A model for the fragile-to-strong transition in water

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A model based on the existence of two different competing local structures in water is described. It is shown that it can explain the transition between fragile and strong behavior that supercooled water has around 220 K. The high temperature behavior is similar to that observed in standard fragile glass-formers. The strong behavior at low temperatures is associated with the existence of a remanent configurational entropy coming from the possibility of locally choosing between the two possible environments.

I. INTRODUCTION

The form of the dependence of viscosity on temperature is among the many properties that make water an anomalous fluid. Water is a fragile fluid when viewed on cooling. This behavior is typical of many substances known as fragile glass-formers. However, close to the glass temperature $T_G$ ($\sim 136$ K) supercooled water shows characteristics of a strong liquid, in which there is an almost temperature independent configurational entropy, that manifests in an Arrhenius dependence of the viscosity $\eta$ as a function of $T$. Thermodynamic constraints limit the transition between these two regimes to occur rather sharply in a temperature range around $\sim 220$ K.

There is by now a good piece of evidence that many of the anomalous properties of water can be rationalized by the use of an effective, two particle, spherical interaction potential, of the core-softened type. This interaction can be viewed as appearing between clusters of water molecules, rather than between single molecules. The main characteristic of this interaction is that it allows for two different equilibrium distances between clusters, depending on pressure. An appropriate, simplified model that capture many of the anomalies of water is provided by spherical particles interacting through a potential consisting of a hard core plus a soft repulsive shoulder. Here we show–using an analytically solvable version of it–that this kind of interaction can also explain the non-standard behavior of $\eta(T)$.

II. HARD SPHERES MODEL

We will use a model of hard spheres as a starting point (in the next section it will be generalized to describe the properties of water). We will suppose that the pure hard sphere system has an ideal thermodynamical glass transition at some temperature $T_0$ when the fluid phase is supercooled, preventing crystallization. A possible scenario for this glass transition is the following. For glassy systems there is a contribution $s_c$ to the entropy–referred to as configurational entropy–that comes from the many different configurations in which the glass can exist. For the case of spheres it comes from the many ways in which the spheres can be accommodated in stable, non-crystalline arrangements. These configurations differ in the value of the specific volume $v$. We will suppose that hard spheres have a configurational entropy per particle $s_c^{HS}(v)$ of the form:

$$s_c^{HS}(v) = \alpha (v - v_0) - \beta (v - v_0)^2.$$  

According to this formula, $s_c^{HS}$ becomes lower than zero for $v < v_0$ and $v > v_0 + \alpha/\beta$, indicating that there are no accessible states in this range, i.e., $T_0$ is the minimum value that $v$ can take. To get the total entropy $s_{tot}$ of the system we should still include the contribution coming from small vibrations around each configuration. However, for our purpose this will not be necessary, since (as we will see below) $\eta$ is given in terms of $s_c$, rather than $s_{tot}$, and $s_c(T)$ is independent of the vibrational contribution to the entropy. The previous form of the configurational entropy implies the existence of an ideal thermodynamical glass transition occurring at $T_0$, where $T_0$ is obtained from $P/T_0 = \partial s_c^{HS} / \partial v|_{v=v_0} = \alpha$. Whereas from microscopic grounds there is no rigorous proof that this transition should occur, the consequences on observable magnitudes that can be predicted from it are consistent with the known phenomenology of glassy systems and with results of numerical simulations. For $T < T_0$, $s_c^{HS}$ is given by

$$s_c^{HS}(T > T_0) = \frac{\alpha^2}{4 \beta T^2} (T^2 - P^2 / \alpha^2) = \frac{\alpha^2}{4 \beta T^2} (T^2 - T_0^2)$$

This expression for $s_c^{HS}$ can be used to calculate transport properties such as the viscosity $\eta$ through the use of

*In Ref. a parabolic form for $s_c$ as a function of density (instead of $v$) is used. The difference between both choices is tiny, and both give rise to an ideal glass transition.
the Adam-Gibbs formula [17]. It states that the value of \( \eta \) is given by
\[
\eta(T) = \eta_0 \exp[A/(Ts_c)],
\]
which for hard spheres becomes
\[
\eta^{HS}(T) = \eta_0 \exp \left[ 4A\alpha^2 \beta T/(T^2 - T_0^2) \right]
\]
where \( \eta_0 \) and \( A \) are constants. This is a behavior typical of a fragile glass-former, in which \( \eta \) increases more rapidly than in a simple thermally activated process, and it diverges when \( T \to T_0 \). The presence of \( s_c \) in (3) reflects the fact that jumps between different basins of the energy landscape become less probable as the number of these basins diminishes.

### III. Core-softened models for water

Properties of water have been studied recently by using models in which particles interact through potentials that allow for two different equilibrium distances between particles, namely \( d_0 \) and \( d_1 > d_0 \) [3]. One possibility is, for instance, to take a strict hard core at \( d_0 \) and a shoulder that vanishes at \( d_1 \) [2]. Here we will use a further simplification of this kind of models in order to be able to extract analytical results [2]. We consider spheres of radius \( r_1 = (d_1/2) \). Pairs of spheres will be allowed to overlap (more than two overlapping spheres will not be allowed), and each time this happens the system will be charged an energy \( \varepsilon_0 \). This may be considered as a limiting case of particles with a core-softened potential, in which there is a low energy hard core at a distance \( 2r_1 \), and a strict hard core at \( 2r_0 \), and we are taking \( r_0 = 0 \). To make the problem analytically tractable, we will also suppose that each time two spheres overlap, they are constrained to have their centers in exactly the same position. This approximation neglects the entropy associated with small vibrations of the particles in each pair.

We are interested in the configurational entropy \( s_c \) of the system, now as a function of the specific enthalpy \( h = P v + \varepsilon \), that includes the internal energy \( \varepsilon \) coming from the existence of overlapping particles. To calculate \( s_c(h) \) we proceed in the following way. Suppose we have a system of \( N \) particles, \( n \) of them in non overlapped positions and \( n' \) pairs of overlapped particles \( (N = n + 2n') \). The configurational entropy will be that of \( n + n' \) hard spheres plus the combinatorial entropy for locating the \( n' \) pairs in the \( n + n' \) possible positions, i.e.,
\[
\tilde{s}_c = \frac{n + n'}{N} s_c^{HS} + k_B \ln \left( \frac{n + n'}{n'} \right)
\]
(here we use \( \tilde{s}_c \) to indicate an entropy functional). Using \( x = n'/N \) and \( \tilde{v} = V/(n + n') = v/(1 - x) \) as independent variables we can write \( \tilde{s}_c \) as
\[
\tilde{s}_c(x, \tilde{v}) = (1 - x) s_c^{HS}(\tilde{v}) + \frac{k_B}{1 - 2x} \ln \left( \frac{1 - x}{1 - 2x} \right) + x \ln \left( \frac{1 - x}{x} \right).
\]

In order to get the thermodynamic value of \( s_c(h) \) at each value of the external pressure \( P \), we have to maximize \( \tilde{s}_c \) for each fixed value of the enthalpy, i.e.,
\[
s_c(h) = \min_{x, \tilde{v}} \left| \tilde{s}_c(x, \tilde{v}) \right|
\]
\[
h = P v + \varepsilon = (1 - x) P \tilde{v} + x \varepsilon_0.
\]

### IV. Results

In Fig. 1 we see \( s_c, x, \) and \( v \) as functions of \( h \) for three different values of \( P \), using expression (3) for \( s_c^{HS}(v) \) with \( \alpha = 2.79 k_B r_1^{-3} \), \( \beta = 0.97 k_B r_1^{-6} \), \( v_0 = 6.37 r_1^4 \) which are values extracted from numerical simulations of hard spheres systems [14]. We also plot in Fig. 1 the limiting cases \( \tilde{s}_c(x = 0) \) and \( \tilde{s}_c(x = 0.5) \), corresponding to all particles in singled or overlapped positions, respectively. The thermodynamic value \( s_c(h) \) can never be lower than \( \tilde{s}_c(x = 0) \) or \( \tilde{s}_c(x = 0.5) \). The states with the lowest enthalpy for \( x = 0 \) and \( x = 0.5 \) have (from (3)) \( h = P v_0 \) and \( h = P v_0/2 + \varepsilon_0/2 \), respectively. These values coincide at \( P_{cr} \equiv \varepsilon_0/v_0 \). In Fig. 1(a), \( P = 0.9 P_{cr}, s_c(x = 0) \) is always greater than \( \tilde{s}_c(x = 0.5) \) and for this reason \( x \) takes values close to 0, indicating that most particles are in singled positions. The obtained \( s_c(h) \) function departs from zero with infinite derivative at \( h = 0.9 \varepsilon_0 \) (because of the combinatorial contribution to the entropy) but it still has a singularity (namely a jump in its second derivative) when \( \partial s_c / \partial h = \alpha/P \). In (b) the value of \( P = 1.1 P_{cr} \) is larger, and at low \( h \) the contributions with \( x = 0.5 \) dominate, indicating that the system has almost all particles coupled in pairs. For higher \( h \), \( x \) goes down to zero, namely paired particles become rare. In (c), the value of \( P = P_{cr} \) is exactly that at which the ground state of the system with \( x = 0 \) and the one with \( x = 0.5 \) are degenerated. In this case, entropy starts from a finite value \( \approx 0.48 k_B \) at \( h_{min} = \varepsilon_0 \), corresponding to the maximum combinatorial entropy of choosing which particles are singled, an which are paired.

To get the values of the thermodynamic variables as a function of \( T \), instead of \( h \), we have only to make use of the relation \( T^{-1} = \partial s_c / \partial h \). The results for the configurational entropy \( s_c(T) \) and the viscosity \( \eta(T) \) (calculated using the Adam-Gibbs formula (3)) are shown in Fig. 2.

### V. Discussion and comparison with water

From Fig. 2(a) we see that for any \( P \), \( s_c \) is finite for all \( T \neq 0 \), i.e., there is no vanishing of \( s_c \) at any finite
temperature, contrary to what happened in the case of simple hard spheres (see Eq. (2)). This is due to the possibility for the system of having particles singled or paired, which always accounts for the existence of a non-zero combinatorial entropy. For \( P = P_{cr} \) the bottoms of the \( s_c \) functions corresponding to \( x = 0 \) and \( x = 0.5 \) coincide (Fig. 3(c)), and this combinatorial entropy can be used up to \( T = 0 \), in such a way that \( s_c \) remains finite, even when \( T \rightarrow 0 \). For \( P \neq P_{cr} \), \( s_c \) goes to zero as \( T \rightarrow 0 \), as the ground state is unique. There is still a phase transition at finite temperatures, signaled by the kink in the \( s_c(T) \) curves in Fig 2(a). The position of this kink in the \( P-T \) plane is given by \( P/T = \alpha \). In the \( \log(\eta)-1/T \) plot (Fig. 3(b)), the kinks mark the transition between a fragile and a strong behavior. At high \( T \), \( s_c \) diminishes rapidly with temperature and the system is fragile. This behavior is equivalent to that of the simple hard sphere system (see Eq. (1)). At low \( T \), the dependence of \( s_c \) on \( T \) is much weaker, indicating a stronger behavior. In this regime, the available configurational entropy is mainly of combinatorial nature.

For this model there is no ideal glass transition, i.e., \( \eta \) is finite at any finite temperature, and \( T_0 = 0 \). However, from an experimental point of view, the glass transition \( T_G \) is conventionally defined as the value of \( T \) at which \( \eta \) takes some large value (this is usually taken to be \( 10^{13} \) poise). In Fig. 3 we show curves of constant \( \eta \) extracted from our model. Each of these may be thought as defining a dynamical glass transition temperature \( T_G \) (that depends on pressure), according to different dynamical criteria. The position of the line of the fragile-to-strong transition is also indicated. We see that \( T_G \) is systematically lower around the critical pressure \( P = P_{cr} \).

This behavior has been observed in numerical simulations of \( SiO_2 \) [19,20], which has a fragile-to-strong transition qualitatively similar to that of water. Notice that \( T_G \) is lower than the temperature of the fragile-to-strong transition only in some range of pressure around \( P_{cr} \), and only in this range the fragile-to-strong transition will be experimentally observable.

One important ingredient that we have not included in the model is the existence of an attractive part in the interaction potential. In real water this attraction generates the liquid-vapor first order coexistence line, and also probably a second first order line in the supercooled region separating two different amorphous configurations [2]. A simple way of analyzing the consequences on our model of an attraction between particles is the following. If the attraction is considered to be long ranged, of van der Waals type, then all the results we have obtained remain valid if we replace \( P \) by a new effective pressure \( P^* \equiv P + \gamma/v^2 \) with some constant \( \gamma \), namely, the attraction acts as an effective pressure (which depends on \( v \)) that has to be added to the external pressure \( P \). In the \( P-T \) phase diagram, this non-uniform transformation of the \( P \) axis produces (if \( v \) decreases rapidly when \( P \) increases) a “folding” that indicates a first order transition [3]. This is the way in which the liquid-vapor coexistence line appears in the van der Waals equation for a fluid. For our model, since \( v(P) \) at \( T = 0 \) has an abrupt discontinuity at \( P = P_{cr} \), the attraction generates also a new first order line ending in a critical point. It seems to be [4] that in water this critical point lies at temperatures higher than \( T_G \), so the first order line determines two different sectors of the glassy phase of water. These two sectors correspond to the experimentally observed high density amorphous (above the first-order line) and low density amorphous (below the first order line) phases [5,6]. In our model, these two phases differ in the fraction of particles that are paired, and thus they can also be named high density and low density amorphous phases.

We have relied for our discussion upon the existence of a thermodynamic phase transition for hard spheres, that is not rigorously proven to occur. However, for slightly different forms for \( s_c^{HS} \) (which may imply the absence of an ideal glass transition) than that given by Eq. (3), our results still remain valid, except for the fact that the sharp fragile-to-strong transition (the kinks in the curves of Fig. 3) becomes a crossover.

The model we have presented explains the transition between fragile and strong behavior of water as appearing from the competition between two different local structures. To be able to solve the problem analytically, we had to make the crude approximation that these structures correspond to singled and paired particles. In real water it is likely that what plays the role of our particles are the so-called Walrafen pentamers [22], which are clusters of five water molecules. These cluster are naturally expected to accommodate at one of two possible distances from each other [4]. It is clear that in this more general case the mechanism for a fragile-to-strong transition may remain basically the same. In fact, from the way we solved the model, it is seen that all what is needed is the existence of two different competing structures, independently of the details of them. At high \( T \) the fragile behavior is associated to the configurational entropy of each structure individually. At low \( T \) the strong behavior appears due to the combinatorial entropy of choosing locally between the two structures.

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FIG. 1. Configurational entropy $s_c$, specific volume $v$, and fraction of pairs of particles relative to the total number of particles $x$ as a function of the enthalpy for three different values of pressure. In order to compare, the limiting cases $\tilde{s}_c(x=0)$ and $\tilde{s}_c(x=0.5)$ are also shown (entropies are given in units of $k_B$, $v$ is in units of $5r_1^3$, where $r_1$ is the radius of the particles, see text for details).
FIG. 2. (a) Configurational entropy $s_c$ as a function of $T$, for different values of $P/P_{cr}$, as indicated. (b) Viscosity $\eta$ vs. $1/T$, calculated according to the Adam-Gibbs formula (expression (3), $\eta_0$ and $A$ are the constants in that expression).

FIG. 3. Pressure-temperature plot, indicating the position of the fragile-to-strong transition (solid line) and contour lines of constant viscosity (dashed lines, the corresponding values of $\varepsilon_0 A^{-1} \ln(\eta/\eta_0)$ are indicated).