

## Bose-Einstein Condensation and the Glassy State

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The distinction between a classical glass and a classical liquid is difficult, since both are disordered. The difference is in the fact that a glass is frozen while the liquid is not. In this Letter an equilibrium measure is suggested that distinguishes between a glass and a liquid. The choice of this measure is based on the idea that in a system which is not frozen symmetry under permutation of particles is physically relevant, because particles can be permuted by actual physical motion. This is not the case in a frozen system. In this Letter it is shown how to generalize naturally the quantum mechanical concept of Bose condensed fraction to classical systems in order to distinguish between the glass and the liquid. It is finite in the liquid and zero in the frozen state. The actual value of the condensed fraction in the liquid may serve also as a measure of the glassiness in the liquid.

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The freezing of a liquid into an ordered solid is characterized by the appearance of Bragg peaks in x-ray scattering from the solid at momenta corresponding to the reciprocal lattice. The strength of the Bragg peaks is thus an equilibrium parameter that distinguishes between the liquid state and the state of a periodic solid. When dealing with a glass the situation is different, because the structure factor that is measured by x-ray scattering is similar to that of a liquid. The usual measures that distinguish a liquid from a glass are various transport parameters, such as the diffusion constant of a tagged particle in the glass or the viscosity of the glass versus the viscosity of the liquid [1,2]. Both are based on the fact that a glass is frozen while a liquid is not. In the following, I will suggest a measure that also distinguishes between the frozen and unfrozen states but is basically an equilibrium measure. This means that the glass I will be considering is not everyday off equilibrium glass but rather thermodynamic glass, whose existence at finite temperature is still debated [3–5]. Since it is sometimes extremely difficult to realize that a given glass is not in equilibrium, the concepts developed in the following may prove useful albeit not in a precise sense even for off equilibrium glass. The idea behind this suggestion is that in a liquid of classical identical particles the symmetry under permutations of particles is physically relevant. Namely, two configurations of the system that differ only in permutations of the particles can be connected by physical continuous trajectories in configuration space which lie entirely in a thermodynamically accessible region of configuration space. Namely, the intermediate configurations of the system are of the same nature as the initial state. In a glass, on the other hand, while symmetry under permutations still formally exists, it seems not to be relevant. The reason is that continuous paths in configuration space connecting two configurations that differ by a permutation which involves a large number of particles

must have intermediate configurations which differ very much from an allowed glass configuration.

The natural parameter that distinguishes quantum systems in which the symmetry under permutations is physically relevant from systems where it is not relevant is the Bose condensed fraction. (I will not go here into the finite temperature description of the quantum mechanical system, since the analogy to be used here between the quantum mechanical and classical systems is between the quantum mechanical ground state and the classical distribution function at a finite temperature.) Consider first this analogy. The following set of Langevin equations describes the stochastic over-damped motion of a classical system consisting of  $N$  particles and enclosed in a cube of volume  $V$  with periodic boundary conditions:

$$\frac{d}{dt}x_i^k = -\gamma \frac{\partial}{\partial x_i^k} W + \eta_i^k, \quad (1)$$

where  $W$  is the potential energy of the system,  $i$  denotes the particle,  $k$  denotes the Cartesian component of a vector, and the noise  $\eta$  obeys

$$\langle \eta_i^k \rangle = 0 \quad \text{and} \quad \langle \eta_i^k(t) \eta_j^l(t') \rangle = 2D \delta_{ij} \delta_{kl} \delta(t - t'). \quad (2)$$

Note that the potential energy is not necessarily an external potential. In fact, the potential energy that I have in mind is a sum of pair potentials. It is well known that the above Langevin equations can be transformed into a Fokker-Planck equation for,  $P$ , the distribution function in configuration space,

$$\frac{\partial P}{\partial t} = \sum_i \nabla_i \cdot [D \nabla_i + \gamma \nabla_i W] P. \quad (3)$$

This has as a steady state solution the Gibbs distribution  $P_S \propto \exp[-W/kT]$ , where  $kT = D/\gamma$ . A standard transformation  $P = P_S^{1/2} \Psi$  [6] leads to an imaginary time Schrödinger equation

$$\frac{\partial \Psi}{\partial t} = -H\Psi. \quad (4)$$

The precise form of  $H$  is not of interest in the following and will not be given here. It is important to note, however, that it is a Hermitian operator, and nonnegative definite, where its only eigenstate with zero eigenvalue is the ground state  $\Psi_G = P_S^{1/2}$ . This defines for the classical system in thermal equilibrium a natural “ground

state.” Clearly the  $\Psi_G$  is symmetric under permutations and therefore is the ground state of the bosonic reduction of  $H$ . Therefore, a Bose condensed fraction  $\xi$  can be defined for the classical liquid as the ground state condensed fraction of some quantum Bose system with a ground state given by  $\Psi_G = P_S^{1/2}$ . Clearly the ground state condensed fraction is a functional of the ground state. This functional is known for many years to be given by [7]

$$\xi = \frac{1}{V} \frac{\int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi_G(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_G(\mathbf{r}'_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\int d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \Psi_G^2(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}. \quad (5)$$

For the benefit of the reader, I will just present here the necessary ingredients needed for a simple proof of the above relation. First, the normalized ground state has to be written in second quantized form as

$$|G\rangle = \left[ N! \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi_G^2(\mathbf{r}_1, \dots, \mathbf{r}_N) \right]^{-1/2} \times \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N) \psi^+(\mathbf{r}_1) \cdots \psi^+(\mathbf{r}_N) |0\rangle, \quad (6)$$

where the  $\psi^+$ 's are local Bose creation operators and  $|0\rangle$  is the vacuum (no particle) state. Then, the creation operator in the single particle zero momentum state is expressed as

$$a_0^+ = V^{-1/2} \int d\mathbf{r} \psi^+(\mathbf{r}), \quad (7)$$

and the condensed fraction is written as

$$\xi = \langle G | a_0^+ a_0 | G \rangle. \quad (8)$$

The rest of the job is done by using the Bose commutation relations

$$[\psi(\mathbf{x}), \psi(\mathbf{y})] = [\psi^+(\mathbf{x}), \psi^+(\mathbf{y})] = 0 \quad (9)$$

and  $[\psi(\mathbf{x}), \psi^+(\mathbf{y})] = \delta(\mathbf{x} - \mathbf{y})$ .

Consider a classical system, described by a potential energy given by a sum of pair potentials, which at temperature  $T$  is in the liquid phase. The corresponding condensed fraction is obviously a functional of the pair potential  $\phi$  and a function of the temperature and the density. In the following, it will be shown that in the liquid state the condensed fraction is nonvanishing. For the liquid the condensed fraction is given by

$$\xi = \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \exp \left[ -(1/2)\beta \left\{ \sum_{i=2}^N [\phi(\mathbf{r}_i - \mathbf{r}_1) + \phi(\mathbf{r}_i - \mathbf{r}'_1)] + \sum_{i,j=2}^N \phi(\mathbf{r}_i - \mathbf{r}_j) \right\} \right] / Q_N V, \quad (10)$$

where  $Q_N$  is the  $N$  particle partition function. Now, multiply and divide the right-hand side of the above by  $Q_{N+1}$  and note next that  $Q_{N+1}$  can be obtained from an integral very similar to that on the right-hand side of Eq. (10). The difference being that the integrand in  $Q_{N+1}$  has an additional factor of  $\exp\{-(1/2)\beta \sum_{i=2}^N [\phi(\mathbf{r}_i - \mathbf{r}_1) + \phi(\mathbf{r}_i - \mathbf{r}'_1) + 2\phi(\mathbf{r}_1 - \mathbf{r}'_1)]\}$ . Because of the short range of  $\phi$ , the last term in the exponent can be dropped when integrating over  $\mathbf{r}_1$  and  $\mathbf{r}'_1$  so that the final result is

$$\xi = \frac{Q_{N+1}}{V Q_N} \frac{G[(1/2)\beta]}{G[\beta]}, \quad (11)$$

where

$$G(\alpha) = \int d\mathbf{r} \left\langle \exp \left\{ -\alpha \sum_{i=1}^{N-1} [\phi(\mathbf{r}_i) + \phi(\mathbf{r}_i + \mathbf{r})] \right\} \right\rangle \quad (12)$$

and where the average is taken with respect to the Gibbs distribution at temperature  $T$  of a system of  $N - 1$  particles interacting via the two body potential  $\phi$ . It is clear that the ratio  $Q_{N+1}/V Q_N$  is of order one. The ratio of the  $G$ 's is also of order one. To see that it will be more convenient to express  $G(\alpha)$  in the form

$$G(\alpha) = \int d\mathbf{r} \left\langle \exp \left\{ -\alpha \int d\mathbf{r}' \phi(\mathbf{r}') [\rho(\mathbf{r}') + \rho(\mathbf{r}' - \mathbf{r})] \right\} \right\rangle, \quad (13)$$

where  $\rho(\mathbf{r}) = \sum_{i=1}^{N-1} \delta(\mathbf{r} - \mathbf{r}_i)$  is the particle density. Since the two particle potential is short ranged the expression for  $G$  can be simplified to

$$G(\alpha) = V \left\langle \exp \left\{ -2\alpha \int d\mathbf{r}' \phi(\mathbf{r}') \rho(\mathbf{r}') \right\} \right\rangle. \quad (14)$$

Each of the  $G$ 's is of order  $V$  and so their ratio is of order one. In fact, for the hard sphere system the ratio of the  $G$ 's is just 1. Thus the condensed fraction is nonvanishing in a classical liquid.

The frozen state is characterized by the fact that each particle is localized in the vicinity of some fixed point in space. The analogy with the quantum mechanical Bose system, this time with a system in which the particles are localized, is still valid, because the localization can be

taken into account by a proper modification of the classical distribution function. The problem of the existence of Bose-Einstein condensation in a Bose solid was discussed extensively in the past [7–13] and these ideas can be borrowed now for the discussion of the frozen state in the classical case. The relevant result for the present discussion is that Bose-Einstein condensation does not exist in a Bose system in which the particles are localized. Therefore it also does not exist in the frozen classical system. For the sake of completeness, an outline of the argument is given in the following.

A reasonable configuration space distribution function corresponding to the frozen system  $P_f$  is given by

$$P_f = P_S \sum_p L[\mathbf{r}_1, \dots, \mathbf{r}_N; p(\mathbf{R}_1, \dots, \mathbf{R}_N)], \quad (15)$$

where the sum on  $p$  is the sum over permutations of the lattice (either periodic or disordered) sites. The function  $L$  is given by

$$L[\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_N] = \prod_{i=1}^N g(\mathbf{r}_i - \mathbf{R}_i, \mathbf{R}_i), \quad (16)$$

where the function  $g(\mathbf{r}, \mathbf{R}_i)$  viewed as a function of  $\mathbf{r}$  is one within some compact singly connected region around the origin and vanishes outside it. Its dependence on  $\mathbf{R}_i$  denotes that the shape and orientation of the region in which the function differs from zero depends on the lattice site. (Even for the more familiar ordered lattice such a form is necessary as  $P_S$  alone is invariant under translations.) Consider the off diagonal correlation function

$$\Phi(\mathbf{r}) = \frac{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi_f(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi_f(\mathbf{r}_1 + \mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N \Psi_f^2(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (17)$$

where  $\Psi_f = P_f^{1/2}$ . The system will exhibit a nonzero condensed fraction if and only if the off diagonal correlation has an infinite range. In order to understand what is going on it is instructive to consider first the case of no overlap. This is the case where  $g(\mathbf{r} - \mathbf{R}_i, \mathbf{R}_i) \times g(\mathbf{r} - \mathbf{R}_j, \mathbf{R}_j) = 0$  for  $i \neq j$ . Each of the  $\Psi$ 's in the integrand in the numerator on the right-hand side of Eq. (17) involves a sum over permutations. The integrand in the numerator on the right-hand side of Eq. (17) will thus involve a double sum over permutations of terms of the form  $L[\mathbf{r}_1, \dots, \mathbf{r}_N; p(\mathbf{R}_1, \dots, \mathbf{R}_N)]L[\mathbf{r}_1 + \mathbf{r}, \dots, \mathbf{r}_N; p'(\mathbf{R}_1, \dots, \mathbf{R}_N)]$ . Because of the condition of no overlap applied to  $\mathbf{r}_2, \dots, \mathbf{r}_N$ , it is evident that any product of two  $L$ 's corresponding to two different permutations is identically zero. In case  $p' = p$ , it is obvious that for  $|\mathbf{r}|$  large enough (larger than the linear size over which  $g[\mathbf{r}, p(\mathbf{R}_1)]$  is different from zero) the product of  $L$ 's is again identically zero. Therefore, the off diagonal correlation (17) vanishes identically for finite large enough distances. For small overlap it will never vanish identically but

will decay over a finite range, so that the condensed fraction is zero [13]. In reality the overlap is small, describing the fact that a particle cannot escape from the cage consisting of its neighbors. So condensation does not exist.

The fact that condensation exists in the liquid state and does not exist in the frozen state implies that a dimensionless parameter,  $g$ , that measures the glassiness of the liquid can be defined

$$g = 1 - \xi. \quad (18)$$

Thus, the glassiness changes continuously from zero in the extremely dilute gas to one in the frozen state. In the following, I will give two examples in which known results from classical liquid theory will be used to obtain the glassiness in liquids with repulsive interactions.

The first example is that of the one-dimensional hard rod problem. It is interesting not only because it can be solved exactly but also because of its special peculiarities, which result from the one-dimensional character of the problem. The one-dimensional hard rod problem is soluble and  $Q_N$  can be obtained exactly [14,15]:

$$Q_N = [L - (N - 1)a]^N, \quad (19)$$

where  $L$  is the total length of the system (not periodic) and  $a$  the length of a single rod. Using Eq. (11) and the fact that the ratio of the  $G$ 's is one in the case of hard cores, it is easy to obtain the condensed fraction

$$\xi = (1 - x)^{-x/(1-x)}, \quad (20)$$

where  $x = Na/L$ . This result of a finite condensed fraction for the hard rod case is actually misleading. The reason is that, because of the strict hard rod condition, symmetry under permutation is obviously irrelevant because the particles cannot be interchanged dynamically and the initial order of the different particles is preserved. Thus the dynamically relevant quantity is  $Q_N/N!$  rather than  $Q_N$ , because the latter takes into account, erroneously, all possible orderings of the particles. This leads, as expected, to a vanishing condensed fraction. This is specific to the hard core one-dimensional system where the condensed fraction vanishes while the particles are not localized and do not form a glass. The last property is a peculiarity of one dimension. Only in one dimension with a hard core interaction symmetry under permutations can be broken in spite of the fact that the system is not frozen. In higher dimensions, the dynamical irrelevance of symmetry under permutations can follow only from localization. To get some idea of what happens in the liquid phase in three dimensions consider next the hard sphere system. I will use here the Percus-Yevick (PY) approximation [16], in spite of its known shortcomings at high densities, because it offers an analytic [17] and reasonable result over a wide range of densities. The PY equation of state is given by

$$p = nkT[1 + \eta + \eta^2]/[1 - \eta]^3, \quad (21)$$

where  $\eta$  is expressed in terms of the hard sphere radius  $R$  and the particle density  $\rho$ ,  $\eta = \pi R^3 \rho / 6$ . Once the pressure is given,  $Q_N$  can be obtained readily, resulting in a straight forward manner in an expression for the condensed fraction

$$\xi = (1 - \eta)^{f(\eta)}, \quad \text{with } f(\eta) = (3/2)[1 - 1/(1 - \eta)^2], \quad (22)$$

and the glassiness will be just

$$g = 1 - (1 - \eta)^{f(\eta)}. \quad (23)$$

Clearly, the above expression cannot be taken seriously for relatively high densities but can be expected to be a semiquantitative description up to medium density range ( $\eta$  about 0.3–0.4).

A number of questions can be raised now concerning all the above discussion. First, to what extent is the definition of  $g$  arbitrary? One can use, of course, more complicated functions of the condensed fraction that interpolate between zero and one. This arbitrariness is trivial, of course, and the same can be done for many traditional definitions of physical quantities. There are, however, more interesting possibilities. Since the system is formally equivalent to a Bose system, one could look also for a superfluid density,  $\rho_S$ , and define perhaps the glassiness as  $g = 1 - \rho_S$ . This, however, will not give us any information about the liquid, since the liquid at a finite temperature is equivalent to a Bose liquid at zero temperature (ground state). In a translational invariant Bose ground state the superfluid density is always one and that definition of glassiness will always lead to zero glassiness in the liquid state. This is different from the situation of a Bose system in the presence of a random potential [18], where  $\rho_S$  changes continuously and becomes zero for strong pinning. There, the ground state for each realization is not translational invariant. Second, why look at such a parameter and not just stay with the viscosity? First, it is always interesting to look at the same phenomena from a new and different angle. This may lead to interesting new insights and connections. The second reason is more practical. I would suggest that perhaps the most interesting regime for the study of glassiness in liquids is that of supercooled liquids. In that regime the direct measurement of viscosity might not be that easy, because it necessitates a macroscopic disturbance of a metastable system. Third, is the glassiness an accessible parameter? From the theoretical point of view the answer is definitely positive. Obviously, approximation schemes that improve on PY for hard core interactions can be used as well as simulations. Established analytical and nu-

merical methods can be used to treat cases with soft interactions including attractive parts, which are of great interest. Last, is glassiness a measurable quantity? It can be measured in simulations, but what about real experiments. Even without checking their relevance to the present problem it is clear that recent Bose-Einstein condensation experiments seem to be out of the question. They are done at extremely low densities, which in any case are not interesting for the case studied here. They are totally not useful for the determination of the condensed fraction in liquid helium, where only indirect measurements exist. For example, the condensed fraction can be obtained from the measured structure factor [19]. This seems to be possible also in our case and is postponed to future publications.

The purpose of the present Letter is just to introduce the basic idea and hopefully it will trigger further activity in the future. I believe that of particular interest will be the study of the glassiness in liquids near their transition point and in the metastable domain of supercooled liquids.

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