Metastable Systems in Thermodynamics: Consequences, Role of Constraints

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Metastable states are not in true equilibrium and so cannot be directly treated by thermodynamics and statistical thermodynamics. To circumvent this difficulty one can specify an equivalent equilibrated state, equivalent in the sense that the observed macroscopic features are indistinguishable from those of the metastable state, and equilibrated because of the imposition of auxiliary constraints which totally block the very slow relaxations that cannot be completed during the time of the experiment. This procedure permits one to treat metastable systems consistently within a completely time independent and causal thermodynamic framework. It also gives a consistent description of the entropy of glassy and similar random metastable systems in which the entropy vanishes as $T \rightarrow 0$ K, and it explains the apparent residual entropy at 0 K obtained in most conventional analyses based upon experiments carried out over irreversible paths (but not always recognized as such).

1. Introduction

Metastable systems are routinely treated by the methods of thermodynamics despite the fact that they are not truly at equilibrium and that thermodynamics applies only to equilibrated systems.[1] In this paper, we will try to clarify the thermodynamic study of metastability and its relation to strict thermodynamics, and to suggest a modest reformulation of the axiomatic basis of the discipline, one that can be applied consistently in all situations, both when the distinctions between the two are important and when they are unimportant. In our development we keep in mind what we take to be the exact equivalence of thermodynamics and statistical thermodynamics, a requirement that is sometimes dropped in studies of metastability. Of course, thermodynamics and equilibrium statistical mechanics can never involve time, and in a consistent thermodynamic formulation of metastability the implicit presence of time as a variable must be excised; as shall be explained, we do this by the introduction of auxiliary thermodynamic variables or constraints.[2] Among the special subjects impacted by this study are the glass transition, residual entropy, fundamental aspects of the third law, and the approach to chemical equilibrium of locally equilibrated systems.

Before proceeding further, it is appropriate to mention that some, but not all, of the ideas expressed below have been touched on by other authors, but nobody seems to have attempted a codification of the whole that could qualify as a universal and internally consistent discipline. Important examples of the presentation of some of these ideas can be found in the recent book by Debenedetti[3] and in the papers of Debenedetti, Corti, Stillinger, Sastry, and Speedy.[4−6] These authors emphasize the importance of introducing constraints in order to convert metastable states into equilibrium states amenable to thermodynamic analysis, and they also discuss the relative time scales whose overlap signals the necessity for constraints, especially in the context of the glass transition.[3] These ideas are similar to our own as they are expressed in the following sections.

2. Metastability

Conventionally, a metastable system is one in which one, or a very few, of its relaxation processes are too slow to measure in at least some thermodynamic experiments. Such systems are metastable because in other longer lasting experiments these slow relaxations can be completed or at least observed. Whether or not one has this additional knowledge should in no way affect the application of thermodynamics.

It is convenient to specify metastability in terms of the characteristic time τ for the slow relaxation and the characteristic time τ_{exp} for an experimental measurement. For metastability, we require

$$\tau \gg \tau_{exp} \tag{1a}$$

When this condition holds under all relevant experimental conditions, the slow relaxation can be implicitly ignored and the system taken as equilibrated although it is technically only metastable because given enough time it would change. True equilibrium may be specified by

$$\tau \ll \tau_{exp} \tag{1b}$$

Discussions of metastability become significant when the two conditions meet, i.e., when either the experimental conditions or the α-relaxation can be altered so that the system passes from one extreme set of conditions to the other. It is only if all, including the designated slow relaxation processes, are rapid with relaxation times $\tau(\text{slow}) \ll \tau_{exp}$ that one has local equilibrium and metastability; otherwise the system is unstable. We recognize that other specifications of metastability have also been introduced, and below we discuss the relationship of our formulation to some of the others.

One's first conclusion might be that, since metastable systems are not at equilibrium, they cannot be treated within the framework of thermodynamics. This could be disconcerting because in a strict sense no system is at equilibrium; any physical system will presumably undergo nuclear transmutation and ultimately end up as an iron mass or possibly become somewhat ephemeral as its protons decay. These are extreme cases of the

inequality (eq 1a), and they pose no problem provided the possibility of transmutation or of proton decay is excised or, equivalently, one has no interest in comparing thermodynamic quantities in the undecayed and decayed states of the system, i.e., a comparison of an actual sample with the sample after proton decay. The important point is that *if one is to study such systems by means of thermodynamics, these very slow relaxation processes must be excised,* either implicitly or explicitly. Excising them implicitly is adequate in this example because they will never enter into any practical application of thermodynamics, i.e., thermodynamic quantities in the undecayed and decayed states are not compared. However, in cases such as liquids converting to glasses, or in the catalysis of mixtures of hydrogen and oxygen to form water, one passes from the condition in eq 1b to that in eq 1a, and it is this crossover that requires careful consideration. For liquids, all of the relaxations are rapid so these issues need not be considered in studies focused entirely on liquids, whereas for glasses they have no effect and so can be excised from studies focused entirely on glasses. It is when studying the conversion of liquid to glass that the switch of the slow relaxations from the condition in eq 1a to that in eq 1b must be considered; *if this conversion is not considered, then the auxiliary constraint, defined below, remains passive, and the present discussion, although needed for theoretical consistency, becomes academic.*

Excision, as discussed above, means that the condition of metastability $\tau \gg \tau_{\exp}$ is converted to

$$\tau \rightarrow \infty \tag{2}$$

a limiting operation which has no physical implications, but important conceptual ones. To effect this conversion, i.e., to convert the metastable system to a true equilibrium system which can be studied by thermodynamics, one most impose constraints (at least conceptually), denoted as auxiliary constraints, in addition to the usual constraints such as constant volume, temperature, and pressure. It is on these auxiliary constraints that we focus. A system held at equilibrium by virtue of auxiliary constraints is said to be in constrained equilibrium or in local equilibrium. Note that it is respect for the temporal implications of eqs 1a, 1b, and 2 that enables one to apply the time-independent analysis of thermodynamics and statistical thermodynamics to the inherently time-dependent problem of metastability.

3. The Equivalent Equilibrated System

One can denote a system in constrained equilibrium that has been arranged to be thermodynamically equivalent to the metastable system as the equivalent equilibrated system. The equivalent equilibrated system must be macroscopically identical to the actual metastable one over the time scales of the experiment. If this cannot be effected, as is the case when the system is unstable, then one cannot make use of thermodynamics to study metastability.

Since in the thermodynamic study of the liquid−glass and hydrogen−oxygen systems one must compare the equilibrium properties in the two limiting states in which first one and then the other of the conditions in eqs 1a and 1b holds, one must find a means of controlling the systems so that they can be taken reversibly from one limit to the other. A reversible path is one in which the system is kept arbitrarily close to equilibrium, and in the study of metastability this means that all of the intermediate states, as well as the metastable end state, must be in constrained equilibrium with the auxiliary constraints properly and reversibly adjusted at each intermediate point. It

is the imposition and reversible adjustment of such auxiliary constraints that gives rise to difficulty and confusion, and it is on the discussion of this procedure that much of our attention is focused.

One must impose external auxiliary constraints to study metastability by means of thermodynamics, i.e., one must study the equivalent equilibrated system rather than the metastable system itself. The auxiliary constraints restrict the fluctuations in the equivalent equilibrated system to those that can actually take place in the metastable system during the experimental times $\tau_{\exp}$; they must do so without appreciably altering those fluctuations that are significant. Equivalently, the auxiliary constraints can be envisaged as imposed barriers that limit the equivalent equilibrated system to those regions of phase space that can actually be accessed by the metastable system during the experimental times $\tau_{\exp}$; the constraints must do so without appreciably altering the accessed regions. This means that we cannot rely simply on the inequality in eq 1a but must have the total dynamic arrest implied by eq 2, i.e., time must truly be eliminated from consideration. This is nontrivial because the metastable system has no automechanism for restricting itself; all it can accomplish by itself is extreme retardation of access to other fluctuations and other regions of phase space, and it requires the imposition of external auxiliary constraints to limit access permanently. The equivalent equilibrated system has fewer allowed fluctuations and a smaller accessible phase space than the actual metastable system, but it is equilibrated because it actually passes through all its allowed phase space; it is equivalent to the metastable system in the sense that it samples almost the exact same regions of phase space as the metastable system does in the time of the experiment. In most cases of metastability the volume of phase space that must be blocked off is far greater than the part accessible in the experiment.

4. Imposition of External Auxiliary Constraints

To prevent conversion to iron, i.e., transmutation to the ultimate equilibrated system, one usually effects the blockage by tampering with the Hamiltonian, i.e., by using a Hamiltonian which completely overlooks those terms which lead to true equilibrium, or more or less equivalently by the imposition of holonomic constraints which alter the Hamiltonian. Clearly if we used the correct Hamiltonian without imposing some other way of blocking the transmutation, our statistical thermodynamic and thermodynamic analysis would be in considerable trouble. On the other hand, if we have a metastable system consisting of a viscous fluid containing a dissolved dye in contact with pure fluid, we are not likely to tamper with the Hamiltonian, but, much more simply, we can envisage the auxiliary constraint as a barrier inserted between the two halves. Thus although the original system was not at equilibrium, the equivalent constrained system which incorporates the barrier is at equilibrium and can be treated by thermodynamics. Both of these operations are external in the sense that the constraints are imposed by external action. As another example, consider the conversion of a liquid to a glass; the greatly retarded relaxations in the glass must be totally blocked in the equivalent equilibrated system that replaces the actual glass, and this might be achieved either by tampering with the Hamiltonian or by imposition of appropriate external fields that hold the molecules in place.

The change that we wish to make in the usual thermodynamic formalism involves the introduction of auxiliary constraints. Such constraints may or may not be readily imposed in a laboratory experiment. This situation is not really new to thermodynamics. For example, when we use thermodynamic

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potentials such as the Gibbs free energy G to specify the condition, $(\delta G)_{T,p} = 0$, of reversibility and equilibrium, the paths prescribed by constant $\{T,p\}$ must be reversible or else along them G, S, and T cannot be defined within the rules of thermodynamics. Since only those states at the G minimum are in equilibrium specified by the laboratory constraints of interest, the neighboring states being probed can be equilibrated only in the sense that they are constrained by the reversible imposition and removal of auxiliary constraints (variables). There is no need, however, to identify the constraints, and they may even be impossible to apply and their variations may only be virtual in a laboratory experiment, but despite this, the analytical basis of much of ordinary thermodynamics depends on the conceptual application of such constraints.[2]

5. Zero-T Entropy and Causality

We examine the nature of thermodynamic functions of state as $T \rightarrow 0$ K. The third law states that the entropy of an equilibrated system vanishes as $T \rightarrow 0$ K, and this is readily understood in statistical thermodynamic terms as meaning that as $T \rightarrow 0$ K the system can exist only in its ground state which is usually not appreciably degenerate, i.e., the log of the degeneracy is far less than 10^{23}. However, there are systems with very low-lying, highly degenerate states that cannot be brought to equilibrium as $T \rightarrow 0$ K. As examples, one has crystals of CO and NO molecules which should have orientational order and zero entropy at true equilibrium at $T \rightarrow 0$ K, but are found empirically to have random orientations and corresponding empirical entropies of order Rln2 at $T \rightarrow 0$ K; such systems are metastable with orientational relaxation times τ far in excess of any conceivable experimental time, and they are therefore subject to the condition of eq 1a. On the other hand, at sufficiently high temperature the orientational relaxation times become very short, the system is at true equilibrium, and the condition of eq 1b is readily satisfied. A degree of controversy has arisen on the best way to treat such systems thermodynamically. We take the entropy of such systems to be zero, others[7,8] identify a nonzero residual 0 K entropy which is close to the entropy the system had when it first fell out of equilibrium at a higher glass transition temperature, T_g, and still others keep track of distinct thermodynamic (nonzero) and statistical thermodynamic (zero) entropies.[9]

We envisage the problem as follows. To compare the high-T and the $T \rightarrow 0$ K entropies, one must create a reversible path between the equilibrated high-T system (condition 1a) and the equilibrium equivalent of the low-T, metastable system (condition 1b). This path is created by means of the reversible imposition of auxiliary constraints through the exchange of work with the constraints. The equilibrium equivalent state at $T \rightarrow 0$ K is one in which all but very local changes (vibrational) are damped out, and so there are very few allowed fluctuations, or equivalently, the accessible phase space has a very small volume. We therefore expect $S \rightarrow 0$ as $T \rightarrow 0$ K. The relevant equivalent equilibrium state at $T \rightarrow 0$ has a very low entropy despite the fact that the many possible random orientational configurations correspond to a high degree of degeneracy; this is because in the metastable state the system does not access these degenerate states within the experimental time, τ_{exp}, and in the corresponding equivalent equilibrium state (subject to auxiliary constraints) it *never* accesses these many degenerate configurations.

Alternative approaches have focused on the fact that as T is decreased toward 0 K the configurational degeneracy of the metastable state remains very high, and that if one were to wait long enough, i.e., if τ_{exp} were very much longer than currently possible, the system at finite T would actually access all these degenerate states (including the ordered state).[1,7,8] Alternatively, one can think of all these degenerate configurations as being accessed by means of a continuous recycling in which the system is heated (above some glass temperature T_g where the degenerate configurations are all accessed) and then cooled back to the initial low temperature below T_g. This process gives potential access to all the degenerate configurations, and these degenerate configurations are then incorporated into the entropy; as $T \rightarrow 0$ K one finds S approaching a finite value, known as the 0 K residual entropy, that depends on the degree of degeneracy. This view of low-T entropy for metastable systems such as CO has been encouraged by the experimental "fact" that in order to obtain identical values of very high-T entropies (for example, for gaseous CO) obtained from glassy CO at $T \rightarrow 0$ K and from crystalline graphite and oxygen at $T \rightarrow 0$ K, it seems as though one must postulate a finite residual entropy at $T \rightarrow 0$ K for the glassy state. We show below that the reason this residual entropy is required by the experiments is that the paths followed in the relevant experiments have not been reversible ones (they have deviated far from equilibrium), and that, consequently, they lead to a spurious apparent entropy. Observational evidence for the nonreversibility of the path includes the fact that the transition temperature T_g depends, albeit slightly, upon heating and cooling rates. Furthermore, one observes a hysteresis loop about T_g, a sure sign of irreversibility and nonequilibration. Additionally, the state in which the metastable system is found (as specified by its measured properties) is path dependent, specifically upon the rate of temperature quench. All this means that the experimental paths followed in such experiments will be irreversible despite the fact that τ_{exp} may be very long (the experiment slow) and despite the fact that the path appears to be almost reversible.

Another example of the shift from truly equilibrated to metastable systems as temperature is lowered is the crossover from liquid above T_g to glass below T_g, T_g being specified by $\tau(T_g) = \tau_{exp}$. In our analysis the entropy of the glass is very small, approaching zero as $T \rightarrow 0$ K, whereas in the more conventional approach described above the entropy of the glass just below T_g (and even as $T \rightarrow 0$ K) is very close to that of the liquid just above T_g. (Here we do not address the question of whether the ground state of the liquid or of a spin glass is highly degenerate.)

Not only do we believe that residual entropy at 0 K is an artifact resulting from apparent entropy measurements along nonreversible paths but we also find this specification incompatible with a *s*trict-constructionist view of the second law which establishes that entropy is a state function. If it is a state function it depends only upon its measured state, not upon the history of the system and certainly not upon its future. Since the system does not visit its alternative degenerate states during the time of measurement, it is unaware of these states, and the principle of *causality* forbids it to be affected by these states. We do not see how potential accessibility can affect an experimentally based state function. Therefore, in contrast to conventional approaches, the present analysis can be used to explain the values of the apparent residual entropy obtained over irreversible paths without violating either causality or the correspondence between thermodynamics and the statistical mechanical principle that in a single trapped microstate the entropy of a system is zero.

6. Work Associated with Imposition of Auxiliary Constraints

The reversible imposition of external constraints, be they regular or auxiliary constraints, involves nonzero reversible work. Thus, reversible work, δW_{rev}, must be associated with the reversible process needed to connect an initial truly equilibrated state at a temperature T_+, subject to the condition of eq 1b, to a final equivalent equilibrium state at T_-, subject to the condition of eq 1a. The so-called transition temperature or glass-transition temperature T_g lies between T_+ and T_-. The entropy change along the reversible (rev) path is given by

$$\Delta S(T_-) = S(T_-) - S(T_+) = \int_{T_+}^{T_-} dU/T + \int_{T_+}^{T_-} \delta W_{rev}/T \quad (3)$$

where S always refers to a truly equilibrated state, be it the liquid, where $S = S(T_+)$, or the equilibrated state equivalent to the glass, where $S = S(T_-)$, and δW_{rev} is positive when the system performs work on the constraint.

In practice, glasses are formed irreversibly (irrev) in the laboratory by simple cooling below T_g without the use of auxiliary constraints, without the expenditure of any work, i.e., $W_{irrev} = 0$. If, as is usually done, one were then mistakenly to accept the unconstrained glass as equilibrated, and the path from liquid to glass mistakenly as reversible, one would then mistakenly invoke the first law to obtain an apparent (app) entropy change

$$\Delta S_{app} =$$
$$S_{app}(glass,T_-) - S(liq,T_+) = \int_{T_+}^{T_-} dU/T + \int_{T_+}^{T_-} \delta W_{irrev}/T \quad (4)$$

Whereas the change of entropy in eq 3 is independent of path, but dependent upon the reversible work needed to impose auxiliary constraints reversibly, ΔS_{app} depends on path (as is seen by examining the term on the right of eq 4) and so cannot be a true entropy change. The difference between the apparent entropy ΔS_{app} and what we take as the thermodynamically meaningful entropy ΔS given in eq 3 is seen to be the work required to impose the auxiliary constraints needed to retain the system at equilibrium. Equations 3 and 4 can be combined to yield

$$S_{app}(glass,T_-) = S(T_-) - \int_{T_+}^{T_-} [\delta W_{rev} - \delta W_{irrev}]/T \quad (5)$$

where $S(T_+)$ and $S(liq,T_+)$ are the same quantity. In many experiments, $\delta W_{irrev} = 0$. The expression in ref 5 is especially interesting because it illustrates that the $S_{app}(glass,T_-)$, commonly accepted as the entropy of the glass, is path dependent since the work performed can be path dependent. Also since the integral on the right is negative, $S_{app} > S$, where S is the entropy of the equilibrated state equivalent to the glass.

Of particular interest is the change from liquid to structural glass which often takes place over such a narrow temperature range that the process can be envisaged as an isothermal one, $T_+ \approx T_g \approx T_-$. In this case, equation 3 becomes

$$S(eq\ gl,T_g) -$$
$$S(liq,T_g) = [U(eq\ gl,T_g) - U(liq,T_g) + W_{rev}]/T_g \quad (6)$$

where (eq gl) indicates the equilibrated state equivalent to the glass, i.e., the constrained glass. Similarly, the apparent entropy measured when the glass is formed irreversibly without work is the corresponding form of eq 4:

$$\Delta S_{app}(T_g) = S_{app}(glass,T_g) -$$
$$S(liq,T_g) = [U(glass,T_g) - U(liq,T_g)]/T_g \quad (7)$$

The energy of the state is specified whether or not the system is in equilibrium, and so the proper specification of the equivalent equilibrated state requires that $U(eq\ gl,T_g) = U(glass,T_g)$. Thus eqs 6 and 7 yield the result

$$S_{app}(glass,T_g) = S(eq\ gl,T_g) - W_{rev}/T_g \quad (8)$$

Note the subtle point that W_{rev}/T_g is independent of path because $dU/T_g = 0$, but that the integral in eq 5 is dependent upon path.

Finally, one might expect that although the glass transition takes place over a small temperature interval, because it is not a first order thermodynamic transition the ΔU's in eqs 6 and 7 should be vanishingly small. And this seems to be the case (the measured $Q_{irrev} \approx 0$). In this case eq 7 yields

$$S_{app}(T_g) = S(liq,T_g) \quad (9)$$

a result widely used but usually without the indication of the *apparent* nature of this entropy. Below we shall discuss the requirement imposed on the auxiliary constraints in this case, the requirement that they alter S but not U.

As indicated above, we expect $S(eq\ gl) \rightarrow 0$ as $T \rightarrow 0$ K, and furthermore, we do not expect much change in $S(eq\ gl)$ between T_g and 0 K; thus eq 8 leads to $W_{rev} \approx -T_g S(liq,T_g)$, emphasizing the well-known fact that entropy can be reduced by the performance of work. Although we also do not expect much change in $S_{app}(glass)$ between T_g and 0 K, eq 9 leads to a high apparent residual 0 K entropy that is nearly equal to that of the liquid above T_g.

The terms "calorimetric entropy" and "statistical entropy" are often used to distinguish between the measured residual entropy and the entropy prescribed by statistical mechanics, which is equal to zero if the system is trapped metastably in a single configuration. These two concepts are consistently united by consideration of the reversible work performed on a system as it passes through T_g on a hypothetical path determined by the reversible imposition of suitable auxiliary constraints.

7. Vapor Pressure

One way to study changes of condensed phases is to keep track of their vapor pressures. The fact that the vapor pressure of the glass is the same as that of the liquid (both near T_g) has been taken as evidence that the two have the same Gibbs free energy (G) and consequently, since they have the same internal energy, that they have the same entropy. But, as we have seen, in our analysis the entropy of the glass cannot be specified in the absence of auxiliary constraints needed for the specification of the equilibrated state corresponding to the glass (which is equivalent to the statement that entropy can be defined only in a true equilibrium state. The equivalent equilibrated state specified by these auxiliary constraints has the same vapor pressure as does the actual metastable supercooled state. The reason for this is that in the presence of the auxiliary constraints, the condition for phase equilibrium is not $\Delta G = 0$, but rather that ΔG be equal to the work needed to impose reversibly the auxiliary constraints needed to transform an equilibrated phase (gas) to an equivalent equilibrated phase (replacing the glass).

8. A Quantitative Example

A specific example of the imposition of auxiliary constraints for the liquid−glass transition can be helpful in reinforcing the

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several points that have been made. In particular, we can address the nature of the auxiliary constraints that must satisfy the requirement that they leave $\Delta U = 0$ for the transition, whereas the corresponding ΔS must be negative and large.

A simple way of considering the intermolecular interactions is to use a model in which they can be represented by internal fields which inhibit rotations so that the independent molecular motions are oscillatory. In the case of rotors the torsional oscillations might be controlled by a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_{\text{fr}} - \nu \sum_{i}^{N} [\lambda_{\text{int}}(T)/2](\theta_i - \theta_i^{\text{o}})^2 \quad (10)$$

where $\mathcal{H}_{\text{fr}}$ is the free rotor contribution, $\lambda_{\text{int}}(T)$ is the mean force constant attributed to the intermolecular forces, θ_i the orientation of the ith molecular rotor, θ_i^{o} is the orientation of the ith molecular rotor just before the liquid turns to glass, and ν is the number of degrees of rotational freedom (2 or 3). The partition function for this system can readily be calculated to be

$$Q_{\text{liq}}(T) = Q_{\text{fr}}(T)Q_{\text{int}}(\lambda_{\text{int}},T)/\text{h}^{3N} \quad (11)$$

Consequently, for the liquid near T_{g} one has (equipartition)

$$U(\text{liq},T_{\text{g}}) = U_{\text{fr}}(T_{\text{g}}) + N\nu kT/2 \quad (12)$$

$$S(\text{liq},T_{\text{g}}) = \\ U_{\text{fr}}(T_{\text{g}})/T_{\text{g}} + Nk \ln Q_{\text{fr}} + kN \ln[\nu(kT/\lambda_{\text{int}})^{1/2}] \quad (13)$$

Next we consider the external fields that must be applied to create an equilibrated state equivalent to the glass at T_{g}. We might envisage the imposition of fields by means of a yet-to-be developed set of X-ray tweezers that are capable of holding molecules (or rotors) within a small range of positions (angles) determined by the liquid just before it turns to glass. This is a very microscopically specific field which varies from molecule to molecule and has the property of freezing the system in a state very similar to (but not exactly identical to) that in which it was last found in the liquid. The effect of such a field might be represented by a simple increase in the torsional force constants holding the molecules in place. Near the glass transition the intermolecular forces clearly play a big role since with a very slight lowering of temperature they can effectively inhibit rotations within experimental times; thus $\lambda_{\text{int}}/kT > 1$. The effect of the external field or auxiliary constraint is to increase this torsional force constant still further, i.e.

$$\lambda_{\text{ext}} > \lambda_{\text{int}} > kT \quad (14)$$

and since the system subject to the external fields is associated with the equilibrated state equivalent to the glass

$$U(\text{eq gl},T_{\text{g}}) = U(\text{liq},T_{\text{g}}) \quad (15)$$

$$S(\text{eq gl},T_{\text{g}}) = S(\text{liq},T_{\text{g}}) + (kN/2) \ln[\lambda_{\text{int}}/\lambda_{\text{ext}}] \quad (16)$$

These results have the desired properties that the $U(\text{eq gl})$ for the equilibrated state equivalent to the glass be the same as that for the liquid, while the corresponding $S(\text{eq gl})$ be reduced by $|kN \ln[\lambda_{\text{int}}/\lambda_{\text{ext}}]|$. The effect of the external fields is to restrict the angular motions of the molecules, and we see from eqs 16 and 13 that this restriction results in a decrease of entropy; the amount of decrease is determined by the choice of λ_{ext}, which in turn is determined by the actually observed restriction of

rotations in the glass. This decrease can readily be interpreted as a decrease in orientational degeneracy. At the same time equipartition assures that $\Delta n = 0$.

Alternative simple models could be envisaged and implemented. For example, we could envisage the X-ray tweezers as restricting the rotational motion found in the liquid to free rotation within a very small angular range about the orientation each molecule last had in the liquid before turning to glass.

9. Maxwell Demon

A Maxwell demon is a microscopic sprite that has the ability to intervene at just the right moment. The standard introduction to these creatures is focused on the problem of separating a mixture of two gases, A and B, without doing any work. It places a barrier in the middle of the container, drills a small hole through it, and places a gate over the hole. Every time the Maxwell demon sees an A molecule approaching from the right or a B molecule approaching from the left, it opens the gate, and eventually the two gases are separated. Alternatively, the Maxwell demon could be the experimenter who waits patiently for that rarest of fluctuations in which all of the A molecules are on one side and all of the B molecules are on the other, and then opportunistically inserts a barrier (auxiliary constraint) without the expenditure of appreciable work. This is analogous to the procedure followed in forming a glass except that the system self-traps itself (for a long period of time) in a single fluctuation (which though unique is very similar to many others). The Maxwell demon does not violate physical law, but it is not a thermodynamic entity. To achieve the final state thermodynamically (reversibly), the experimenter must introduce the auxiliary constraints reversibly with the expenditure, at least conceptually, of work, and this means that he, she, or it must allow all relevant fluctuations to take place en route to the final state, and not merely catch the system in a lucky (or unlucky) fluctuation.

10. Summary

Metastable systems are not in true equilibrium. Consequently, one cannot directly treat them by thermodynamics and statistical thermodynamics. Furthermore, when one has need to calculate the thermodynamic change of state from a truly equilibrated state to a metastable state, as in studies of the glass transition, one cannot find a reversible path over which to do so because a reversible path must always be infinitesimally close to equilibrium.

Despite the fact that the metastable system is out of equilibrium, we seek a way to apply thermodynamics and statistical thermodynamics to the study of such systems. We require that the thermodynamic and statistical thermodynamic results agree, and that the analysis be independent of time. We also require that the analysis not violate causality, by which we mean that a state function can depend only upon the behavior of the system during the time of the experiment and cannot depend on changes brought about in the future.

A metastable state is taken as a state in which nearly all relaxations take place rapidly compared to the time constant τ_{exp} of the experiment, but for which one (or a small number) of relaxations have long relaxation times such that $\tau(T) \gg \tau_{\text{exp}}$. Such a system is said to be locally equilibrated. The system is truly equilibrated if $\tau(T) \ll \tau_{\text{exp}}$. If many modes relax on times scales large or comparable to τ_{exp}, the system is said to be unstable.

To carry out thermodynamic studies on a metastable system one must excise the slow relaxation, that is one must block it completely. Thus, we must change the actual physical condition

$\tau \gg \tau_{exp}$ to $\tau \rightarrow \infty$. This has the effect of replacing the metastable system with an equivalent equilibrated system which can be studied by thermodynamics and statistical mechanics. The equivalent equilibrium system is held at equilibrium by means of the imposition of external auxiliary constraints which completely block the slow relaxation without in any other way appreciably altering the metastable system. This means that the auxiliary constraints must allow the system in constrained equilibrium to traverse the same parts of phase space in the time τ_{exp} as does the metastable system.

We not only replace the metastable system by an equivalent equilibrium system, but we can also specify a reversible path between a truly equilibrated state and an equivalent equilibrium state representing the metastable state. We do this by imposing the auxiliary constraints reversibly, and this process requires work, work that is absent in the irreversible process by which the metastable state (glass) is actually formed. A problem long recognized in the study of metastable states (glasses) is that their properties may be dependent upon their histories of preparation (rates of temperature quench), and according to the present analysis this means that the equivalent equilibrated state needed to match the experimentally obtained metastable state will be dependent upon the history of preparation. Consequently, the reversible work needed to impose the appropriate auxiliary constraints will vary from experiment to experiment.

One of the consequences of this analysis is that there are no residual 0 K entropies in glasses (random systems). Near 0 K the system cannot access many configurations, i.e., the majority of alternative microstates, despite the fact that there may exist many degenerate configurations. What counts in determining the entropy is the number of configurations that can be accessed during the experiment, not the number of degenerate states that could be accessed if one waited long enough or cycled the system back and forth between the metastable and the truly equilibrated state. The reason that conventional treatments have required nonzero residual 0 K entropies for glasses is that they have often (but not always) mistakenly (we believe) taken the glass to be equilibrated, and consequently, the path over which the glass has been formed, as reversible. One practical difficulty with this approach is that the residual 0 K entropy may depend somewhat on the rate at which the experimental cooling takes place. The present approach, on the other hand, can explain the so-called measured residual entropy without violating causality or requiring that thermodynamics be in any way inconsistent with the statistical mechanical concept that a system trapped in a single microstate have zero entropy.

We have shied away from including $T = 0$ K and have restricted the discussion to $T \rightarrow 0$ K; $T = 0$ K is in many ways singular.

It is only in comparing metastable with stable states (e.g., glass with liquid) that the present discussion of metastablility is important; if one is safely in the $\tau \gg \tau_{exp}$ regime, the discussion of constrained equilibrium and equivalent equilibrium states is academic since the auxiliary constraint plays an entirely passive role. However, auxiliary constraints might be implied even in the following problem. One studies a chemical equilibrium but, when finished, the experimenter opens the container and flushes the contents down the drain. Does this last act of flushing, which converts what seemed like an equilibrated system to a metastable one, have to be included in the studies? Strictly speaking, yes, an auxiliary constraint is needed, one that prevents the experimenter from destroying the experiment because we have insisted that all relaxation be blocked. Imposing this auxiliary constraint may seem trivial in the case described, but it becomes significant

in those many cases where the experimenter intervenes too soon. We see again that although the implied imposition of auxiliary constraints is ubiquitous, in many cases they need not concern us except insofar as they enable us to formulate a self-consistent thermodynamics. It might be noted that no external auxiliary constraints are needed to describe a first-order transition, although sometimes such constraints are introduced for computational reasons.

11. Brief Historical Perspective

Nernst[10] was the first to formulate a statement of the third law of thermodynamics. In 1920 Lewis and Gibson[3] first proposed that a glass should retain an "entropy of mixing" down to very low temperatures, and in 1921 Wietzel,[11] studying fused silica, provided apparent experimental support for this claim. Gibson and Giauque,[12] and then later Simon and Lange,[13] provided further evidence with their low-tempereature studies of glycerol. Thus, in the early 1920s considerable interest in the thermodynamics of glasses had already developed, but the explanation of the observed phenomenon was tentative at best. In 1925, Pauling and Tolman[8] set forth the first rationalization of the apparent large residual entropy of a glass based on the idea of many equivalent disordered configurations (high degeneracy), an idea still advanced by many today.

Years later, Davies and Jones,[14] as well as Wilks,[15] concluded that a glass was not in an equilibrium state—not even in metastable equilibrium—and (as we find) that the transition to the glassy state was irreversible and not treatable by the usual methods of thermodynamics. These authors recognized that a quasithermodynamic treatment of a glass required the introduction of an additional variable denoted as a degree of advancement of reaction (roughly equivalent to our auxiliary constraint), and they combined this with an irreversible thermodynamic approach based on the affinity function introduced by De Donder.[16] Frenkel[17] also introduced an additional variable in an irreversible thermodynamic treatment based upon the concept of local equilibrium with respect to all variables except the additional (auxiliary) one. They did not, however, attack the problem of residual entropy and its noncausal overtones. The use of constraints in the study of metastable systems was later examined by Reiss.[2]

The distinct features of the present analysis are the following: The auxiliary constraints are used to bring the system into true equilibrium (equivalent equilibrated state). The irreversibility of glass formation is characterized by the absence of the reversible work needed to impose the auxiliary constraints reversibly, and this absence coupled with the small observed heat of transition leads to the measurement of a large apparent glass entropy. The present analysis shows the glass entropy to be small, and allows the actual entropy of the 0 K glass to be set at zero, thus reconciling the thermodynamic and statistical thermodynamic pictures and allowing the theory to be compatible with causality, and above all to be compatible with the experimental facts.

In our analysis both the supercooled liquid and the glass are treated on equal footing as metastable states, the difference being that the supercooled liquid requires few auxiliary constraints to restrain it from crystallizing, while the glass requires many additional auxiliary constraints to restrain it from accessing the large number of nearly degenerate states, each of which specifies the distinct glass in which the system is actually stuck in different experiments. In this analysis one understands that the heat capacity anomaly observed at T_g, the temperature at which the glass becomes a liquid, is associated with the removal of a

large number of auxiliary constraints, while the fact that no anomaly is observed at the melting point when the supercooled liquid becomes a stable liquid is due to the fact that very few auxiliary constraints must be removed.

One customary way of treating such problems is to take the liquid as a metastable system because it can access all of the nearly degenerate liquid states, and the glass as an out-of-equilibrium system because it cannot access all of the nearly degenerate glassy states within experimental times; however, in such a formulation the glass cannot be regarded as being in thermodynamic equilibrium, and, therefore, thermodynamics cannot be consistently applied to the glass. Our way of addressing these problems is to constrain the glass so as to allow it to access all of the nearly degenerate configurations associated with a particular glassy state, but to restrict it from accessing (even over long times) configurations associated with other glassy states; in statistical thermodynamic terms this means that both the liquid and the glass are permitted to access *all allowed* parts of phase space, but the part of phase space allowed (because of the auxiliary constraints) to the glass is very much more limited.

In still another approach, stable and metastable states for one-component systems can be specified by pressure, temperature, and density (for multicomponent systems we add variables of composition); the properties of such systems (liquids and supercooled liquids) are independent of path of formation, while in out-of-equilibrium states (glass) the properties are dependent upon the paths of formation. In this formulation, too, one cannot apply thermodynamics to the glass and it is even not clear how to treat the supercooled liquid. In contrast, in our formulation the difference between supercooled liquid and glass, as described above, merely lies in the number of auxiliary constraints needed, and any path in which the auxiliary constraints are imposed reversibly and that leads to the appropriate specific glassy state may be used. Additional constraints are equivalent to additional variables that must be specified.

As we mentioned at the outset, aspects of our formulation of metastability have been implied by various authors focused on specific phenomena such as the glass transition, but the method seems not to have been presented or pursued within a consistent and universal framework. In one such picture, each particular glass has been envisaged as a system at constrained equilibrium, and the liquid envisaged as a collection of its glasses (with the auxiliary constraints, denoted as order parameters, removed).[14,6] Recently Speedy[6] has implemented these ideas by imposing auxiliary constraints that hold his simulation liquid in distinct glassy configurations, but in comparing the entropy of the glass with that of the liquid he does not take account of the work involved in imposing and removing the auxiliary constraints reversibly, although he does make mention of our view that such reversible work is crucial.

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