Abstract. Starting for the Stillinger and Weber expression for the free energy of supercooled liquids, we extend the free energy to the case in which two time scales separate and the system is in quasi-equilibrium. The concept of an effective temperature, different from the kinetic temperature, is naturally introduced. An example of hypothetical quasi-equilibrium phase diagram is presented for the case of SPC/E water.

1. Introduction

The study of the properties of undercooled liquids is a topic of current research. Under the name of undercooled liquids we will indicate liquids whose relaxations start to show a separation between different timescales. The idea of considering the dynamics of undercooled liquids as similar to the vibrations of a disordered solid on short timescales, while attributing the slow dynamics to rare change in the global structure (i.e. the atomic position of the disordered solid assumed as the reference for short time vibrations) is old [1]; in particular, the fruitful reformulation of Goldstein [2] of these ideas in terms an energy landscape has led to the introduction of a formalism [3] that is particularly suitable for the study of liquids via Monte Carlo or Molecular Dynamics simulations [4].

In Sec. 2 we describe such formalism, showing that it is particularly suitable to investigate the connections between the statics and the dynamics of equilibrium systems. In Sec. 3 we show that such formalism can be extended to systems in quasi-equilibrium via the introduction of a temperature for the slow degrees of freedom that can be measured both via dynamics and
via statics. In Sec. 4 we speculate on the possibility of quasi-equilibrium, quench-rate dependent critical points.

2. Free energy for a supercooled liquid

The phase space of a system can be in general partitioned in different ways, giving rise to equivalent rewritings of the free energy \[5\]. In general, we will consider systems with an hamiltonian \( H \) and therefore disregard the momentum space as it can be trivially integrated out; we will therefore concentrate on the \( fN \)-dimentional configuration space \( W \), where \( f \) is the number of spatial degrees of freedoms of a particle and \( N \) is the number of particles. What makes us prefer or introduce a particular partition is its physical relevance ad interpretation.

Stillinger and Weber introduced such a partition \[3\] in the spirit of the Goldstein picture of undercooled liquids dynamics (see Fig. 1). They associate to each configuration the configuration reached following a steepest descent path to minimize the potential energy. Such configuration is called an Inherent Structure (IS) and corresponds to a local minimum of the potential energy (Fig. 2). While to each IS we can associate its potential energy \( e_{IS} \), the converse is not true: to each energy level \( e_{IS} \) there will be associated a degeneracy \( \Omega(e_{IS}) \) counting the number of local minima with energy \( e_{IS} \) \[6\] (Fig. 2). Following the reasoning of Goldstein we can already argue that \( e_{IS} \) is a good candidate to be a slow variables of the system, as it is associated to the global structure of a liquid and not to its vibrational excitations. Defining the configurational entropy \( s_{conf} = k_B \ln(\Omega(e_{IS})) \), we can write the Helmotz free energy of the system at temperature \( T \) and volume \( V \) as \[3\]

\[
F(T, V) = e_{IS}(T, V) - Ts_{conf}(e_{IS}, V) + f_{vib}(e_{IS}, T, V)
\] (1)

where \( e_{IS} \) is the energy of the typical minima at \( (T, V) \), \( s_{conf} \) for each fixed \( V \) will depend implicitly on the temperature via the \( T \) dependence of \( e_{IS} \) and \( f_{vib} \) is the average free energy of the typical basins at \( (T, V) \). At fixed \( V \), \( f_{vib} \) will depend on the shape of the basins (we assume that the shape
of the basin can be parametrized by $e_{IS}$ and on the average kinetic energy (therefore on $T$). The validity of such approximations has been carefully checked and confirmed via numerical simulations of different atomic and molecular model systems [7–12].

For real systems $s_{conf}$ has been often approximated by the difference of the entropy of the liquid and the entropy of some reference solid phase [13]. For computer liquids we have access to the IS configurations and can therefore estimate the “true” $s_{conf}$. In particular, we can use thermodynamic integrations using the relation

$$ds_{conf} = \frac{de_{IS}}{T} + \frac{df_{vib}}{T} = \frac{de_{IS}}{T} \left(1 + \frac{\partial f_{vib}}{\partial e_{IS}}\right)$$

for the differential of $s_{conf}$ obtained using the extremum condition $\delta F = 0$. To calculate $F$, first an accurate estimate of $e_{IS}$ must be obtained by minimizing the potential energy of equilibrium configurations of the liquids. The estimate of $f_{vib}$ includes two steps: first, the harmonic contribution $f^h$ valid at low temperatures is obtained calculating the normal mode frequencies $\omega_i$ ($i = 1..fN$ [14]) near the IS minima; the exact calculation for a collection of harmonic oscillators gives us the estimate [15]

$$f^h = -k_B T << \ln \left(\frac{\hbar \omega}{2 \pi k_B T}\right) >>$$

where the average $<<..>>$ [16] is intended both on the IS configurations and on all the $fN$ modes. For systems like binary mixture Lennard Jones, $f^h$ is already a good estimate for $f_{vib}$ [7]. In the case of a molecular liquid, the SPC/E model for water [17], measurable deviations are found [8]. Still, deviations are small and can be estimated as perturbative corrections to the ideal harmonic oscillator behavior [18]. In practice, what it is found is that heating up IS’s one can estimate the anharmonic corrections $e_{anhar} = aT^2 + bT^3 + ...$ to the ideal harmonic behavior $e = e_{IS} + (f/2)k_B T$. 

Figure 2. Sketch of the Stillinger-Weber partition of the configuration space $W$. The configurations indicated as $IS^i$ are local minima of the potential energy; all the configurations of the basin $W^i$ are associated to $IS^i$ via steepest descent.
Figure 3. The free energy of undercooled liquids can be expressed in terms of the energy levels $e_{IS}$ of the inherent structures $IS$, to their degeneracy $\Omega(e_{IS})$ and to the shape (in harmonic approximation, to the curvature $\omega$) of the associated basins.

Therefore, once $e_{is}$ and $f_{vib}$ have been estimated, we can reconstruct $s_{conf}$ by thermodynamic integrations. The behavior of $s_{conf}$ is related to the possibility of an ideal glass transition [13]. If $s_{conf}$ becomes zero at some finite temperature $T_K$ (the so-called Kauzmann temperature [19]), this means that the liquid is in a metastable state, trapped in the basin of a single minima; therefore diffusivity is zero and the thermal vibrations around the disordered structure (the IS of the minimum) are the only sort of motion taking place. A precise functional dependence has been proposed by Adam and Gibbs [20] among $s_{conf}$ (a static quantity) and the diffusion coefficient $D$ (a dynamic quantity):

$$D \propto e^{-\frac{A}{T_{conf}}}$$

where $A$ is almost constant with $T$ [20, 21]. Up to now, the Adam-Gibbs relation (Eq. 4) has always been found to be consistent with simulation results [8, 9, 11, 12] (see Fig. 2).

3. Free energy for quasi-equilibrium states

Attempts to construct thermodynamics for out-of-equilibrium states have not yet come to a success; in particular, for glassy systems the history of the system cannot in general be disregarded so that no static theory with a small number of parameters can be constructed [5]. In the case of undercooled systems, where a separation between two different time scales becomes sharper and sharper, it is possible to generalize in a straightforward way the expression for the free energy. In the case of simulated liquids, quenching at low $T$, the time evolution of $e_{IS}$ is slow, with a decay compatible with a logarithmic or a very small power-law decay [7], while the short time dynamics has a much faster timescale and is vibrational in character (see Fig. 3). We can then treat our system as two subsystems in contact: a vibrational subsystem, linked to the fast vibrations in a basin, and the configurational subsytem of the local minima $IS$’s, whose dynamics is reflected by the slow decay of $e_{IS}$ (see Fig. 3). On the timescales
Figure 4. Adam-Gibbs plot of diffusivity $D$ versus $1/Ts_{conf}$ [8]. The plot shows that there is a strong correspondence among the dynamics and the statics of undercooled liquids [22, 23]. For the sake of clarity, the values of $D$ have been shifted by multiplying by powers of 5 from $5^0$ (the lowermost curve $\rho = 0.95\, \text{g/cm}^3$) to $5^5$ (the uppermost curve $\rho = 1.40\, \text{g/cm}^3$)

where the vibrational subsystem comes in equilibrium with the external heat-bath at temperature $T_{bath}$ (in this sense, the vibrational subsystem is canonical [24]), $e_{IS}$ is almost constant (in this sense, the configurational subsystem is almost microcanonical [24]).

If we assume that the basins corresponding to a given $e_{IS}$ visited in out-of equilibrium are the same (or have the same characteristics) of the ones visited in equilibrium, we can use the expression of $f_{vib}(e_{IS}, T)$ obtained in equilibrium to take account of the vibrational part of the free energy. Obviously, the vibrational temperature will be equall to the external bath temperature $T_{bath}$. The configurational part corresponds to the almost microcanonical subsystem of the energy levels $e_{IS}$ together with their degeneracies $\Omega(e_{IS})$. Now, we can write in general the free energy of this subsystem as $e_{IS} - T_{int}s_{conf}(e_{IS})$ where $T_{int}$ (we will indicate $T_{int}$ as the internal temperature) can be in general different from $T_{bath}$ [5]:

$$F = e_{IS} - T_{int}s_{conf}(e_{IS}) + f_{vib}(e_{IS}, T_{bath}). \quad (5)$$

$T_{int}$ interpreted as a parameter that “optimizes” the free energy [26] given the constraints that the energy of the minima is $e_{IS}$ and that the vibrational subsystem has temperature $T_{bath}$. Therefore, we can derive an expression of $T_{int}$ [7, 27] extremizing the generalized free energy:

$$\frac{\partial F}{\partial e_{IS}} = 0 \rightarrow T_{int}(e_{IS}, T_{bath}) = \frac{1 + \frac{\partial f_{vib}}{\partial e_{IS}}}{\frac{\partial s_{conf}}{\partial e_{IS}}}. \quad (6)$$
Figure 5. (a) The typical decay of a correlation function in undercooled liquids. The fast relaxation corresponds to the vibrational dynamics and can be treated in the harmonic approximation using the instantaneous normal mode approach (b) Typical decay of $e_{IS}$ after a deep quench. A slow logarithmic law is compatible with numerical data [7, 25].

Figure 6. Quenching the system (i.e. lowering rapidly the external temperature $T_{bath}$ of the heat bath), vibrational degrees of freedom come rapidly at a canonical (NVT) equilibrium with the bath, while the subsystem corresponding to structural changes (the IS’s) relaxes slowly and can be treated as an almost microcanonical (NVE) system in which $e_{IS}$ does not change over the characteristic vibrational timescales.

Up to now, we have a theoretical prescription for $T_{int}$ that is self consistent with our writing of the generalized free energy. At this point, two questions naturally arise: first, is it possible to write the free energy in terms of experimentally measurable quantities? And then, can we measure $T_{int}$?

Regarding the first problem, we recognize that already in the 30’s an approach to the construction of an out-of-equilibrium free energy for ex-
Experimental glasses had been attempted by Davies and Jones [28] in terms of “frozen observables”, i.e. quantities that maintain values typical of high temperatures after quenching; a successful implementation of such ideas is found in [29], who uses the “more” concrete enthalpies of shock compressed hard-sphere liquids [30] to calculate the equilibrium configurational entropy.

Regarding the measurement of $T_{\text{int}}$, we can resort to dynamics measurements: it is in fact known both from theory [31], numerical simulations [7] and experiments [32], that out of equilibrium systems can exhibit at least two temperatures. A simple way to measure such temperatures is through the application of linear response theory [33]. Let’s consider a perturbed Hamiltonian $H_P = H - \lambda B$, where $H$ is the unperturbed Hamiltonian, $B$ is a generic observable and $\lambda$ is a small parameter. Linear response theory predicts [34] that, switching on the perturbation at time $t = 0$, we have

$$< A(t) >_P = \frac{-\lambda}{k_B T} [C_{AB}(t) - C_{AB}(0)]$$

where $< A(t) >_P$ (the response of the system) is the time evolution of the average of an observable $A$ in presence of the perturbation and $C_{AB}(t) = < A(t)B(0) >$ is the correlation function (the decay of fluctuations) between the observables $A$ and $B$ in absence of the perturbation. Therefore, from the slope of a parametric plot of $< A >_P$ versus $\lambda C_{AB}$, the temperature is measured from the dynamics of the system (see Fig. 3).
While at short times such temperature coincides with \( T_{bath} \), at long times a temperature \( T_{\text{eff}} \neq T_{bath} \) is measured in quenching experiments. In the case of binary-mixture Lennard Jones system, it has been verified that \( T_{\text{eff}} = T_{\text{int}}(e_{IS}, T_{bath}) \) \[7\]. In general, \( T_{\text{eff}} \) tends to be higher than \( T_{bath} \) and of the order of the temperature at which the system is in equilibrium exploring basins of depth \( e_{IS} \). Somehow, the configurational part of the system “remembers” the temperature at which was originated.

4. Out of equilibrium phase diagram for SPC/E water

Equation 5 and 6 allow to develop, using the inherent structure formalism, an expression for the free energy for disordered materials even in out-of-equilibrium states; for such free energy, the “history” of the system is described by its \( e_{IS} \) value. In this section we present a preliminary application to the case of SPC/E water.

The low temperature of SPC/E water has been object of a massive computational investigations in order to investigate the slow dynamics of molecular liquids \[35\] and to check the liquid-liquid critical point scenario \[36\]. In particular, the properties of the energy landscape have been thoroughly analyzed in order to find connections between the dynamics and the statics of such a system \[8, 22, 37\].

The profile of the energy of SPC/E versus the volume develops a change in concavity already in the region numerically accessible (see Fig. 4), suggesting the possibility of a phase transition hindered by the entropic terms. Low temperature extrapolations predict indeed a liquid-liquid critical point a temperature of \( \sim 130 \) K and a specific density of \( \sim 1.1 \) g/cm\(^3\) \[38\]. Such a transition would be located beyond the predicted Kauzmann line for SPCE water \[8\] and therefore unaccessible to equilibrium studies \[39\].

To derive an expression for the free energy in the low temperature region of SPC/E water, we select for simplicity the harmonic approximation, where \( f_{\text{vib}}(e_{IS}, V, T_{bath}) \approx f^h = -k_B T_{bath} < < \ln \left( \frac{\hbar \omega(e_{IS}, V)}{2 \pi k_B T_{bath}} \right) >> \) (Eq. 3). We use the data for \( s_{\text{conf}} \) at \( T = 210 \) \[8\] as reference entropy to obtain an expression for \( s_{\text{conf}}^h \):

\[
s_{\text{conf}}^h(e_{IS}, V) = s_{\text{conf}}^{T=210}(V) + \int_{210}^{T(e_{IS}, V)} \frac{de_{IS} + df^h}{T},
\]

where \( T(e_{IS}, V) \) is the temperature at which a system at volume \( V \) in equilibrium has \( IS \)'s of energy \( e_{IS} \). We obtain then the generic expression for the free energy in harmonic approximation:

\[
F^h(e_{IS}, T_{bath}, V) = e_{IS} - T_{\text{int}}(e_{IS}, T_{bath}, V)s_{\text{conf}}^h(e_{IS}, V) + f^h(e_{IS}, T_{bath}, V).
\]
First, we check the equilibrium phase diagram for $F^h$. No phase transition is found in the physical region where $s_{conf} > 0$. We then perform an ideal experiment: we consider the free energy of state point $s$ in equilibrium at a temperature $T_{eq}$ after a sudden quench at $T_{bath} = 100K$ (well below the Kauzmann locus). After a rapid quench, $e_{IS}$ has not time to change on the timescales of vibrations, so that $e_{IS}$ and $s_{conf}$ remain to their equilibrium values, while $f_{vib} \approx f^h(e_{IS}(T_{eq}), T_{bath} = 100K)$.

The value of the internal $T_{int}$ can be calculated from Eq. 6 and will be in general different from the temperature $T_{eq}$ at which the quench has started. In the harmonic approximation, Eq. 6 becomes

$$T_{int} = T_{eq} \frac{1 - a T_{bath}}{1 - a T_{eq}}$$

where $a = \frac{\partial<<k_B \ln[\omega(e_{IS}, V)]>>}{\partial e_{IS}}$ and $T_{eq}$ is the temperature at which minima of depth $e_{IS}$ are populated in equilibrium.

In the case of SPC/E water, as can be inferred from Fig. 4, $a$ is small (order $10^{-2}K^{-1}$) such that $T_{int} \approx T_{eq}$, differing from the case of the binary mixture Lennard-Jones [7] where $a$ is relevant and $T_{int} < T_{eq}$ significantly.

Therefore, for SPC/E water in the harmonic approximation, it is not possible to “shift up” the critical point above the Kauzmann line. This is true for two reasons: first, in SPC/E water the vibrational part $f_{vib}$ of the free energy has a very small dependence both on $V$ and on $e_{IS}$ compared to the remaining term. Therefore, if we ignore $f_{vib}$, the phase diagram stays almost unchanged. The only way then to get a phase transition is to “kill” the entropic term $T_{int}s_{conf}$; but from Eq. 6 we see that, as $\partial f_{vib}/\partial e_{IS} << 1$,
Figure 9. (a) example of the linear dependence of $e_{IS}$ versus $1/T$ (b) the average logarithm of the basin’s curvature is approximatively linear in $e_{IS}$

$T_{\text{int}} \approx T_{eq}$ where $T_{eq}$ will be approximatively equal to the temperature at which the quench is started as the change of $e_{IS}$ is logarithmically slow. So, for systems where $f_{\text{vib}}$ does not vary much with $e_{IS}$ (i.e. the shape of the basins does not vary much), the temperature of the slow degrees of freedom of the systems after a quench stays almost the same as the starting temperature of the quench. In order to decrease drastically the internal temperature (and therefore decrease the entropic term of the free energy hindering eventual critical points), one has to resort is a system with a strong dependence of the shape of the basins with $e_{IS}$. In the extreme case $\partial f_{\text{vib}}/\partial e_{IS} >> 1$, we would have the ideal situation $T_{\text{int}} \approx T_{\text{bath}}$. The possibility of the appearance of critical points in out-of-equilibrium situation is a new issue that deserves to be further addressed and investigated.
5. Acknowledgments

We thank Robin Speedy for stimulating discussions and acknowledge partial support from INFM-PRA-HOP, INFM Iniziativa Calcolo Parallelo and MURST-PRIN98.

References

1. J. Frenkel  *Kinetic theory of liquids* Dover publications, New York 1955
2. M. Goldstein,  *J. Chem. Phys.* 51, 3728 (1969).
3. F.H. Stillinger and T.A. Weber,  *Phys. Rev. A* 25, 978 (1982);  *Science* 225, 983 (1984); F. H. Stillinger,  *Science*. 267, 1935 (1995).
4. M.P. Allen and D.J. Tildesley  *Computer simulation of liquids*, Clarendon Press, Oxford 1987
5. R.G. Palmer,  *Reviews of Modern Physics* XX, 669 (1982/83)
6. Note that a rigorous analysis requires the definition of a density of states $d(e_{IS})$ such that $d(e_{IS})\Delta$ are the number of $IS$ with energy between $e_{IS}$ and $e_{IS} + \Delta$ [40].
7. F. Sciortino, P. Tartaglia  *Phys. Rev. Lett.* 86, 107 (2001).
8. A. Scala, F.W. Starr, E. La Nave, F. Sciortino, and H.E. Stanley,  *Nature* 406, 166 (2000).
9. R.J. Speedy,  *J. Chem. Phys.* 114, 9069 (2001)
10. S. Buchner and Andreas Heuer,  *Phys. Rev. Lett.* 84, 2168 (2000).
11. S. Sastry,  *Nature* 409, 164 (2001)
12. I. Saika-Voivod, P. H. Poole, F. Sciortino,  *Nature* (in press).
13. P.G. Debenedetti  *Metastable liquids*, Princeton University press, 1999
14. Note that there are three spurious zero frequency modes corresponding to the translation of the system.
15. L.D. Landau, E.M. Lifits,  *Statistical Physics* Moscow : Mir
16. Note that for the derivation of the free energy of the equilibrium liquid we are always assuming that self averaging for all observables. This is not in general the case for systems with complex landscapes at low temperatures [41]
17. H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma,  *J. Phys. Chem.* 91, 6269 (1987).
18. R.P. Feynmann,  *Statistical mechanics: a set of lectures*, Benjamin-Cummings, London, 1982
19. A.W. Kauzmann,  *Chem. Rev.* 43, 219 (1948).
20. G. Adams and J.H. Gibbs,  *J. Chem. Phys.* 43, 139 (1965).
21. S. Corezzi,  *cond-mat* 0106513
22. E.La Nave A.Scala, F.W.Starr, F.Sciortino, H.E.Stanley,  *Phys. Rev. Lett.* 84, 4605 (2000)
23. L.Angelani, R. Di Leonardo, G. Ruocco, A. Scala, F. Sciortino  *Phys. Rev. Lett.* 25, 5356 (2000)
24. J.W. Gibbs  *Elementary principles in statistical mechanics*, New York: Charles Scribner’s Sons - London : Edward Arnold , 1902
25. L. Angelani, R. Di Leonardo, G. Parisi, G. Ruocco  *cond-mat* 0011519: R. Di Leonardo, L. Angelani, G. Parisi, G. Ruocco, A. Scala, F.Sciortino,  *cond-mat* 0106214
26. E.T. Jaynes,  *Phys. Rev.* 106, 620 (1957);  *Ibidem* 108, 171
27. Franz
28. R.O. Davies and G.O. Jones,  *Adv. Phys.* 2, 370 (1953).
29. R.J. Speedy,  *Phys. Chem. B* 103, 4060 (1999)
30. F.H. Stillinger, E. DiMarzio, R.L. Kornegay,  *J. Chem. Phys.* 40, 1564 (1964).
31. L. F. Cugliandolo, J. Kurchan and L. Peliti  *Phys. Rev. E* 55, 3898-3914 (1997).
According to the Adam-Gibbs expression (Eq. 4), at the Kauzmann line corresponding to \( s_{\text{conf}}(V, T) = 0 \) diffusion becomes zero and the system cannot evolve anymore.