Glasses: a new view from QED coherence

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Abstract

Stuck in the marshes of the Kauzmann paradox, glasses have always been a puzzle for condensed matter theorists. We show that in the new picture of condensed matter, which takes into account the coherent interaction mechanisms of QED, glasses are nothing but liquids, whose non coherent fraction is highly depleted, very close to zero near \( T_g \), the temperature of glass formation. Using the recently developed QED theory of liquid water, we are also able to give a successful account of the surprising finding of two low-temperature water amorphs and of their phase-transition.

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1 Introduction

Physicists have been, and still are, greatly embarrassed when they are pressed to define glasses, these elusive physical systems which look like solids, since they keep, as crystals do, their volume and shape, but unlike crystals they notably lack a microscopic space order. However, in spite of such apparent lack of order, their entropy approaches that of crystals below a temperature that is usually rather high, a surprising fact that has been referred to as the Kauzmann paradox. For many substances, including water, the Kauzmann temperature is higher than 100 K.

Quite apart from this "entropy puzzle", the very definition of the "glassy state" gets entangled in some rather thorny theoretical problems. Whereas, in fact, the transition from the glass to the solid is well behaved according to the usual thermodynamical rules (the transition occurs on a sharply defined line in a $p-T$ plane and is accompanied by the release of a well defined heat of transition), the glass-liquid transition occurs as a gradual evolution in phase space. Indeed, at a given pressure, the transition spans a temperature interval, usually one or two tens of Kelvin wide. Sometimes, as in the case of water, which we shall analyse in this paper, more than one glass phase exist and the transition between them obeys the laws of orthodox thermodynamics, being first-order.

Traditionally, glasses have been thought to belong to the realm of liquids, since they admit a surface tension, as indicated by the increase of the length of a fissure produced in a glass plate. Thus a glass could be considered as a liquid possessing an infinite (actually an enormously high) viscosity. When the temperature decreases many liquids, including water, exhibit a rapid increase in viscosity, associated with the divergence of all relaxation times. As a result, it is a matter of convention to define which is the threshold of viscosity, beyond which the liquid becomes a glass or, alternatively, how long the experimentalist should wait before declaring the formation of the glass.

The slowing down of many thermodynamical transformations that has been observed when a piece of matter approaches the "glassy state" is at the center of what Anderson has termed a "change of paradigm", in Kuhn's acception. According to this view, the enormous increase in viscosity just blocks the evolution of the macroscopic system in its phase-space, so that the system, so to say, gets stuck in one of its microscopic configurations, becoming unable to "explore" the full ensemble of its allowed configurations. In other words, the system loses its "ergodicity", thus making the concept of entropy void.

In order to obtain an understanding of such "localization in phase-space", as Anderson has christened this concept, the potential energy surfaces are pictured as steeply discontinuous landscapes. When kinetic energy, i.e. temperature, is low enough, the system finds it more and more difficult to migrate from one to the next, thus causing an increase of viscosity. According to the new paradigm, localization in phase-space should explain also the Kauzmann paradox, since in
that space the system "knows" its own small "hole" and nothing else and, as a result, its "effective" entropy is indeed very small.

We believe, however, that this interpretation of the thermodynamics of glasses runs into some difficulties when confronted with the ease with which the low density amorph (LDA, a glass of H$_2$O) makes a transition towards the recently discovered high density one (HDA). Since this transition occurs between two glasses below the Kauzmann temperature (where their entropy is very small), it must be dynamically driven, i.e. the change $\Delta G$ of the Gibbs potential must be mainly due to a change of enthalpy $\Delta H$, induced by applying a large external pressure. Thus we must accept that for glasses there are two types of transformation: one associated with diffusive processes that become slower and slower with the decrease of temperature; the other induced by changes in non-thermal variables (such as pressure) that occur within "reasonable" time spans, in which significant density changes are observed ($\rho_{LDA} \approx 0.92$ g/cm$^3$, $\rho_{HDA} \approx 1.3$ g/cm$^3$) in spite of the small change in $G$ ($\Delta G \approx 2.5$ kJ/mole, corresponding to 26 meV per molecule), indicating that during the transition the system did not have to climb very steep slopes in phase space. This dual nature of glass transformations brings to mind an old fashioned model of glasses, the so-called "extended Glarum model" [6],[7], which pictures the glass as a basic non-entropic "continuum" containing a number of "defects" capable to diffuse among a number of "sites". With the decrease of temperature, the "defects" and the "sites" become scarcer and scarcer, thus lengthening the diffusion times. In such model the transport properties depend on the "defects", while the "continuum" contributes essentially to the structure which is assumed to be quite heavy, thus rather insensitive to molecular agitation. However, this "defect and hole" theory has been criticized (see, for instance, Ref.[3]) on the ground that it is hard to reconcile the assumed "continuum" with the molecular structure that, according to the generally accepted picture of condensed matter, forms the glass.

In recent times a new approach to condensed matter has been developed, based on Quantum Electrodynamics (QED) [8], that allows us to give a fresh look to all the above problems. In this theory an ensemble of molecules or atoms, beyond a critical density and below a critical temperature, become unstable against rearranging itself in a new ground state, where the molecules become a coherent matter field that oscillates, in tune with the e.m. field, between two selected molecular levels. In this way the molecules restructure themselves since their configuration becomes a superposition of the two molecular levels. The minimum space-domain where such coherent oscillations take place, the Coherence Domain (CD), has the size of the wavelength of the electromagnetic mode resonantly coupled to the transition between the two molecular configurations. At room temperature the thermal fluctuations extract from the "coherent ground state" a number of molecules that can’t any longer follow the coherent oscillation: they appear and behave as a dense gas occupying the interstices among the CD’s, forming a non-coherent fraction, whose size decreases with temperature. We can
thus see that the non-coherent fraction plays the same role as the "defects" of the phenomenological Glarum model.

Within such framework, we have analysed the dynamics and thermodynamics of water in detail [9], obtaining good agreement between theory and experiment. In particular we have found that the non-coherent fraction (see Fig.6 of Ref.[9] and Fig.1 of this paper) practically vanishes at a temperature as high as 135 K: one can see that a decrease from 1% to 0.1% is obtained in the interval 150 ∼ 120 K, thus reproducing a very peculiar feature of the "glassy transition".

A careful inspection of Fig.1 renders it reasonable to identify the "glass" with the liquid where the coherent fraction has become just "very close" to one. Of course, in this configuration viscosity becomes enormous, for in a coherent system it is impossible to move one molecule without affecting all the others, that are phase-related to it. However, contrary to the conventional vision, high viscosity (and in particular the high observed deviations from Arrhenius activation) is the consequence and not the cause of the formation of glass, due to the fact that the allowed phase-space shrinks to the coherent ground-state, losing the entropy of the incoherent phase. One may say that in the new view the glass is not just a "piece of ill-condensed matter" as Anderson puts it, but on the contrary it is matter in a well condensed state, where all molecules oscillate in unison and are not bound to be spatially ordered. The hindered translational degrees of freedom of the glass make its entropy negligible, thus explaining the Kauzmann paradox in a natural way. Even though throughout this paper we shall illustrate our general theory of glasses in the only case we have studied in sufficient depth, i.e. liquid water, the basic ideas we have just discussed must also be applicable to other glass-forming systems, whose basic molecular structure may be quite different from that of H$_2$O.

This much in the way of Introduction. The rest of the paper is organized as follows: in Sect.2 we summarize the main results of Ref.[9]; Sect.3 discusses within the coherent QED framework the principal features of a glass, while Sect.4 contains a derivation of the thermodynamics of the transition between the two amorphs of water.

2 QED structure of water

In the framework laid down in Refs.[8,9] we have worked out a theory of liquid water, whose main points we shall now summarize.

The electronic spectrum of water is very rich (see Fig.2), making it rather difficult to select the level $|B\rangle$, that is going to be the partner of the ground state $|0\rangle$ in the coherent oscillations induced by the quantized electromagnetic field. As explained at length in Chap.3 of Ref.[8], the main ingredients of a coherent process are:
1. the direct transitions $|0\rangle \leftrightarrow |B\rangle$, whose amplitude is governed by the coupling constant:

$$g_B = \left(\frac{2\pi}{3}\right)^{1/2} \frac{e}{m_e^{1/2}} \left(\frac{N}{V}\right)^{1/2} \frac{f_{0B}^{1/2}}{\omega_B}.$$  \hspace{1cm} (1)

where in the natural units system ($\hbar = c = k_B = 1$) $m_e$ is the electron mass, $N/V$ the number density of the system, $\omega_B$ the energy difference $E_B - E_0$, and $f_{0B}$ the oscillator strength of the transition $|0\rangle \leftrightarrow |B\rangle$;

2. the "photon mass" term $\mu(\omega)$, that arises from the virtual transitions from the ground state to all other intermediate states $|n\rangle$, induced by the photon modes of frequency $\omega$, whose value is

$$\mu_B(\omega) = -\frac{1}{2} \frac{e^2}{m_e} \left(\frac{N}{V}\right) \frac{1}{\omega_B^2} \sum_{n\neq B} f_{0n} \frac{\omega^2}{\omega_n^2 - \omega^2}.$$  \hspace{1cm} (2)

Defining $\mu_B(\omega_B) = \mu_B$, one finds [8] that, when

$$g_B^2 \geq g_{B,\text{crit}}^2 = \frac{8}{27} + \frac{2}{3} \mu_B + \left(\frac{4}{9} + \frac{2}{3} \mu_B\right)^{3/2},$$  \hspace{1cm} (3)

the ensemble of molecules becomes dynamically unstable: the molecules begin to oscillate between $|0\rangle$ and $|B\rangle$ in a spatial region whose minimum size is the wavelength of the resonant electromagnetic mode:

$$\lambda_B = \frac{2\pi}{\omega_B}.$$  \hspace{1cm} (4)

which will be called the "Coherence Domain" (CD) of the system. The oscillation $|0\rangle \leftrightarrow |B\rangle$, in tune with the corresponding e.m. mode, will dynamically evolve (see Ref.[8]) to a "renormalized" frequency:

$$\omega_r < \omega_B,$$  \hspace{1cm} (5)

that guarantees that the e.m. field stays where the molecules are, and is not radiated away, thus decreasing the energy of the ground state: an impossible undertaking!

Eq.(3) determines the minimum critical density for which the transition from the "perturbative" ground state to the "coherent" ground state occurs. Thus each level $|B\rangle$ has its own "critical density" and the competition among the levels will obviously be gained by the level, let’s call it $|1\rangle$, that has the lowest critical density, since at this density the ensemble of molecules will start oscillating collectively between $|0\rangle$ and $|1\rangle$, preventing all other levels from participating in the "e.m. dance". As it will be shown in Sect.4, the influence of macroscopic variables, such as pressure, upon the terms appearing in Eq.(3) may lead the ground state $|0\rangle$
to change partner in the coherent oscillation, giving rise in such way to phase-
transitions, that considerably enrich the phase diagram. It is interesting to note
that at zero pressure Eq.(3) selects among the different levels of the H$_2$O molecule
the excited state at 12.06 eV, whose critical density is 0.88 g/cm$^3$.

The theory of Refs.[8,9] shows that for $g \simeq g_{\text{crit}}$, the e.m. potential (averaged
over different directions) $A$ obeys the equation (differentiating with respect to
the adimensional time $\tau = \omega t$)

$$\frac{i}{2} \frac{d^3 A}{d\tau^3} + \frac{d^2 A}{d\tau^2} + i\mu \frac{dA}{d\tau} + g^2 A = 0,$$

that, for very small $g^2$, admits for $\mu < -0.5$ (and thus $\rho > \rho_{\text{crit}}$) runaway solu-
tions, namely $A$ grows exponentially, reaching in times of the order of $10^{-14}$ sec
a limiting value corresponding to a physical configuration where:

1. the electron clouds of the water molecules are described by the coherent
state:

$$|\text{coh.}\rangle = \cos \gamma |0\rangle + \sin \gamma |1\rangle,$$

with $\cos^2 \gamma = 0.873$. Should one wish to produce a (incoherent) su-
perposition of this type in a thermal way, he would need an oven kept
at $7 \cdot 10^4$ K and would be, of course, compelled to accept heavy con-
tamination from many other levels;

2. the oscillation of the matter field is in tune with a corresponding os-
cillation of the e.m. field. According to (5), the common frequency
of oscillation is lower (indeed, much lower) than the original value
$\omega = 12.06$ eV at the start of the runaway process. While the wave-
length $\lambda$ remains unchanged, the ”renormalized” frequency attains the
remarkably reduced value:

$$\omega_r = 0.26 \text{ eV}.$$  

As a consequence this dynamically generated e.m. field cannot be
radiated, since the mass of its ”photon”, instead of vanishing, has an
imaginary value:

$$m^2 = \omega_r^2 - \vec{k}^2 \ll \omega^2 - \vec{k}^2 = 0.$$  

We note that the renormalization of the frequency (Eq.8) is absolutely
-crucial for the consistency of the full physical picture, since by Eq.(9)
the e.m. field is prevented from leaving the system and lower further
its energy. Thus this dynamical configuration does represent the state
of minimum energy.
3. The overall energy gain that such configuration achieves can be understood as follows. The positive energy that is required to produce the coherent e.m. field and to excite 12.7% of the molecules to the level at 12.06 eV is more than compensated by the negative energy of the interaction between the e.m. field and the current generated by the oscillating molecules; the sum of these three terms becomes negative when the density exceeds a critical threshold, becoming more and more negative with increasing density. As a consequence, the molecules crowd as close as they are allowed by the highly repulsive short-range forces originating from the molecular hard cores. Since the excited state $|12.06 \text{ eV}\rangle$ is spatially quite more extended than the ground state $|0\rangle$, the intermolecular distance is larger than would be predicted from the standard molecular size. In Ref.[10] this problem has been thoroughly discussed. The energy gained in the process of condensation is released out and accounts for the first-order character of the vapour-liquid transition. The analysis of Ref.[9] shows that the energy gain $\Delta E$ per molecule at the center of a CD is

$$\Delta E = \omega_r = 0.26 \text{ eV}.$$  \hspace{1cm} (10)

Due to the space variation of the e.m. vector potential $A$, $\Delta E$ exhibits the modulation as a function of the distance $r$ from the center of the CD shown in Fig.3. Moreover, the equilibrium condition between the molecular and the e.m. fields demands that the molecules are assembled in the central part of the CD up to a radius which is $3/4$ of the total radius, given by Eq.(4).

4. Given an ensemble of CD’s, energy minimization requires that the fields of the different domains be in tune. This phase-matching allows the fields in the interstices to interfere to yield energy minimization. In such configuration the molecules at the boundary of each CD are acted upon not only by the e.m. field of their own CD but also by the tails of the fields of neighbouring CD’s. The profile of the total energy is depicted in Fig.4. In this way the coherence of a single domain is propagated throughout condensed matter on a macroscopic scale.

5. At $T \neq 0$ the coherent ground state is subject to the thermal aggression of the environment, absorbing energy and momentum from the collisions with external particles or from external radiation. These energy-momentum transfers excite single molecules out of the coherent state to one of the single-particle states described by an appropriate excitation curve. In Fig.5 we report the curve used in Ref.[9]. Thus for each $T$ we may compute the non-coherent fraction $F_{nc}(T)$ of molecules extracted from the coherent ground state, the coherent fraction being obviously given by $F_c(T) = 1 - F_{nc}(T)$. In Fig.1 we plot $F_c(T)$, as
derived from the excitation spectrum assumed in Ref.[9]. The non-coherent fraction comprises the molecules extracted from the regions where $|\Delta E|$ is smaller. An inspection of Fig.4 shows these regions to be located at the periphery of the CD’s which, as a result, shrink when $T$ increases. Thus we may write for the ”effective” radius of the CD as a function of $T$:

$$R_{CD}(T) = R_{CD}(0)[F_c(T)]^{1/3}, \quad (11)$$

where Eq.(4) informs us that $R_{CD}(0) = \frac{3\pi}{4\omega_0}$. Please note, however, that the two fractions are not sharply divided, but their boundaries are somewhat blurred, so that the transition from the coherent to the non-coherent fraction is rather smooth.

The requirement of phase-matching among CD’s for energy minimization keeps the CD’s tightly packed, in such a way that the non-coherent fraction remains trapped in the interstices of an array of CD’s, that form a kind of cage preventing the non-coherent ”gaseous” phase to leave the system as a free gas. Of course, the non-coherent fraction is not an ideal gas, but rather a Van der Waals’ gas, since significant short range attractive forces act between the molecules. When $T$ increases, the non-coherent fraction increases its pressure, which appears as the vapour tension of the liquid. At the boiling point the pressure of the non-coherent fraction succeeds in breaking the ”cages” of the CD’s and in coming to the open. Thermodynamical equilibrium then requires that a new ”non-coherent phase” be established at the expense of the coherent one; all the energy supplied to the system from the outside gets spent to accomplish just this. The new non-coherent phase also finds its way out of the liquid, and the process keeps on going until the complete vaporization of the liquid is achieved.

To end this Section, we would like to recall that, apart from the successful analysis of the dynamics and thermodynamics of water carried out in Ref.[9], QED finds another remarkable corroboration from the striking phenomena of Single Bubble Sonoluminescence [11], which we have shown to arise from the electrodynamic nature of the interactions among the molecules of H$_2$O in Ref.[12].

3 H$_2$O at low temperature: supercooled water and glass

In this Section we shall discuss some peculiar properties of liquid water at low temperature, as predicted by the QED theory outlined in the previous Section, according to which most molecules now belong to the coherent fluid.
As a consequence of the two-fluid picture of water characteristic of our approach, all physical variables are given by the weighted combination of the "coherent-phase" value, which is independent of temperature, and the value in the "non-coherent phase", typical of a dense gas. For instance, in the case of an extensive variable $X$, such as the free energy or the entropy, one has:

$$X(T) = X_c F_c(T) + X_{nc}(T) F_{nc}(T),$$

where $X_c$ is independent of temperature, since the internal temperature of the coherent phase is zero. The thermodynamic potentials, like the specific heat, derivatives with respect to temperature of extensive quantities, can thus be written:

$$\frac{dX}{dT}(T) = [X_c - X_{nc}(T)] \frac{dF_c}{dT} + F_{nc}(T) \frac{dX_{nc}}{dT}.$$  

At low temperature $F_{nc}(T)$ can be neglected, so that the thermodynamic potentials are proportional to $\frac{dF_c}{dT}$, whose temperature behaviour can be seen in Fig.1b. It is interesting to compare this behaviour with that of the typical specific heat of a glass, shown in Fig.6. Both show a characteristic $\lambda$-shape: the curve increases steeply in the region of the supercooled liquid and drops to zero below the "glassy transition". In our approach this peculiar shape is a consequence of the T-dependence of the filling by the non-coherent fraction of the interstices of the CD’s.

In order to understand the dynamics of the "glassy transition", let us analyse the behaviour of the shear viscosity $\eta$ at low temperature, where the non-coherent fraction $F_{nc}(T)$ has become quite small. The main point is that the coherent fluid behaves like an infinitely viscous liquid, since below the gap threshold it is impossible to accelerate a single molecule without collectively accelerating the whole CD. Thus the observed viscosity of the liquid should, according to our theory, be ascribed to the non-coherent fluid that lingers in the interstices between CD’s: it is just the flow of the non-coherent fluid, which acts as a kind of lubricant, which allows the array of CD’s to follow the stream of the liquid. When $F_c(T) \to 1$ ($F_{nc}(T) \to 0$) the "lubricant" disappears, viscosity becomes very large and the liquid vitrifies. It is clear, therefore, that this process is not sharp in temperature, like the usual thermodynamic phase transitions, but it actually starts when the non-coherent fraction becomes small enough to make viscosity exceed a fixed large value. In order to have a rough idea of the phenomenon, we consider the crude model where the CD’s are rigid clusters of water molecules floating in the non-coherent fluid, streaming in a channel of width $R$ and where the size of the average interstice between CD’s is $\delta$. From the usual definition of shear viscosity $\eta$, one gets:

$$\frac{\eta_{tot}(T)}{R} = \frac{\eta_{nc}(T)}{\delta},$$

(14)
hence
\[ \eta_{\text{tot}}(T) = \frac{\eta_{\text{nc}}(T)}{\delta/R} \propto \frac{\eta_{\text{nc}}(T)}{F_{\text{nc}}(T)}, \]  
(15)

implying that when \( F_{\text{nc}} \to 0 \) the viscosity \( \eta_{\text{tot}}(T) \) will diverge. Inspection of Fig.1a shows that our model for \( F_{\text{nc}}(T) = 1 - F_c(T) \) approaches the vanishing limiting value for \( T \simeq 135 \) K. In Fig.7 the interval \( 100 \text{ K} < T < 200 \text{ K} \) of Fig.1a has been magnified: one can see that at \( 150 \text{ K} \ F_{\text{nc}} \simeq 1.6 \cdot 10^{-2} \), whereas at \( 135 \text{ K} \ F_{\text{nc}} \simeq 10^{-3} \), showing that by decreasing the temperature by approximately 15 K \( \eta \) increases by an order of magnitude. Thus the non-sharp nature of the glassy transition is just the consequence of the non-sharp disappearance of the non-coherent fluid.

The above discussion allows us also to understand the large increase of viscosity observed [13] when a shear stress is exerted upon a layer of water whose thickness is smaller than a threshold value, which at room temperature is about 500 \( \AA \). We note that at this temperature Eq.(11) yields for the CD diameter just such value; thus when the width of the channel is about the CD diameter no room is left for the ”lubricant” and \( \eta \) is bound to rise very sharply.

All other transport variables, from the self-diffusion coefficients to the thermal relaxation times, which critically depend on \( F_{\text{nc}}(T) \), are expected to parallel the behaviour of \( \eta \), thus producing the kind of universal behaviour that is typical of all supercooled liquids just above vitrification.

The problem of the divergence of viscosity at low temperature has been recently analysed for a Lennard-Jones liquid [14] in the conventional framework of the free energy landscapes discussed in the Introduction. It is interesting to observe that for the viscosity and the relaxation time these authors derive a behaviour very close to the Arrhenius one, which is almost universally inadequate to describe the observed transport properties near the glassy transition, the Kauzmann paradox and the \( \lambda \)-shape of heat capacity. It is quite reasonable that the dynamics discussed in Ref.[14] is at work within the non-coherent fluid, producing the divergence of \( \eta_{\text{nc}} \) in Eq.(15). However, it seems equally reasonable that the non-Arrhenius behaviour of the viscosity is the necessary consequence of the fast (in temperature) depletion near \( T_g \) of the non-coherent phase and, thus, can only be understood in a conceptual framework which recognizes the role of coherence.

4 The tale of two glasses: LDA and HDA

As mentioned in the Introduction, a challenge to the usual understanding of liquid has been posed by the discovery of a high density variety of amorphous solid water [3]. The existence of a liquid-liquid phase transition, which gives rise to a kind of ”liquid polymorphism”, has been suggested in Refs.[15],[16]. Hence, the generally accepted conceptual framework is hard put to explain how two different intermolecular organizations may arise from the same basic molecule,
capable of well defined electric polarizations, sources of equally well defined fields of force. Moreover, since the phase transition occurs at very low temperature, where diffusive processes are very slow, the transformation must be dynamically driven, for the application of an appropriate pressure transforms a mesoscopic metamolecular complex into a different one in a short time in a non-diffusive way.

We now show that such stringent requirements, strongly suggested by the empirical evidence, are naturally accounted for in the QED approach we have followed in this paper. In Ref.[9] it was found that the excited level at 12.06 eV, ”winner” of the competition for the partnership with the ground state in the coherent, collective oscillation, is actually closely trailed in the race by a level at 11.5 eV, whose critical density is at 1 g/cm$^3$. This level, whose electronic configuration is $4p$, is less extended than the ”winner”, which is $5d$. Should the level at 11.5 eV have won the race, the resulting liquid would clearly have been denser than the actual liquid water. In Table 1 we summarize the main features of the two levels.

| Level 1 | Level 2 |
|---------|---------|
| $\omega$/eV | 12.06 | 11.5 |
| electronic configuration | $5d$ | $4s$ |
| $\rho$ (g/cm$^3$) | 0.88 | 1.0 |

Table 1.

At low temperature, where due to the smallness of the non-coherent fraction the entropic contribution is negligible, the free energy per molecule $f$ is the sum of three contributions:

\[
f = \frac{F}{N} \simeq \frac{E}{N} = -\delta_c - \delta_{SR,attr} + \delta_{SR,rep},
\]

which we are now going to briefly discuss:

1. $-\delta_c$ is the gap produced by the coherent oscillation between the ground state and the chosen level. From the discussion in Ref.[8]

\[
\delta_c = \omega \epsilon,
\]

where $\epsilon$ satisfies the quartic equation:

\[
2\epsilon^4 + \epsilon^3 - 3\epsilon^2(1 + \mu_r) - \epsilon(2g^2 + 1 + 2\mu_r) + (1 + 2\mu_r)^2 = 0.
\]

Since $\delta_c$ is expected from thermodynamics to be in the range of tenths of eV, whereas $\omega$ exceeds 10 eV, $\epsilon$ must be quite small, thus allowing us to drop in Eq.(18) $\epsilon$-powers higher than 1, yielding:

\[
\epsilon \simeq \frac{(1 + 2\mu_r)^2}{1 + 2g^2 + 2\mu_r}.
\]
For the level $|1\rangle$ one can show that this approximation differs from the exact solution by less than 5%. Also, in the region of $n = N/V \simeq 1/m \mu_2 \text{cm}^{-3}$ the gap $\delta_c$ has a very mild dependence on $n$, so that we shall assume $\delta(n) \simeq \text{const.}$

2. $\delta_{SR,\text{attr}}$ denotes the attractive effect of the short-range (Van der Waals) interaction, which prevails at distances not too close to the molecular hard core. From the energy functional

$$E_{SR}[n] = \frac{1}{2} \int d^3 \vec{x} \, d^3 \vec{y} \, \psi^\dagger(\vec{x})\psi(\vec{x})V_{SR}(\vec{x} - \vec{y})\psi^\dagger(\vec{y})\psi(\vec{y}), \quad (20)$$

where $|\psi| \simeq n^{1/2}$ and the potential is free from singularities, we get:

$$\delta_{SR,\text{attr}} = \alpha n^2. \quad (21)$$

3. $\delta_{SR,\text{rep}}$ arises from the interaction between the hard cores, which repel each other due to the combined effects of the Coulomb repulsion and of the Pauli principle. Using the repulsive part of a typical Lennard-Jones interaction:

$$V_{SR,\text{rep}}(r) = \epsilon \left( \frac{r_0}{r} \right)^{12}, \quad (22)$$

and carrying out the analysis reported in Ref. [17], we obtain the functional dependence

$$\delta_{SR,\text{rep}} = \beta n^{7/3}. \quad (23)$$

Thus Eq.(10) takes the form:

$$f = -\delta_c - \alpha n^2 + \beta n^{7/3}. \quad (24)$$

From the equation of state:

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial (F/N)}{\partial (V/N)} = n^2 \frac{\partial f}{\partial n}, \quad (25)$$

we get:

$$p = n^3 \left[ -2\alpha + \frac{7}{3}\beta n^{1/3} \right], \quad (26)$$

that for $p = 0$ yields:

$$\alpha = \frac{7}{6}\beta n_0^{1/3}, \quad (27)$$

$n_0$ being thus the density at zero pressure. By combining (25) and (17), we obtain:

$$f = -\delta_c - \alpha n^2 \left[ 1 - \frac{6}{7} \left( \frac{n}{n_0} \right)^{1/3} \right]. \quad (28)$$
which at \( p = 0 \) reduces to
\[
f_0 = -\delta_c - \frac{\alpha}{7} n_0^2.
\] (29)

In addition we have
\[
p = 2\alpha n^3 \left[ \left( \frac{n}{n_0} \right)^{1/3} - 1 \right].
\] (30)

Let us now analyse the problem of the two water glasses in the above framework. We have (See Ref.[9]) \( \delta_{cLDA}^L = 0.26 \text{ eV} \) and \( \delta_{cSR}^H = 0.24 \text{ eV} \) at \( p = 0 \). Thus:
\[
f_{LDA} = -\delta_{cLDA} - \delta_{SR}^L \left[ 7 - 6 \left( \frac{n}{n_0} \right)^{1/3} \right],
\] (31)
\[
f_{HDA} = -\delta_{cHDA} - \delta_{SR}^L \left( \frac{n_0}{n_0} \right)^2 \left[ 7 - 6 \left( \frac{n}{n_0} \right)^{1/3} \right],
\] (32)
\[
p_{LDA} = 14\delta_{SR}^L n \left( \frac{n}{n_0} \right)^2 \left[ \left( \frac{n}{n_0} \right)^{1/3} - 1 \right].
\] (33)

Note that in the above equations the coefficient \( \alpha \) of the Van der Waals attraction, being independent of density has been assumed as universal. Eq.(33) gives us in a straightforward manner the pressure of the transition \( \text{LDA} \rightarrow \text{HDA} \) when we equate the density \( n \) to the threshold value prescribed by eq.(3) for the level \( |2\rangle \) at 11.5 eV (see also Table 1). By putting \( \rho_{cLDA}^2 = 0.94 \text{ g/cm}^3 \) and \( \rho_{cHDA} = 1 \text{ g/cm}^3 \), eq.(33) gives us:
\[
p_{LDA \rightarrow HDA} \approx 3.4 \text{ kbar},
\] (34)
in excellent agreement with the value \( p_{LDA \rightarrow HDA} = 3.2 \text{ kbar} \) measured by Bellissent-Funel [14].

From the thermodynamic measurements of Ref.[10] we are able to derive the parameters of the coherent process involving level \( |2\rangle \), that gives rise to the HDA. By equating the Gibbs potentials per molecule
\[
g = \frac{G}{N} = f + \frac{pV}{N} = f + \frac{p}{n}
\] (35)
of the two glasses, we get:
\[
\delta_{cHDA} = \delta_{cLDA} - \delta_{SR}^L \left[ \left( \frac{n_0^H}{n_0} \right)^2 \left( \frac{n_0^L}{n_0} \right)^{1/3} \right] + \frac{p}{n} \left( \frac{n_0^L}{n_0^H} \right) - 1.
\] (36)

Inserting in this equation \( p_{HDA \rightarrow LDA} = 0.5 \text{ kbar} \), measured in Ref.[16] and \( \rho_{cHDA}^2 = 1.17 \text{ g/cm}^3 \), we get:
\[
\delta_{cHDA} = 0.13 \text{ eV} = \frac{1}{2} \delta_{cLDA}.
\] (37)
in good agreement with the value that can be obtained from Eq. (17).
Thus we find that in the HDA the electrodynamical gap \( \delta^c_{HDA} \) is weaker than in the LDA, but at high pressures one can obtain higher densities with less energy expense, since the size of the molecular levels involved in the coherent oscillations selected by QED is smaller.

5 Conclusions

In this paper we have attempted to show that the new picture of condensed matter afforded by a full utilization of the general equations of QED, and in particular of their coherent solutions, provides us with an approach to the physics of the glassy state that seems both simple and powerful. In a nutshell, according to our theory, a glass is nothing else than a liquid, i.e. a molecular system whose coherent oscillations involve the valence electrons, which has (almost) completely lost its non-coherent fraction, thus becoming enormously viscous. Instead of ill-condensed matter, as Anderson sees it, a glass appears to us a perfectly condensed liquid. We have shown that such view is supported by the peculiar T-dependence of the function \( F_{nc}(T) \), the non-coherent fraction, that we have determined for water (but whose qualitative structure should be quite general), which reproduces the typical shapes of the specific heat near the "glassy transition" and the basic undefiniteness of \( T_g \), the glass transition temperature. The extreme viscosity of the glass is thus seen as the manifestation of the phase coherence of the matter field, which suppresses all local motions, which would result in large fluctuations of the phase itself.

In the last Section we have been able to give a successful theory of the non-diffusive transition between the LDA and the HDA of water, simply in terms of the pressure induced change of the coherent oscillations of the water molecule. We have identified a different excited level at 11.5 eV that, being smaller in size than the one at 12.06 eV, involved in the coherent oscillations of liquid water, leads to a denser glass. The quantitative agreement with the experimental observations of Ref. [16] is, we believe, a further corroboration of the power, simplicity and correctness of this approach, which we hope to extend soon to other interesting types of glass.

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