation mentioned earlier, or at least call for physically-motivated constraints on interaction functions $\Phi$ to avoid this kind of thermodynamic degeneracy with kinetic disparity.

The possibility of attaining the reverse situation raises a group of open questions. Specifically, are there pairs of distinct potential energy landscapes that lead to an identical transport or relaxation property at all temperatures, but possess distinct thermodynamic properties? Perhaps the answer is that none exist.

It is now appropriate to return to identification of a $Q_N$ modification to yield a description of the metastable supercooled liquid. This involves a projection operation
-----
**View15. Projection operation for supercooled liquid**
that in principle can be based upon the configuration space tiling by basins. In particular basins can be divided into two groups, those whose inherent structures contain identifiable crystalline particle clusters of "significant" size, versus those that do not and thus are consistently amorphous. Only the latter basin set, to be designated by L, should be retained if the properties of the supercooled liquid are the objective, because this is the subset of configuration space within which a supercooled liquid remains if it has not nucleated. This strategy implements theoretically the absence of crystal nucleation and growth that is the primary laboratory criterion for successful supercooling. By clusters of "significant" size it would be logical to mean those equal to or larger than the critical nucleus size at the temperature of maximum nucleation rate in the supercooled liquid of interest.

After projecting the crystal-containing basin set out of consideration, the resulting configurationally restricted partition function \( Q_{N,l}(\beta) \) that describes both the stable liquid above \( T_m \) and the metastable supercooled liquid below \( T_m \) can also be exhibited as a \( \varphi \) quadrature. The corresponding integrand as before will possess an exponential form that contains a modified enumeration function \( \sigma_l(\varphi) \) and a modified vibrational free energy function \( f_{vib,l}(\varphi, \beta) \) for the basin subset \( L \). Once again that quadrature in the asymptotic large-system regime will be dominated by its integrand maximum, now at \( \varphi_l^*(\beta) \), to be located as before by equality of slopes. This projection operation is not limited by dynamic slow-down as temperature declines, so in principle it can predict supercooled liquid properties down to absolute zero. For \( T \geq T_m \), the projection should have virtually no effect on the position of the integrand maximum, \textit{i.e.}, \( \varphi_l^*(\beta) \equiv \varphi^*(\beta) \). For \( T < T_m \) \( (\beta > \beta_m) \) it should provide a smooth extrapolation into the supercooled regime.

The obvious question now is how this bears on the ideal glass transition hypothesis.

**View16. Nominal requirement for ideal glass transition**

The graphical construction for the metastable state function \( \varphi_l^*(\beta) \) helps to supply an answer. The curve for \( \beta[\varphi + f_{vib,l}(\varphi, \beta)] \) has a positive bounded slope \textit{vs.} \( \varphi \) for all \( 0 < \beta < \infty \), and that slope increases without bound as \( \beta = 1/k_BT \) increases (\textit{i.e.}, diverging to \( +\infty \) as \( T \) declines toward \( T = 0 \)). In order for an ideal glass transition to arise at positive temperature, the \( \sigma_l(\varphi) \) enumeration function curve would also have to exhibit a positive finite slope at \( \varphi_{\min,l} \), its low-\( \varphi \) endpoint.

However, the earlier observation concerning independence of rearrangement energy costs in separate macroscopic subvolumes and the implication for inherent structure enumeration leads to a contrary conclusion. Specifically, \( \sigma_l(\varphi) \) will have a leading-order fractional-power singularity at its lower end, producing a diverging slope at that point.

**View17. Effect of local rearrangements on enumeration; no ideal glass transition**
lower end. This forces any "transition" implied by the graphical construction down to 

\( T = 0 \). In other words, no ideal glass transition is possible in the conventional 
interpretation of that concept, at least for atomic and molecular glass formers whose 
interactions have limited spatial range.

In the interests of promoting broader discussion about glass transition issues, it seems 
appropriate to describe a somewhat peculiar situation that arises in polymer 
chemistry/physics. This concerns the structural multiplicity that arises in "atactic"

*View18. Atactic polypropylene example*

polymers, illustrated here by the simple case of atactic polypropylene. The relevant 
chemical bonding structures are illustrated in View18. They involve two choices for 
attaching pendant methyl groups to every other site along the interior of the linear carbon 
backbone (shown in a zig-zag all-trans conformation for ease of visualization). These 
binary choices result from the tetrahedral bonding directions at every other one of those 
interior backbone carbons. If the polymer is formed from 500 propylene monomers, 
there exist \( 2^{498} \) distinguishable choices for attaching the methyl groups. It is 
straightforward to show that in a liter of 500-mer atactic polypropylene molecules with 
these structural choices, if they are independent, the chance that any two of the molecules 
will have identically the same stereochemical bonding geometry is absurdly small, 
specifically about \( 4 \times 10^{-106} \). Consequently there would be only single representatives 
of the possible molecular structures present in that liter, and thus the equivalence classes 
for inherent-structures/basins would involve no permutations of different molecules. 
Nominally it would seem that the enumeration of distinguishable inherent structures 
would then require a function of the type \( \exp[bN \ln N + aN + O(1)] \) for \( N \) atactic polymer 
molecules. At present it is unclear how these would be distributed with respect to the 
intensive depth parameter \( \varphi \). Although the corresponding \( \Phi \) must have a global 
minimum, it will certainly not involve a spatially periodic structure. A remaining open 
question is what the low-temperature equilibrated behavior of this macroscopic system 
must be, especially regarding equilibrium phase transitions, and whether a projection 
operation would even be required to describe liquid supercooling. In particular it is 
unclear whether the global energy minimum might exhibit some partial long-range spatial 
order.

The estimate just mentioned for structure redundancy in a single liter of 500-mer 
atactic polypropylene can be turned around to produce another bizarre number. One can 
alternatively ask how many liters of the polymer would be required so that there is only a 
probability of 1/2 that all molecules are structurally distinct. The answer corresponds to a 
filled cube of polymer that is approximately \( 3 \times 10^{13} \) kilometers on a side! Of course this 
does not account for self-gravitational collapse.

One of the glass transition "issues" that deserves some thought and discussion is the 
distinction between the broad modeling opportunities offered by mathematics on the one 
hand, and the possibly severe constraints on those opportunities required by physical
realism on the other hand. For the former, the kinds of postulated interactions between particles or other degrees of freedom can be very diverse, including specifically very long-range interactions. In particular those unconstrained models can readily generate ideal glass transitions. However the Born-Oppenheimer interaction functions for real substances present a much narrower set of possibilities, and the arguments presented here indicate that for the latter, ideal glass transitions are not a realistic inference.
Topics, objectives:

- Real glass-forming substances of interest
- Experimental $T_g$s versus "ideal glass $T_g$s"
- Born-Oppenheimer potential energy "landscapes"
- Landscape tiling by steepest-descent basins
- Landscapes with identical thermodynamics, different kinetics
- Canonical ensemble modified for supercooled states
- Realistic interactions and ideal glass transitions
- Atactic polymer dilemma
GLASS-FORMING SUBSTANCES
[vitrification by liquid supercooling and/or compression]

(1) Elements: \( S, Se, Te \)

(2) Network formers: \( SiO_2, B_2O_3, As_2S_3, ZnCl_2 \)

(3) Concentrated aqueous electrolytes: \( Ca(NO_3)_2 \cdot 4H_2O \)
   \( Mg(OAc)_2 \cdot 4H_2O \)
   \( H_2SO_4 \cdot 3H_2O \)

(4) Organic molecules: toluene
   salol
   ortho-terphenyl
   ethanol
   glycerol

(5) High mol. wt. polymers: polypropylene, polystyrene,
   polyvinyl chloride (PVC)

(6) Colloidal suspensions: silica spheres,
   poly methylmethacrylate spheres,
   \( N \)-isopropylacrylamide microgel spheres

(7) Metallic glasses: \( Ni_{81}B_{19}, Al_{90}Fe_5Ce_5, Pd_{43}Cu_{27}Ni_{10}P_{20} \)
KAUZMANN TEMPERATURE  

Heat capacity \( (C_p) \) of supercooled liquid in \( T_g \leq T \leq T_m \) exceeds that of the stable crystal. The discrepancy widens as \( T \) declines:

\[
\Delta S(T) = S_{scl}(T) - S_{crys}(T) \\
= \Delta S(T_m) - \int_T^{T_m} [C_{p,scl}(T) - C_{p,crys}(T)] \frac{dT}{T}.
\]

Liquid-crystal molar entropy difference fixed at \( T_m \) by melting enthalpy. Temperature integration determines entropy difference below \( T_m \):

Simple extrapolation below the experimentally limiting \( T_g \) suggests that \( \Delta S \) vanishes at \( T_K > 0 \), the "Kauzmann temperature":

\[
\Delta S(T) = 0 \text{ at } T = T_K > 0
\]
IDEAL GLASS TRANSITION?

Observations concerning an "ideal glass transition" at $T_K > 0$:

(1) The transition at $T_K$ would be second order by conventional standards. It concerns a behavior switching for the amorphous glass, not a transformation to the thermodynamically stable crystal.

(2) Enthalpy of the "ideal glass" remains above the enthalpy of the crystal at $T_K$ according to:

$$\Delta H(T_K) = H_{scl}(T_K) - H_{crys}(T_K)$$

$$= \Delta H(T_m) - \int_{T_K}^{T_m} \left[ C_{p,scl}(T) - C_{p,crys}(T) \right] dT,$$

based upon the same simple heat capacity extrapolation.

(3) However this does not imply a positive entropy of transition from the glass to the crystal at $T_K$, because a reversible direct transition path between the two does not exist.
A wide range of properties is available experimentally to monitor kinetic slowdown as $T$ declines below $T_m$. These include:

- shear viscosity $\eta(T)$;
- self diffusion constant $D(T)$;
- stress relaxation time $\tau_{\text{stress}}(T)$;
- dielectric relaxation time $\tau_{\text{die}}(T)$.

The rate of increase of these properties as $T$ declines toward $T_g$ is typically distinctly non-Arrhenius. A frequently invoked fitting function for that temperature dependence is the Vogel-Tammann-Fulcher (VTF) form, e.g.,

$$ \eta(T) \approx \eta_0 \exp \left[ \frac{A}{T - T_0} \right]. $$

For many glass formers these VTF fits lead to $T_0 \approx T_K$, apparently strengthening the case for an ideal glass transition at positive temperature.

The VTF parameters can be used to classify glass formers qualitatively on a one-dimensional scale from "strong" to "fragile" extremes:

- strong (nearly Arrhenius): large $A/T_0$; $T_0/T_g \approx 0$,
- fragile (distinctly non-Arrhenius): small $A/T_0$; $T_0/T_g \approx 1$. 

KINETIC SLOWDOWN PHENOMENOLOGY
ADAM-GIBBS RELATION
[G. Adam and J.H. Gibbs, J. Chem. Phys. 43, 139-146 (1965)]

BASIC CONCEPTS: Structural relaxation as $T$ approaches $T_g$ involves restructuring within independent "cooperatively rearranging regions" (CRRs). The average number of particles in a CRR is inversely proportional to $\Delta S_{conf}(T)$, the liquid's configurational entropy relative to that of the crystal. The time between "relevant" CRR rearrangements depends exponentially on CRR size.

AVERAGE RELAXATION TIME:

$$\bar{\tau}_{relax}(T) = \tau_0 \exp \left[ \frac{B}{\Delta S_{conf}(T)} \right]$$

[Usually assumed that $\Delta S_{conf}(T) \approx \Delta S(T)$.

IMPLICATION: Kinetic properties of glass formers can be extracted from thermodynamic (static) properties.
POTENTIAL ENERGY "LANDSCAPE" PROPERTIES

- For $N$ molecules described by configuration coordinates $X_1...X_N$, the interactions can be accurately described by nuclear Coulomb repulsions plus the Born-Oppenheimer approximation to the electronic ground state (exception: metals). The resulting potential energy function $\Phi(X_1...X_N)$ includes both intramolecular and intermolecular interactions.

- If each molecule has $\nu$ degrees of freedom, $\Phi$ defines a hypersurface in the $\nu N$-dimensional configuration space, the "potential energy landscape".

- Assuming $\Phi$ is differentiable away from any nuclear confluence, it generates a tiling of configuration space by steepest-descent basins. Each basin consists of all points that descend to a common relative minimum of $\Phi$ (an "inherent structure"): 

- Basin enumeration, structureless particles, large-$N$ regime:
  $$\Omega_N \sim N! \exp[\alpha N + o(N)], \quad \alpha > 0.$$
CANONICAL PARTITION FUNCTION

• For the case of a single-component macroscopic system consisting of $N$ structureless particles confined to volume $V$, the canonical partition function is:

$$Q_N(T) = \exp[-F_N(T,V)/k_BT]$$

$$= [\lambda^{3N}/N!]^{-1} \int_{V} \int_{V} d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp[-\Phi(\mathbf{r}_1 \ldots \mathbf{r}_N)/k_BT] ,$$

where: $F_N$ is the Helmholtz free energy,

$$\lambda = \hbar/(2\pi mk_BT)^{1/2}$$

is the mean thermal de Broglie wavelength.

• This equilibrium generating function provides a temperature-weighted sampling of the entire $\Phi$ landscape, biased strongly toward the basins describing the stable phase at the prevailing $T,V$.

• Because the number of distinct $\Phi$ basins rises exponentially with $N$, Newtonian dynamics would take exponentially long to visit examples of each. Instead, "thermal equilibration" for a single system really just involves visiting a very small representative subset of basins.
PARTITION FUNCTION REDUCTION TO A BASIN-DEPTH QUADRATURE

• Express $Q_N$ as a sum over distinguishable basins ($\beta = 1 / k_B T$):

$$Q_N = \lambda^{-3N} \sum_{a} \exp(-\beta \Phi_a) \int_{B_a} d\mathbf{R} \exp[-\beta \Delta_a \Phi(\mathbf{R})] ,$$

$B_a$: multidimensional region for basin $a$,
$\Phi_a$: $\Phi$ value at basin $a$ inherent structure,
$\Delta_a \Phi$: intrabasin $\Phi$ increment ($\Phi - \Phi_a$).

• Classify inherent structures (basin bottoms) by $\varphi = \Phi / N$, with an enumeration function $CN! \exp[N \sigma(\varphi)]$ for the large-$N$ regime. Here $C$ is an order-unity normalization constant.

• Define mean vibrational free energy per particle for basins in depth range $\phi \pm d\phi$:

$$\exp[-N\beta f_{vib}(\varphi, \beta)] = \lambda^{-3N} \left( \int_{B_a} d\mathbf{R} \exp[-\beta \Delta_a \Phi(\mathbf{R})] \right)_{\varphi \pm d\varphi}$$

• Transformed canonical partition function, large-system regime:

$$Q_N = C^{\varphi_{\text{max}}}_{\varphi_{\text{min}}} \exp \{ N[\sigma(\varphi) - \beta \varphi - \beta f_{vib}(\varphi, \beta)] \} d\varphi .$$
Partition function $Q_N$, and consequently Helmholtz free energy $F_N$, are dominated by the region of the $\varphi$ integrand maximum. This maximum is determined at any temperature by the variational criterion:

$$d\sigma(\varphi) / d\varphi = \beta\{1 + [df_{\text{vib}}(\varphi, \beta) / \partial \varphi]\}.$$

At any given $\beta = 1/(k_B T)$ let $\varphi^*(\beta)$ stand for the position of the integrand maximum. A graphical solution of the determining equation corresponds to matching slopes given by the two members of the above equation:
DISTINCT POTENTIAL LANDSCAPES WITH IDENTICAL THERMODYNAMICS, BUT DIFFERENT KINETICS

• In the $3N$-dimensional configuration space $V \times V \times \ldots \times V$ of particle configurations $\mathbf{R} = \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$, introduce a continuous divergence-free displacement field $S(\mathbf{R})$:
  \[ \nabla_{\mathbf{R}} \cdot S(\mathbf{R}) = 0 \ . \]

• The resulting transformation of positions from $\mathbf{R}$ to $\mathbf{R} + S(\mathbf{R})$ amounts to a multidimensional "stirring" of an incompressible fluid in the available configuration space.

• The two potential functions $\Phi(\mathbf{R})$ and $\tilde{\Phi}(\mathbf{R}) = \Phi[\mathbf{R} + S(\mathbf{R})]$ have the same number of basins and inherent structures with equal depths before and after the transformation. The basins become distorted, but retain their connectedness, content, and intrabasin classical vibrational free energy.

• Therefore $Q_N(\beta) \equiv \tilde{Q}_N(\beta)$ . However the Newtonian dynamics on the two landscapes are expected to differ.
POTENTIAL ENERGY LANDSCAPES CONSTRUCTED FROM SIMPLE MODULAR UNITS

Define a simple one-dimensional landscape module that has unit width, net altitude increase of unity, and a single interior minimum:

\[ P(x) = -\left( \frac{9}{16} \right) \cos(\pi x) + \left( \frac{1}{2} \right) \cos(2\pi x) + \left( \frac{1}{16} \right) \cos(3\pi x) , \quad (0 \leq x \leq 1) . \]

The mirror-image version has a net altitude decrease of unity:

\[ P(1-x) = \left( \frac{9}{16} \right) \cos(\pi x) + \left( \frac{1}{2} \right) \cos(2\pi x) - \left( \frac{1}{16} \right) \cos(3\pi x) , \quad (0 \leq x \leq 1) . \]

These modular functions have vanishing slopes and equal downward curvatures at both endpoints \( x = 0,1 \).

These modules can be translated horizontally and vertically and spliced together to produce model potential landscapes in many ways over larger \( x \) intervals, exhibiting many local minima.
PARTITION FUNCTION MODIFICATION
FOR SUPERCOOLED LIQUIDS

- Because they are free from obscuring effects of intrabasin vibrations, use inherent structures to divide basins into those that contain local crystalline order vs. those that do not. The latter set $L$ hosts the stable liquid, and should suffice to describe the supercooled liquid.

- Define a "liquid" canonical partition function including only basin set $L$:

$$Q_{N,l}(\beta) = (\lambda^{3N}N!)^{-1} \int \mathcal{L} d\mathbf{R} \exp[-\beta \Phi(\mathbf{R})]$$

$$= \lambda^{-3N} \sum_{a \in L} \exp(-\beta \Phi_a) \int \mathcal{B}_{a} d\mathbf{R} \exp[-\beta \Delta_a \Phi(\mathbf{R})] .$$

- Reduction to $\varphi$ quadrature:

$$Q_{N,l}(\beta) = C_l \int_{\varphi_{\text{min},l}}^{\varphi_{\text{max},l}} \exp\{N[\sigma_l(\varphi) - \beta \varphi - \beta f_{\text{vib},l}(\varphi, \beta)]\} d\varphi .$$

- The large-$N$ asymptotic value of $\ln Q_{N,l} = -\beta F_{N,l}$ is determined by the integrand maximum now at $\varphi_l^*(\beta)$ which is the root of:

$$d\sigma_l(\varphi) / d\varphi = \beta [1 + [\partial f_{\text{vib},l}(\varphi, \beta) / \partial \varphi]] .$$
CONDITIONS REQUIRED FOR POSITIVE TEMPERATURE IDEAL GLASS TRANSITION

• As a function of $\varphi$, $\beta \varphi + \beta f_{\text{vib}, l}(\varphi, \beta)$ has a positive bounded slope for $T > 0$.

• In order for a positive-temperature ideal glass transition to occur, the enumeration function $\sigma_l(\varphi)$ would also have to possess a positive bounded slope in the vicinity of its low end at $\varphi_{\text{min}, l}$.

• Graphical representation of matching slopes at a hypothetical $T > 0$ ideal glass transition:

![Graphical representation showing matching slopes at a hypothetical $T > 0$ ideal glass transition.](image-url)
ENUMERATION FOR BASIN SET $L$ NEAR $\varphi_{\text{min},l}$

[P.G. Debenedetti, F.H. Stillinger, and M.S. Shell, 

- Suppose that $\sigma_l(\varphi)$ has a finite positive slope near $\varphi_{\text{min},l}$:

  $$\sigma_l(\varphi) = A(\varphi - \varphi_{\text{min},l}) + O[(\varphi - \varphi_{\text{min},l})^2] .$$

- For $\varphi$ just above $\varphi_{\text{min},l}$, in order for $\xi N$ ($0 < \xi << 1$) distinct inherent structures to lie below $\varphi$, one requires:

  $$N(\varphi - \varphi_{\text{min},l}) = (1/A)\ln(\xi N^2) + O(1) ,$$

  *i.e.*, the potential energy interval required to contain $\xi N$ inherent structures would have to increase logarithmically as system size $N$ increases.

- That conclusion contradicts the principle that the medium has essentially independent $O(1)$-energy local rearrangement excitations in different macroscopic sub-volumes, which implies that the required interval width does not grow as $N$ increases.

- Consequently the initial slope of $\sigma_l(\varphi)$ at $\varphi_{\text{min},l}$ must diverge. The matching slope criterion then eliminates any $T > 0$ ideal glass transition.
ATACTIC POLYPROPYLENE EXAMPLE

- Linear carbon backbone offers two choices for each methyl group attachment:

- For a 500-mer this leads to $2^{498}$ distinct chemical structures.

- One liter of 500-mer contains $2.58 \times 10^{22}$ molecules. If these have been chosen at random, the chance that any two have identical chemical structures is $4 \times 10^{-106}$.

- Basic questions: Could the absolute $\Phi$ minimum ever be determined? How elongated is the spectrum of relaxation times?