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# Universal properties of supercooled fluids

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**Abstract.** Supercooled fluids from sufficiently repulsive particles exhibit a universal behaviour, which originates from an experimentally unobservable singularity, and consists of a combination of power laws with a saturation law. Many experimental results are explained and a new correlation length is predicted.

## 1. Introduction

It is well known experimentally that glasses and ‘glass transitions’ exhibit universal properties [1, 2]. Some of these have been explained theoretically by investigating a fluid of hard particles [3]. The explanation is based on the identification of a singularity, which is connected to the Kirkwood instability [4–8]. Here the universal properties which the singularity yields are investigated. These follow from two main features: power laws and a saturation law. The argument goes as follows: near the singularity many thermodynamic quantities diverge according to power laws. However since at the singularity the pressure would diverge, no physical system can exist at the singularity. Hence the density  $\rho$  nearly assumes the density  $\rho_\infty$  of the singularity, which is therefore called the fictive density. In short  $\rho$  saturates. Consequently this saturation of  $\rho$  occurs in all quantities which depend on  $\rho$ . The combined effect is shown to explain many experiments on glasses, including all those experiments on static properties which were discussed in Jäckle’s review article [1]. The saturation law also explains why the singularity has never been observed experimentally, although it exists for most substances. Infinitely many phase transitions occur near the singularity. In the classical fluid the Kauzmann paradox [9] allows the entropy of the fluid to become smaller than that of the crystal. This can be repaired by quantum corrections.

## 2. Model

Let us consider  $N$  particles in a  $D$ -dimensional volume  $V$  which interact via an isotropic repulsive two-particle potential  $U(r)$ . The corresponding Mayer function  $g(r)$  [10, 11] at temperature  $T$  has the Fourier transform  $\tilde{g}(k)$ , which has an absolute and relative maximum at  $k_0$ , with  $\tilde{g}(k_0) > 0$ . This is typically the case for potentials with a relatively hard core especially for hard sphere potentials, but not for Coulomb potentials. If the system is cooled, this is done sufficiently rapidly that the system remains in the fluid state if possible.

### 3. Classical fluid

Here the thermodynamic properties will be investigated in terms of the activity  $\gamma$ .  $\ln \gamma$  can be written in terms of Mayer cluster diagrams. These can be classified into those which are topologically more complicated than loops, and those which are not [12, 13]. The latter can be summed as a geometric series. Finally  $\ln \gamma$  is the following function of the density  $\rho$ :

$$\ln \gamma = -\rho \tilde{g}(k=0) - \frac{\rho^2}{2} \int d^D k \frac{\tilde{g}^3}{1 - \rho \tilde{g}} + \text{diagrams topologically more complicated than loops.} \quad (1)$$

Since the denominator in this equation vanishes for  $\rho = 1/\tilde{g}(k_0)$ ,  $\ln \gamma$  exhibits a singularity at that density. The topologically more complicated diagrams than loops can, depending on the explicit choice of the potential  $U$ , have the following effects on the singularity:

(i) They can compensate for the singularity, so that  $\ln \gamma$  is a regular function of the density. This case is highly non-generic in the space of  $U(r)$  and will not therefore be considered in the following.

(ii) If they do not compensate for the singularity, there are two alternatives: they can modify the singularity either quantitatively (this is likely to be the case in three dimensions) or qualitatively. The latter would be surprising, since in Yukawa potentials  $U(r)$  computer simulations exhibit just such a singularity in three dimensions and at high dimension the topologically more complicated diagrams vanish altogether.

In this sense the qualitative properties of fluids near  $\rho = 1/\tilde{g}(k_0)$  can be derived from equation (1). The following is an investigation of the singularity. Formally at leading order near the singularity

$$\tilde{g}(k) = \tilde{g}(k_0) - a(k - k_0)^2. \quad (2)$$

Therefore

$$\ln \gamma = -\rho \tilde{g}(k=0) - \Omega_D \tilde{\rho}^{-1/2} \quad (3)$$

where

$$\tilde{\rho} = 1 - \rho \tilde{g}(k_0) \quad (4)$$

and

$$\Omega_D = -\sqrt{\frac{\rho_\infty^3}{4a}} k_0^{D-1} (k_0 r)^{1-D/2} J_{D/2-1}(k_0 r) \tilde{g}(k_0)^3. \quad (5)$$

Here the fact that the term proportional to  $\tilde{\rho}$  only contributes near  $\tilde{\rho} \approx 0$  is taken into account by replacing  $\rho$  with  $\rho_\infty$ . The latter denotes the value of the density at the singularity for a given temperature. (Technically this is a tricky but correct notation which simplifies the procedure for taking derivatives.) Hence the following equations,

which describe the thermodynamics near the singularity, can be derived. The pressure  $P_f$  of the fluid reads

$$P_f/T = \rho + \frac{1}{2}\tilde{g}(k=0)\rho^2 + \Omega_D\rho\tilde{\rho}^{-1/2} + \frac{2}{\tilde{g}(k_0)}\Omega_D(\tilde{\rho}^{1/2} - 1). \quad (6)$$

The chemical potential  $\mu_f$  is

$$\mu_f/T = \ln \rho + \tilde{g}(k=0)\rho + \Omega_D\tilde{\rho}^{-1/2} - D/2 \ln(MT) \quad (7)$$

where  $M$  is the mass of the particle divided by the square of Planck's constant. The compressibility  $\kappa_f$  is

$$\kappa_f = -\frac{1}{V} \frac{dV}{dP} = \frac{2}{\Omega_D\rho^2 T\tilde{g}(k_0)}\tilde{\rho}^{3/2}. \quad (8)$$

The free energy per particle  $f_f$  is

$$f_f/T = \ln \rho + \frac{1}{2}\tilde{g}(k=0)\rho - \frac{D}{2} \ln(MT) - 1 - \frac{2}{\rho\tilde{g}(k_0)}\Omega_D(\tilde{\rho}^{1/2} - 1). \quad (9)$$

The entropy per particle  $\sigma_f$  is

$$\sigma_f = -\ln \rho - \frac{1}{2}\tilde{g}(k=0)\rho + \frac{D}{2} \ln(MT) + \frac{D+2}{2} + \Omega_D \left( T \frac{d\tilde{\rho}}{dT} \tilde{\rho}^{-1/2} - 2 \right) \frac{1}{\rho\tilde{g}(k_0)}. \quad (10)$$

The specific heat per particle  $c_f$  is at fixed  $\rho$

$$c_f = \frac{D}{2} - \frac{\Omega_D}{2} \left( T \frac{d\tilde{\rho}}{dT} \right)^2 \tilde{\rho}^{-3/2}. \quad (11)$$

The two-particle correlation function  $g_2(r)$  reads

$$g_2(r) = b \exp(-w(r)/T) \quad (12)$$

where

$$b = \exp[-U(r)/T] \quad (13)$$

and

$$w(r) = -\sqrt{\frac{\rho}{a}} k_0^{D-1} (k_0 r)^{1-D/2} J_{D/2-1}(k_0 r) \tilde{g}(k_0) \tilde{\rho}^{-1/2}. \quad (14)$$

Here  $J_{D/2-1}(k_0 r)$  is the Bessel function. Thus  $g_2$  has sharp peaks at almost periodic positions, and has infinitely many local maxima and minima. At each distance  $r$ , the next local maximum,  $r_{\max}$ , and minimum,  $r_{\min}$ , are well defined. Thus the local order parameter

$$q(r) := 1 - g_2(r_{\min})/g_2(r_{\max}) \quad (15)$$

is well defined and decays with increasing distance from one to zero. Since the envelope of the Bessel function is approximately

$$\sqrt{\frac{2}{\pi k_0 r}} \quad (16)$$

the local order parameter reads

$$q(r) = 1 - \exp[-\omega_D (k_0 r)^{(1-D)/2} \bar{\rho}^{-1/2}] \quad (17)$$

where

$$\omega_D = \sqrt{\frac{8}{\pi \alpha \rho}} k_0^{D-1} \tilde{g}(k_0). \quad (18)$$

Let us define the correlation length as the distance at which  $q(\xi) = 1 - 1/e$ , then it diverges with the power law

$$k_0 \xi \approx \omega_D^{2/(D-1)} \bar{\rho}^{-1/(D-1)}. \quad (19)$$

These equations contain two extraordinary features:

### 3.1. Irreversibility

At sufficiently small  $\bar{\rho}$ ,  $c_f$  becomes negative, thus  $d\sigma_f/dT$  becomes negative. Since at large  $T$   $\sigma_f(T)$  grows monotonically,  $\sigma_f$  exhibits a local minimum, at  $T_{\min}$  say. This can be explained as follows: In this calculation, all possible configurations of the particles have been integrated with their respective weights. At temperatures below  $T_{\min}$ , the total weight of these configurations is too large for one phase, since the entropy must decrease with decreasing temperature. Hence the total weight of the configurations must be distributed onto sufficiently many phases, so that for all phases and phase transitions, the entropy, which is the logarithm of the total weight of the respective configurations, decreases with decreasing temperature. Therefore the increase in entropy which occurs at temperatures below  $T_{\min}$  is identified as a configurational entropy  $\sigma_{\text{conf}}$ , which is a lower bound for the logarithm of the number of phases, which occur with decreasing temperature. Since these phases need not exhibit any symmetry because the system is cooled sufficiently rapidly, the phases are identified as glass phases. Thus, the order parameter of such a phase is the mean overlap of an actual configuration of particles with a reference configuration of the phase. These order parameters are not described by this theory yet, and their investigation remains a major challenge. The part of the specific heat which corresponds to  $\sigma_{\text{conf}}$  will not be observed in experiments. The number of phases per particle increases without bounds as the singularity is approached. In other words to each phase (metastable or stable) there corresponds a reference configuration (a configuration at which there is a local maximum of the distribution function in configuration space) just as in the case of ferromagnetism, the Ising model or the Ising spin glass (thus separate averaging over non-ergodic components is necessary).

### 3.2. Kauzmann paradox

Consider the curve in the temperature-density plane, on which  $d\bar{\rho}/dT\bar{\rho}^{-1/2}$  is constant. In a physically interesting system, the density will not change too much on that line at sufficiently low temperature, since the inter-particle distances are then nearly constant. This condition requires some potential in addition to the purely repulsive one. For the purpose of investigating the singularity, it does not make much difference whether this additional potential is an external one of a box, for example, or whether it is a slight modification of  $U(r)$ . In the latter case the potential  $U(r)$  exhibits a local minimum, at  $r = r_0$  say. Thus the potential is attractive at  $r > r_0$ . Here and in the following we assume such a modified potential. Hence at sufficiently low temperature, the entropy becomes negative and, for arbitrarily small temperature, the entropy can become arbitrarily small. On the other hand, the entropy of the crystal is finite. This is the Kauzmann paradox. This paradox motivates the investigation of quantum corrections.

### 4. Semiclassical fluid

The free energy can be written as an expansion in  $\hbar$ . In this expansion, the leading correction to the classical free energy per particle reads [14]

$$f_{\text{qm}} = \frac{1}{24T^2M} \langle (dU/dr)^2 \rangle. \quad (20)$$

Here  $\langle \dots \rangle$  denotes the average according to the Boltzmann distribution. Let us consider the forces  $F_{ij} = -dU/dr_{ij}$ . For states at which the quantum corrections become relevant, the solid-state virial theorem [15] is a sufficient approximation,

$$\sum_{i,j}^N r_{ij} F_{ij} = PV. \quad (21)$$

At a crude but sufficient approximation, only the interaction of the immediate neighbours contributes significantly, and their mean distance is  $r_{ij} = \rho^{-1/D}$  and their number is  $D$ , thus

$$F_{ij} = \frac{2P}{\rho^{1-1/D}D}. \quad (22)$$

Inserting this into equation (20) yields the general expression for  $f_{\text{qm}}$  in this equation

$$f_{\text{qm}} = \frac{P^2}{6T^2M D^2 \rho^{2-2/D}}. \quad (23)$$

#### 4.1. Small corrections

If the corrections are sufficiently small,  $P = P_f$  can be inserted into equation (23), thus at leading order in  $\tilde{\rho}$ ,

$$f_{qm} = \frac{\phi}{\tilde{\rho}} \quad (24)$$

where

$$\phi = \frac{\Omega_D^2 \rho^{2/D}}{6MD^2}$$

$$\sigma_{qm} = \frac{\phi}{\tilde{\rho}^2} \frac{d\tilde{\rho}}{dT} \quad (25)$$

$$c_{qm} = -\frac{2T\phi}{\tilde{\rho}^3} \left( \frac{d\tilde{\rho}}{dT} \right)^2 \quad (26)$$

$$P_{qm} = \frac{\tilde{g}(k_0)\phi}{\tilde{\rho}^2 \rho^2} \quad (27)$$

This approximation is valid for  $P_f \gg P_{qm}$ , or

$$T \gg \frac{\Omega_D}{6\tilde{\rho}^{3/2} MD^2 \rho^{4-2/D}} \quad (28)$$

#### 4.2. Large corrections

Since from thermodynamics  $P = \rho^2 df/d\rho$  and  $f = f_f + f_{qm}$ , the general expression for  $f_{qm}$  assumes the form

$$f = f_f + \frac{1}{6\rho^2 MD^2 T^2} \left[ \rho^2 \frac{df_f}{d\rho} + \rho^2 \frac{df_{qm}}{d\rho} \right]^2 \quad (29)$$

Inserting  $P_f = \rho^2 df_f/d\rho$  and  $f - f_f = f_{qm}$  and considering the vicinity of the singularity at which  $P_f \approx T\rho\Omega_D\tilde{\rho}^{-1/2}$  yields the differential equation

$$\sqrt{f_{qm}} = A\tilde{\rho}^{-1/2} + B \frac{df_{qm}}{d\rho} \quad (30)$$

with

$$A = \frac{\Omega_D}{\sqrt{6MD}} \quad (31)$$

and

$$B = \frac{\rho}{\sqrt{6MDT}} \quad (32)$$

Only the qualitative features of the solution  $f_{qm}$  of the preceding differential equation will be derived. Consider  $f_{qm}$  as a function of  $\tilde{\rho}$ , while  $\rho \approx \text{constant}$ , then

$$\sqrt{f_{qm}(\tilde{\rho})} = A\tilde{\rho}^{-1/2} - B\tilde{g}(k_0) \frac{df_{qm}}{d\rho} \quad (33)$$

If  $\tilde{\rho} \rightarrow \infty$ , the term proportional to  $A$  vanishes, and hence  $f_{qm} \rightarrow 0$ . If  $\tilde{\rho} \rightarrow 0$ , the term proportional to  $A$  diverges, and hence  $f_{qm} \rightarrow \infty$ . In between,  $f_{qm}(\tilde{\rho})$  is a monotonically decreasing function. Thus there is a range of sufficiently small  $\tilde{\rho}$  in which the small corrections are valid. This range will be investigated in the following.

### 4.3. Reparation of the Kauzmann paradox

The corrected entropy reads

$$\sigma = \sigma_f + \sigma_{qm} = -\ln \rho + \frac{D}{2} \ln(MT) + \frac{D+2}{2} + \Omega_D \left( T \frac{d\tilde{\rho}}{dT} \tilde{\rho}^{-1/2} - 2 \right) \frac{1}{\rho \tilde{g}(k_0)} + \frac{\phi}{\tilde{\rho}^2} \frac{d\tilde{\rho}}{dT}. \quad (34)$$

Consider a system at constant pressure and temperature. Then equation (40) holds and thus the entropy is together with  $\rho \approx \rho_\infty = 1/\tilde{g}(k_0)$

$$\sigma \approx -\ln \rho + \frac{D}{2} \ln(MT) + \frac{D+2}{2} + \Omega_D (2\tilde{\rho}^{1/2} - 2) + \frac{2\phi}{T\tilde{\rho}} \quad (35)$$

or

$$\sigma \approx -\ln \rho + \frac{D}{2} \ln(MT) + \frac{D+2}{2} + \Omega_D \left( 2 \frac{\Omega_D T}{\tilde{g}(k_0) P} - 2 \right) + \frac{2\phi \tilde{g}(k_0)^2 P^2}{\Omega_D^2 T^3}. \quad (36)$$

With (40)  $d\tilde{\rho}/dT$  is positive. Hence the function  $\sigma(T)$  diverges for  $T \rightarrow 0$  as well as for  $T \rightarrow \infty$ . In between it assumes a minimum at  $T_{\min}$ . Furthermore at sufficiently low temperature,  $\ln T$  will be dominated by  $T^{-3}$  in the previous equation for  $\sigma(T)$ . Thus at sufficiently low temperature,  $\sigma(T_{\min}) > \sigma_{\text{crystal}}(T_{\min})$ , and the Kauzmann paradox is thus repaired.

In principle there is still the possibility that at intermediate temperatures the entropy of the semiclassical fluid becomes smaller than that of the crystal. For a given potential  $U$  there is always a sufficiently large mass  $M$  such that the entropy becomes negative at some intermediate temperature. However the entropy cannot become arbitrarily small as in the classical fluid. Therefore it would be very surprising if there should still be a Kauzmann paradox possible within the semiclassical fluid.

### 4.4. Interpretation and experimental significance of quantum corrections

The fact provided by the analysis is that near the singularity quantum corrections become relevant. Typically in statistical physics quantum effects only occur at relatively low temperature, whereas here it depends on the material and the experimental conditions (e.g. pressure) under consideration, whether or not the singularity with its quantum effects occur at relatively high temperatures.

One might ask whether these quantum effects can be modelled by considering one particle in a fixed surrounding or whether it is necessary to model a system of several or many particles. The analysis of the free energy suggests that only a system of particles can model the quantum corrections. And in particular the existence of the many glass phases suggests that slow dynamics is relevant and hence the tunnel effect is important and thereby relaxation times decrease (relatively to the respective classical relaxation times) and hence more fluctuations can take place in finite time and therefore the entropy increases (relatively to the entropy corresponding to a respective classical model).

In addition to this theoretical evidence there is experimental evidence for the answer of this question, that in general the quantum corrections near the singularity cannot be modelled by considering a single particle with its fixed surroundings.



For the case of *o*-terphenyl the Kauzmann temperature  $T_K$  [3] has been measured [16, 17] to be approximately 200 K. Let us assume for simplicity that a molecule is in a hard box formed by its neighbouring molecules. Then its energy is

$$\frac{p^2}{2m} = \frac{3}{2}k_B T \quad \text{or} \quad \frac{p_x^2}{2m} = \frac{1}{2}k_B T.$$

Thus its de Broglie wavelength is  $\lambda = 0.2042 \text{ \AA}$ . The mean square root displacement of an *o*-terphenyl molecule at that temperature has been measured [18] to be  $\sqrt{\langle R^2 \rangle} = 0.424 \text{ \AA}$ . Thus at 200 K the quantum effects of a one-particle model are relatively small, and it turns out that only at  $T < 100 \text{ K}$  is  $\lambda > \sqrt{\langle R^2 \rangle}$  and the quantum effects are relatively large for a single-particle model.

Thus from these experiments for *o*-terphenyl the quantum effects for a single-particle model are relatively small at  $T_K$  and since the quantum effects are relatively large at  $T_K$  according to this investigation, the quantum effects at the structural glass transition for *o*-terphenyl are due to collective phenomena. Hence this transition has to be understood as a macroscopic quantum phenomenon at relatively high temperature.

#### 4.5. Irreversibility

The discussion of irreversibility remains essentially the same as for the case of the classical fluid.

### 5. Universal properties

#### 5.1. Fictive density and temperature

In the temperature–density plane, the singularity occurs on the curve defined by  $\bar{\rho} = 0$ . The respective temperatures  $T_\infty$  and densities  $\rho_\infty$  are called fictive since these points cannot be reached experimentally, because on that curve the pressure diverges. At these points  $\rho_\infty$  the Kirkwood instability, i.e. the instability of the uniform density distribution with respect to infinitesimal density fluctuations, would occur, if they could be reached experimentally. Here it has already been shown that near  $\rho_\infty$  the relevant physics occurs, i.e. many (mostly metastable phases occur), while  $\rho_\infty$  itself cannot be reached. This explains why the Kirkwood instability has never been observed experimentally, although it should be very universal since repulsive potentials are relevant in many substances. This also explains qualitatively why carbon can be transformed to diamond at high pressure, namely the system approaches the Kirkwood instability as the pressure increases, and thus the relative stability of any metastable phase decreases. Apparently the diamond phase is stable at high pressure.

These power law divergencies are known from hard sphere systems and other systems of repulsive particles [19–21].

#### 5.2. Coexisting phases

The number of phases grows without bounds independently of the details of the potential. The logarithm of the number of phases is approximately

$$\sigma_{\text{cont}} \approx \sigma(T) - \sigma(T_{\text{min}}) \approx \bar{\rho}^{-2} \quad (37)$$

and is thus universal. Since this behaviour of the entropies is the cause for the apparent Kauzmann paradox, the Kauzmann paradox is also universal.

When the Kauzmann paradox occurs, quantum corrections become relevant. For comparison note that quantum corrections also become relevant when the uncertainty relation is violated. This occurs for a system of particles which interact via a Yukawa potential below a temperature which diverges like  $\rho^{-5.5}$  [22].

It has been found from experiments on glasses that many coexisting phases exist [23]. Furthermore it is known from mode coupling theory [24] that a dynamic instability exists at which certain modes have diverging relaxation times. The states which are thereby frozen in can be identified with the phases. Here also the number of these phases is estimated.

### 5.3. Implicated saturation of the specific heat

When the singularity is approached by decreasing temperature, the specific heat decreases due to equation (11) with a power law. Since the configurational entropy does not contribute to the specific heat, there is a saturation of this decrease at a lower level, when the formation of phases becomes significant. This saturation of  $c(T)$  is observed experimentally at the glass transition [1].

### 5.4. Saturation law for $\rho$

Consider a system at constant pressure. At high temperature,  $\tilde{\rho} \approx 1$ , hence  $P_f/T \approx \rho + \tilde{g}(k=0)/2\rho^2$ , and thus  $\rho(T)$  is a monotonically decreasing function.

As the temperature approaches  $T_\infty$  from above however,  $\tilde{\rho}$  needs to be considered. In that case,

$$\frac{P_f}{T} \approx \Omega_D \rho \tilde{\rho}^{-1/2}. \tag{38}$$

From  $\tilde{\rho} = 1 - \rho \tilde{g}(k_0)$  it follows that

$$\frac{P_f}{T} \approx \frac{\Omega_D}{\tilde{g}(k_0)} (\tilde{\rho}^{-1/2} - \tilde{\rho}^{1/2}) \approx \frac{\Omega_D}{\tilde{g}(k_0)} \tilde{\rho}^{-1/2}. \tag{39}$$

Hence when  $P = P_f$  the universal relation at leading order in  $\tilde{\rho}$  is given by

$$\tilde{\rho} \approx \left( \frac{\Omega_D T}{\tilde{g}(k_0) P} \right)^2 = \left( \frac{\Omega_D T \rho_\infty}{P} \right)^2. \tag{40}$$

From  $\tilde{\rho} = 1 - \rho \tilde{g}(k_0)$  it follows that

$$\rho = \frac{1 - \tilde{\rho}}{\tilde{g}(k_0)} \approx \frac{1}{\tilde{g}(k_0)} = \rho_\infty. \tag{41}$$

This relationship states that at leading order in  $\tilde{\rho}$ ,  $\rho$  is constant. This saturation of  $\rho(T)$  is observed experimentally at the glass transition [2].

### 5.5. Other implicated saturations

Consider a system at constant pressure. In general all power laws previously derived are universal. However other saturations occur due to the saturation of the density in all those quantities which depend on the density. These are also universal because they occur independently of the details of the potential.

The following saturations may be derived in detail. For each case we investigate the effect of saturation and therefore consider the factor  $\rho^{3/2}$  in  $\Omega_D$  separately.

(i) *The compressibility* According to equation (8), the compressibility is proportional to  $\tilde{\rho}^{3/2} 1/\rho^{7/2}$ . The first factor decreases with a power law when the singularity is approached by decreasing the temperature. The second factor decreases at relatively high temperature with decreasing temperature, while it saturates at  $1/\tilde{g}(k_0)^{7/2}$ , near the singularity. Altogether the compressibility exhibits a saturation effect and a power law. This saturation of  $\kappa(T)$  as well as a decreasing factor of  $\kappa(T)$  is observed experimentally at the glass transition [2].

(ii) The velocity of sound can be expressed as

$$c_p = \frac{1}{\sqrt{\kappa\rho}} \propto \sqrt{\frac{\rho^{5/2}}{\tilde{\rho}^{3/2}}} \quad (42)$$

For the same reasons as those given earlier, the velocity of sound exhibits an increase with a saturation effect, and an increasing power law. This saturation of  $c_p(T)$  as well as a decreasing factor of  $c_p(T)$  is observed experimentally at the glass transition [1].

(iii) Furthermore it is known from experiments [1] that the shear modulus  $G$  also increases at the glass transition and saturates at a higher value. Since  $G$  is the inverse of an anisotropic response which corresponds to the isotropic compressibility  $\kappa$ , it is conceivable, that its saturation occurs in an analogous manner.

So far all static properties of glasses, which were presented by Jäckle's review [2] article have been explained at least qualitatively.

(iv) From the earlier derivation it follows that the form of the two-particle correlation function is the same for any potential at a given dimension. Therefore  $g_2$  is universal near the singularity.

In addition the power law, by which the correlation length diverges, is universal, while the prefactor depends on the potential. Furthermore the saturation law for  $\rho$ , equation (40), implies

$$k_0\xi \approx \left( \frac{\omega_D P}{\Omega_D T \rho_\infty} \right)^{2/D-1} \quad (43)$$

This correlation length has not yet been found experimentally to my knowledge. Perhaps the reason is that there is no known ordered structure which decays with distance according to that correlation length.

### 5.6. More quantitative features

(i) Near the singularity, equation (38) can be inserted into equation (8), thus the compressibility is given by

$$\kappa_r(T, P) = \frac{2T^2 \Omega_D^2}{\rho^2 P^3 \tilde{g}(k_0)^4} \quad (44)$$

Therefore

$$\frac{d\kappa_f}{dT} > 0 \quad \text{and} \quad \frac{d\kappa_f}{dP} < 0 \quad (45)$$

both in agreement with experiments on glasses [2].

(ii) Let us consider the thermal expansion coefficient

$$\alpha = \frac{1}{L} \frac{dL}{dT} \quad (46)$$

where  $L$  is the length of the probe. With the previous results

$$\alpha = \frac{1}{\rho^{-1/D}} \frac{d\rho^{-1/D}}{d\rho} \frac{d\rho}{dT} = \frac{1}{\rho D} \left( \frac{2\bar{\rho}}{\bar{g}(k_0)} \left[ \frac{1}{T} - \frac{d\bar{g}(k_0)/dT}{\bar{g}(k_0)} \right] + \rho \frac{d\bar{g}(k_0)/dT}{\bar{g}(k_0)} \right) \quad (47)$$

or

$$\alpha \approx \frac{1}{D} \frac{d\bar{g}(k_0)/dT}{\bar{g}(k_0)}. \quad (48)$$

Let us first note that near the singularity  $\alpha$  depends on the relative change of the Mayer function only, and not on collective properties like harmonic oscillations or the density, as it does away from the singularity. In this sense this relation is universal. The Mayer function itself, however, is non-universal. It is conceivable that for physically relevant potentials  $(d\bar{g}(k_0)/dT)/\bar{g}(k_0)$  is small, and so is  $\alpha$ . This is typical for glasses [2].

### 5.7. Comparison with a model for the structural glass transition

The existence of the decisive singularity [3] has been derived and the singularity is represented by equation (2) in a well defined and systematic approximation. A singularity of the form of equation (2) has been assumed for a model of the structural glass transition [25]. This model [25] on the one hand, as well as with the neglect of topologically more complicated diagrams than loops in equation (2) in this analysis can, however, be characterized as mean field approximations. Therefore both investigations exhibit certain important common features like the existence of an extensive number of phases and the Kauzmann paradox.

Here for a class of many-particle systems specified by the respective two-particle potentials, the conditions for the existence of the decisive singularity are derived. This theoretical result can also be of practical predictive potential. For example, for particles interacting with Coulomb forces, the Fourier transform of the Mayer function  $\bar{g}$  is proportional to  $-k^{-2}$  and hence there is no such singularity. Since metals mainly interact with Coulomb forces, they rarely form glasses as is well known experimentally. Furthermore the relevance of quantum corrections due to collective phenomena and at relatively high temperature can be derived for this class of many-particle systems. In particular the quantum corrections can repair the Kauzmann paradox which remains to be explained in [25].

## 6. Conclusion

For quite general sufficiently repulsive isotropic two-particle potentials, the static behaviour of a supercooled fluid is investigated. It is shown that the thermodynamics are dominated by a singularity, which is related to the Kirkwood instability. Hence universal power laws and a universal saturation law are derived. The combination of both explains all experiments on the static quantities of supercooled fluids and glasses which were discussed in Jäckle's review article. Furthermore it explains why the singularity itself cannot be observed experimentally, as well as the Kauzmann paradox and its solution by quantum corrections. It implies the existence of many phases near the singularity and provides an estimation of their number. A new correlation length, its increase and saturation are predicted, which if found experimentally would contribute to the understanding of supercooled fluids and glasses.

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