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Connections between some kinetic and equilibrium theories of the glass transition

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Connections between the static density-functional theory of the glass transition and the dynamic mode-coupling theory of the glass transition are discussed. In three dimensions, some approximate equivalences are established. These equivalences are made more precise by examining high-dimensionality liquids and glasses. The similarities with early static and dynamic mean-field theories of the spin-glass transition are emphasized. Some speculations on the relationship between structural glasses and Potts glasses are also included.

I. INTRODUCTION

The dynamics of glasses and of the glass transition are some of the most interesting areas of investigation in modern condensed matter physics. The field has been marked by a proliferation of theoretical approaches ranging from simple scenarios to attempts at full-scale microscopic theories. A fully unified picture has yet to emerge. In this paper we hope to narrow the range of discussion. We will examine the connections between two recent microscopic approaches to the glass transition in simple fluids. The particular system usually investigated by these microscopic theories is a system of hard spheres on which we also will concentrate. At first sight the two approaches are entirely distinct. One is a dynamical mode-coupling theory (MCT);[1-6] the other[7] is an equilibrium theory based on the density-functional theories (DFT) of freezing.[8,9] We will show that the two approaches are related in a formal way. While in their approximate incarnations they are not precisely equivalent, the theories do become equivalent for an infinite dimensional system. We will also argue that in a certain controlled, perturbative sense the theories are, in principle, both exact for the infinite-dimensional glass.

The understanding of the relations between the theories provides a new view of the validity of both theories for finite-dimensional systems. A debate has been raging about whether the glass transition is "static" or "dynamic." Although this cannot be settled by our analysis, the present study does suggest the distinction may not be as clear as some would wish. Similarly, there has been a great deal of discussion of the possible analogies between glasses and spin glasses. The mode-coupling theory of glasses is rather close in spirit to the dynamical analysis of spin glasses.[10-13] It is also related to the early dynamical theory of Edwards and Anderson.[14] The density-functional theory is related to the mean-field approach of Thouless, Anderson, and Palmer.[15] The connections established here help sharpen both the analogy and discrepancy between spin systems and continuous fluid systems. The "discontinuous" nature of the fluid glass transition in the approximate theories is the hallmark of the differences. This discontinuous nature of the transition points to a closer connection with Potts glasses[16-20] rather than with Ising spin glasses. Another feature of the structural glass problem is that the spatial randomness is self-generated rather than put in by hand as in the random spin models. This suggests a connection with frustrated but regular magnetic lattice problems.[21] The connection of structural glasses with regular frustrated systems is the touchstone of the curved space approach due to Nelson.[22] The topological curved space approach is not inconsistent with the theories we consider, but also does not focus on the same relationships.

The organization of the paper is as follows. In Sec. II we review the formal structures of density-functional theory and mode-coupling theory. Although the mode-coupling theory can be derived via dense gas kinetic theory, we will show how it arises from a field theory.[23] The nonlinearities in this field theory arise, in part, from the nonlinearities of the equilibrium density functional. We will argue that the mode-coupling theories are a dynamical but perturbative treatment of the field theory while the density-functional treatment is a static or classical treatment of this theory. A (Boltzmann-type) H theorem for the kinetic theory[24] allows one to connect a dynamic transition with the existence of nontrivial minima of the free energy. In Sec. III we discuss concrete approximations made in the two theories. Both approximate theories describe the glassy solid as systems of Einstein oscillators. The stability criteria found in both theories will be related. In Sec. IV the theories will be investigated for high dimensionalities. In this limit for the relevant densities an exact free-energy functional is known.[25,26] (The glass transition is a "dilute" gas phenomenon in high dimension.) Finally, in Sec. V we summarize our picture and speculate on the connections with Potts glasses and on the dynamics of finite-dimensional glasses.

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II. FREE-ENERGY FUNCTIONALS AND MODE-COUPLING THEORIES

A. Basic equations of density-functional theory

The most systematic route to the calculation of the structure of fluids begins from the free energy as a functional of the inhomogeneous density $n(\mathbf{x}), F(n(\mathbf{x}))$. Recently, free-energy functionals have been used as the starting point for the theory of freezing.[8,9] (A variety of approximate forms for the free energy of an inhomogeneous fluid have been developed.) In the theory of freezing one tries to find minima of a given free-energy functional corresponding to a nonuniform density field. Generally the Euler-Lagrange equation $\delta F/\delta n=0$ is a nonlinear integral equation. For ordinary freezing the analysis is simplified through the consideration of solutions of the integral equation with specified periodicity. It is not obvious, however, that periodic solutions exhaust the complete solution space. Other solutions would correspond with *aperiodic* crystals—inhomogeneous densities which are free-energy minima but which do not have any apparent order. If the free-energy barriers between different aperiodic solutions are extensive in system size we would have true equilibrium phases. If the barriers are merely very large, the solutions would still be relevant because the dynamical transitions between different minima would be very slow.

Freezing into an aperiodic crystal has been studied as a possible origin of the glass transition.[7] A similar but distinct picture has been used to discuss freezing into quasicrystals.[27] The search for generic aperiodic solutions of a nonlinear integral equation is a demanding task. A simpler approach has been used. Starting with a random close packed structure an inhomogeneous density field is constructed. This trial density contains a flexible parameter which allows the description of both a uniform and a nonuniform state. Since the free energy can be computed as a function of this parameter, one can find the point at which aperiodic inhomogeneous solutions become possible. Singh *et al.*[7] carried out this procedure using the free energy obtained by expanding the solid-state free energy around the uniform liquid. The low-order approximation used was

$$F[n(\mathbf{x})]=F_0[n]+F_{\rm int}[n]\ , \tag{2.1}$$

with F_0 the ideal gas entropy term,

$$F_0[n]=\int d\mathbf{x}\, n(\mathbf{x})[\ln n(\mathbf{x})-1]\ , \tag{2.2a}$$

and $F_{\rm int}$ the lowest-order-interaction term,

$$F_{\rm int}[n]=-\tfrac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\, n(\mathbf{x})C(\mathbf{x}-\mathbf{x}')n(\mathbf{x}')\ . \tag{2.2b}$$

In Eq. (2.1) we have neglected a constant term which contributes to the uniform liquid free energy. For $d\rightarrow\infty$, this constant is identically zero. These free energies have been normalized with k_BT, where k_B is Boltzmann's constant and T is the temperature. In Eq. (2.2b), $C(\mathbf{x})$ is the liquid-state direct correlation function.[28] In Fourier space, $C(q)$ is related to the static structure factor $S(q)=1+nh(q)$, with $h(q)$ the pair correlation function, by $nC(q)=1-1/S(q)$.

Other free-energy functionals have been proposed to describe the liquid-glass transition. Here we concentrate on the one given by Eqs. (2.1) and (2.2), since it is most directly related to the MCT of the glass transition.

B. Dynamic density-function theory

A dynamical theory based on the free energies given in Sec. II A can be derived from either kinetic theory or from more phenomenological arguments.[22,29] We will follow the latter course here, noting that a concrete connection between the two possible approaches can be established. The dynamic DFT given here can be used to derive the MCT of the glass transition that is already in the literature.

To begin we first note that in solving the static DFT for glass transition one makes an Einstein oscillator approximation for the aperiodic solid. To make a connection with this theory we discuss here a dynamic DFT for tagged or self-particle motion in a dense liquid. In this description it is relatively simple to make approximations analogous to those used in DFT. As a consequence, the dynamic DFT given here leads to a MCT equivalent to that given by Sjölander and Turski[30] for self-particle correlation functions. We base our description of the dynamical theory of the glass transition on these equations which are somewhat different than the current MCT of the glass transition.[1-6] Dynamic DFT can also be used to derive these theories. Further, we argue below that these two MCT effectively become identical in the limit of large dimensions.

We first write down a set of hydrodynamiclike equations for the self- (or tagged-) particle number density $n_s(\mathbf{x},t)$ and self-momentum density $\mathbf{g}_s(\mathbf{x},t)$. For simplicity, and to make the connection with static DFT and the usual MCT, we only keep nonlinearities in these equations that arise from terms with the free energy. The basic dynamical equations are[31]

$$\partial_t n_s(\mathbf{x},t)+\frac{1}{m}\nabla\cdot\mathbf{g}_s(\mathbf{x},t)=0 \tag{2.3a}$$

and

$$\partial_t g_{s\alpha}(\mathbf{x},t)=-n_s(\mathbf{x},t)\frac{\partial}{\partial x_\alpha}\frac{\delta F_s}{\delta n_s(\mathbf{x},t)}-\nu g_{s\alpha}(\mathbf{x},t)+f_{s\alpha}(\mathbf{x},t)\ . \tag{2.3b}$$

The equations for the fluid density and fluid momentum density $\mathbf{g}$ are (again, neglecting irrelevant nonlinearities)[22,29]

$$\partial_t n(\mathbf{x},t)+\frac{1}{m}\nabla\cdot\mathbf{g}(\mathbf{x},t)=0 \tag{2.3c}$$

and

$$\partial_t g_\alpha(\mathbf{x},t)=-n(\mathbf{x},t)\frac{\partial}{\partial x_\alpha}\frac{\delta F}{\delta n(\mathbf{x},t)}-\int d\mathbf{x}'\,\Gamma_{\alpha\beta}(\mathbf{x}-\mathbf{x}')g_\beta(\mathbf{x}',t)+f_\alpha(\mathbf{x},t)\ . \tag{2.3d}$$

In these equations m is the mass of the particles, $f_{s\alpha}$ and f_α are Gaussian random forces, ν is a bare relaxation rate which for hard spheres is given by $2/3t_E$ with t_E the Enskog mean free time between collisions, and $\Gamma_{\alpha\beta}$ is the fluid dissipative kernel that is given elsewhere.[22] In Eq. (2.3b), F_s is the free energy for the tagged-particle—fluid system. To leading order in an expansion around a uniform fluid,

$$\frac{\delta F_s}{\delta n_s(\mathbf{x},t)}=k_B T\left\{\ln n_s(\mathbf{x},t) - \int d\mathbf{x}_1\, C(\mathbf{x}-\mathbf{x}_1)n(\mathbf{x}_1,t)\cdots\right\} . \tag{2.4}$$

C. Formal connections between DFT and a MCT

A formal connection between the static DFT and the dynamic DFT or MCT can be established. To make the connection, we first note that the most general way to solve static DFT is to look for nontrivial solutions of the equation

$$\frac{\delta F[n]}{\delta n(\mathbf{x})}=0 \tag{2.5}$$

for the density $n(\mathbf{x})$ for a fixed number of particles. Aperiodic solutions to this equation would then correspond to metastable glassy states.

The dynamical MCT approach calculates the density correlation function (dcf), $\langle \delta n(\mathbf{x},t)\delta n(\mathbf{x})\rangle$, where $\delta n(x)=n(x)-n_0$, with n_0 the uniform fluid density, and the angular brackets denote an ensemble average. A glassy state exists if the dcf does not decay for $t\to\infty$,

$$\lim_{t\to\infty}\langle \delta n(\mathbf{x},t)\delta n(\mathbf{x}')\rangle\neq 0 \quad \text{(glass)} . \tag{2.6}$$

The most reasonable way to interpret Eq. (2.6) is that the density field in the glassy state is not uniform. To make a connection with Eq. (2.5) we note that the deterministic version of Eq. (2.3), with $f_\alpha=0$, can be derived from the nonlinear revised Enskog kinetic equation. It has been proven[24] that the only stationary solutions of this equation are specified by densities that must satisfy the equation,

$$\nabla\frac{\delta F[n]}{\delta n(\mathbf{x})}=0 . \tag{2.7}$$

The gradient operator in Eq. (2.7) reflects the fact that the gradient of the generalized pressure must be zero in a (meta) stable state. Equations (2.5) and (2.7) are identical, except possibly for a constant. If we assume the fluctuating forces in Eq. (2.3) will not modify this scenario, then formally it appears that static and dynamic theories lead to identical descriptions of the glassy state.

Finally, we remark that a purely dynamical transition is also possible. Indeed, Das *et al.*[32] have argued that in a mode-coupling approximation a transition is also possible in a theory with a quadratic free energy. We do not dispute this claim, but wish to point out that the dynamical theories can also be consistent with static DFT.

III. CONNECTION OF NAIVE MODE-COUPLING THEORY AND NAIVE DENSITY-FUNCTIONAL APPROACH

The complete mode-coupling theories as well as the complete density-functional theory lead to equations of formidable complexity. Thus when the theories are implemented further approximations are generally made. In order to show the connections in a concrete way equivalent approximations must be made in both theories. The way we will choose to do this is based on an Einstein oscillatorlike approximation in the density-functional theory and a single-particle motion approximation in the mode-coupling theory (which we will dub "naive" mode-coupling theory). A mode-coupling theory along these lines was originally put forward by Sjölander and Turski,[30] but our version is different in that self-consistency is rigorously enforced leading to a sharp transition.

In the MCT theories this approximation is most naturally implemented in a theory based on tagged- (or self-) particle motion. The tagged-particle motion is coupled to fluid fluctuations and to obtain a closed equation we will use the Vineyard approximation[27,33] to relate fluid density fluctuations to tagged-particle density fluctuations. Such an approximation is only valid at large wave numbers (approximately molecular scale wave numbers) and as a consequence our approximation violates known long wavelength properties of the fluid density correlation function. For applications of MCT to the glass transition this drawback is not serious since the mode-coupling integrals are approximately dominated by the large wave-number behavior of the integrals. In fact, cf. Sec. IV, for $d\to\infty$ this approximation appears to become exact.

In examining these theories it is useful to bear in mind the analogies to the older theories of spin glasses. The naive mode-coupling theory is quite analogous to Edwards and Anderson's old dynamical treatment of spin glasses.[14] The simple version of density functional theory is rather close to their early static work.[34] These theories are now known to be incomplete but they did identify properly the occurrence of a transition in the mean-field limit. The way in which the simple static and dynamic theories coincide[14] there is *nearly* reproduced in the structural glass theories.

A. Naive mode-coupling theory

The fundamental mechanism for the glass transition in the MCT is a feedback between slow density fluctuations. In the naive MCT the basic object is the propagator describing the decay of tagged particle fluctuations. This decay is determined by the velocity autocorrelation function (VACF). Here we use Eq. (2.3b) to derive a mode-coupling approximation for the VACF. In the glassy limit this equation reduces to an equation appropriate for a harmonically bound particle with a spring constant that can be related to the spring constant obtained from DFT.

Equation (2.3b) immediately leads to an equation for the tagged-particle velocity $\mathbf{v}_s(t)$. In a Fourier representation one obtains from Eqs. (2.3b) and (2.4),

$$(\partial_t+\nu)v_{s\alpha}(t)=\frac{1}{m}\int\frac{d\mathbf{q}}{(2\pi)^3}iq_\alpha C(q)n_s(-\mathbf{q},t)n(\mathbf{q},t)+f_{s\alpha}(t)\ . \tag{3.1}$$

Here we are interested in an equation of motion for the VACF,

$$C_{s\alpha\beta}(t)=\langle v_{s\alpha}(t)v_{s\beta}\rangle\ , \tag{3.2}$$

where the angular brackets denote an equilibrium ensemble average. In general, MCT will lead to an equation for C_s of the form

$$(\partial_t+\nu)C_{s\alpha\beta}(t)+\int_0^t d\tau\,\Sigma(t-t)C_{s\alpha\beta}(\tau)=0\ . \tag{3.3}$$

where $\Sigma(t)$ is a mode-coupling self-energy. It corresponds to an additional friction mechanism arising from the excitation of structural diffusion modes in the fluid.

The simplest mode-coupling approximation for Σ can be calculated from Eq. (3.1) in the standard way. One obtains[35]

$$\Sigma_0(t)=\frac{n}{3\beta m}\int\frac{d\mathbf{q}}{(2\pi)^3}q^2C^2(q)S(q)\Gamma_{s0}(q,t)\Gamma_{f0}(q,t)\ . \tag{3.4}$$

Here $\Gamma_s(q,t)(\Gamma_f(q,t))$ is the propagator for self- (fluid) density fluctuations and the subscript 0 denotes lowest order propagators. From Eq. (2.3) one obtains, as $q\to 0$,

$$\Gamma_{s0}(q,t)=e^{-D_0q^2t}\ , \tag{3.5a}$$

with $D_0=(\beta m\nu)^{-1}$ the bare self-diffusion coefficient. As discussed above, Eqs. (3.3), (3.4), and (2.3) are not yet complete since $\Gamma_f(q,t)$ appears. In terms of propagators the Vineyard approximation is[33]

$$\Gamma_f(q,t)=\Gamma_f^v(q,t)=\Gamma_s(q,t)\ . \tag{3.5b}$$

Finally, the self-consistent MCT replaces the bare propagators in Eq. (3.4) by exact self-density propagators.[35] From Eqs. (3.4) and (3.5b),

$$\Sigma(t)\simeq\frac{n}{3\beta m}\int\frac{d\mathbf{q}}{(2\pi)^3}q^2C^2(q)S(q)[\Gamma_s(q,t)]^2\ . \tag{3.6}$$

We note that in using Eq. (3.6), vertex corrections are neglected.

We next use Eqs. (3.3) and (3.6) to predict the existence of a glassy state. First note that in the liquid phase,

$$\Gamma_s(q,t\to\infty)\to 0\ \ \text{(liquid)}\ . \tag{3.7a}$$

Physically this condition represents that the probability of finding the tagged particle is uniform for long times in the liquid phase. In a glassy state the tagged particle vibrates around an aperiodic lattice site and

$$\Gamma_s(q,t\to\infty)\neq 0\ \ \text{(glass)}\ . \tag{3.7b}$$

If the glass is a harmonic solid then

$$\Gamma_s(q,t\to\infty)=e^{-q^2/4\alpha}\ , \tag{3.8a}$$

with α a spring constant that can be related to the long-time limit of the self-energy by

$$\alpha=\frac{\beta m}{2}\Sigma(t\to\infty)\ . \tag{3.8b}$$

From Eqs. (3.8) and (3.6) the self-consistent equation for α is

$$\alpha=\frac{n_0}{6}\int\frac{d\mathbf{q}}{(2\pi)^3}q^2C(q)h(q)\exp(-q^2/2\alpha)\ , \tag{3.9}$$

where we have used $C(q)S(q)=h(q)$, with $h(q)$ the equilibrium liquid-phase pair correlation function.

Equation (3.9) is the naive MCT equation for the glass transition. For low densities only the trivial solution, $\alpha=0$, is possible. For higher densities nontrivial solutions are possible and a stable glass phase is predicted.[36] In Sec. III B we show that static DFT leads to similar equations for the glass transition.

B. Einstein-oscillator approximation in density-functional theory

1. Variational equations

The quantitative implementation of the density-functional theory by Singh *et al.*[7] is based on a simple one-parameter trial density function $n(\mathbf{x})$. The motivation for this trial form is the picture that in a glass each atom vibrates around a local lattice site in a quasiharmonic fashion. Thus, in this theory there is an ideal, vibrationless lattice whose structure resembles that of the dense random packings which were first exhibited by Bernal.[37] We specify this aperiodic packing by a set of positions $\{\mathbf{x}_i\}$.

Only the pair distribution function corresponding to the set $\{\mathbf{x}_i\}$ enters into the final variational criterion. We will call this distribution $g_{id}(x)$. It is tabulated for various computer generated aperiodic packing.[38,39] The trial density function is a sum of Gaussians centered about these aperiodic lattice positions:

$$n(\mathbf{x};\alpha)=\sum_{i=1}^{N}n_G(\mathbf{x}-\mathbf{x}_i) \tag{3.10a}$$

where N is the number of particles and

$$n_G(x)=\left[\frac{\alpha}{\pi}\right]^{3/2}e^{-\alpha x^2}\ . \tag{3.10b}$$

If α is zero the trial density becomes a uniform one with the same average density as the ideal lattice. If α is fairly large each Gaussian can be identified with a single particle and α is inversely related to the mean-square displacement of each particle. In this sense if α is large the theory resembles an Einstein oscillator picture of an aperiodic solid.

In Ref. 7 the variational analysis using this trial function was carried out numerically. In order to make formal contact with the mode-coupling theories it is useful to find explicitly the self-consistent equation for α. We will analyze the free-energy functional given by Eqs. (2.1) and (2.2). The variational equation consists of two terms

$$0=\frac{\partial F}{\partial\alpha}=\frac{\partial F_0}{\partial\alpha}+\frac{\partial F_{\text{int}}}{\partial\alpha}\ . \tag{3.11}$$

In this approach the values of α obtained are large. As a consequence the separate Gaussians do not overlap and therefore

$$\frac{F_0}{N}=\frac{1}{N}\int d\mathbf{x}\,n(\mathbf{x})[\ln n(\mathbf{x})-1]$$

$$\simeq\frac{3}{2}\ln\frac{\alpha}{\pi} \tag{3.12a}$$

and we have

$$\frac{\partial F_0/N}{\partial\alpha}=+\frac{3}{2}\cdot\frac{1}{\alpha}\ . \tag{3.12b}$$

It is useful to write the interaction part of the free energy in Fourier space because of its convolution structure:

$$\frac{F_{\text{int}}(\alpha)}{N}=-\tfrac{1}{2}\int\frac{d\mathbf{q}}{(2\pi)^3}C(q)\,|\,n_G(q)\,|^2S_0(q)\ . \tag{3.13}$$

Here $n_G(q)$ is the Fourier transform of Eq. (3.13) and is essentially a Debye-Waller factor:

$$n_G(q)=\exp(-q^2/4\alpha)\ . \tag{3.14}$$

The function $S_0(q)$ in Eq. (3.13) is the structure factor of the ideal aperiodic lattice

$$S_0(q)=\overline{\frac{1}{N}\sum_{i,j=1}^{N}e^{i\mathbf{q}\cdot(\mathbf{x}_i-\mathbf{x}_j)}}=1+n_0h_0(q)\ , \tag{3.15}$$

where the bar denotes that $S_0(q)$ is determined by the distribution $g_{id}(r)$.[40] In giving Eq. (3.15) we have used that the assumed glassy state is isotropic in indicating that $S_0(q)$ is a function of $|\,\mathbf{q}\,|$ only. In this equation, $h_0(q)$ is the ideal lattice correlation function. From Eq. (3.13) we obtain

$$\frac{\partial F_{\text{int}}/N}{\partial\alpha}=-\frac{1}{4\alpha^2}\int\frac{d\mathbf{q}}{(2\pi)^3}q^2C(q)S_0(q)\exp(-q^2/2\alpha)\ . \tag{3.16}$$

Using Eqs. (3.11), (3.12), and (3.16) the self-consistent equation for α is

$$\alpha=\tfrac{1}{6}\int\frac{d\mathbf{q}}{(2\pi)^3}q^2C(q)S_0(q)\exp(-q^2/2\alpha)\ . \tag{3.17}$$

This equation for an effective spring constant α can be compared with those derived by the dynamical theories.

Notice that this formula can be thought of as a fluctuation formula for the spring constant since it is derived from the equilibrium distribution about a lattice site.

The variational principle gives a self-consistent equation for the effective spring constant, Eq. (3.17), remarkably similar to the self-consistency condition of naive mode-coupling theory, Eq. (3.9). Notice that the only difference is a self-interaction term. We will see in Sec. III B 2 that an alternate route to α based on equilibrium theory gives precisely the same result as the dynamical theory.

2. Spring constant via response from density-functional theory

While the result just derived for α is the unambiguous result from the application of the variational principle, an alternate expression for an effective spring constant can be obtained from the density-functional theory. We call the spring constant obtained in this way the dynamical spring constant since it is obtained by calculating the response of the system to a force acting to displace a tagged particle.

Consider an aperiodic packing with the centers of vibration at $\{\mathbf{x}_i\}$. Single out a single atom at $\mathbf{x}_1$ and exert a force $\mathbf{F}$ on it. The atom will be displaced by an amount $\delta\mathbf{x}_1$ before mechanical equilibrium is re-established. We can estimate the free energy involved in this change. If the other atoms are not allowed to readjust their positions the new density field is given by

$$n(\mathbf{x})=n_G(\mathbf{x}-\mathbf{x}_1-\delta\mathbf{x}_1)+\sum_{i=2}^{N}n_G(\mathbf{x}-\mathbf{x}_i)\ . \tag{3.18}$$

Equation (3.18) is a reasonable approximation if α is large.[36,41] Under the assumption that the α value is large there is no change in the ideal gas part of the free energy but the interaction part does change:

$$\Delta F_{\text{int}}=-\int d\mathbf{x}\,d\mathbf{x}'[n_G(\mathbf{x}-\mathbf{x}_1-\delta\mathbf{x}_1)-n_G(\mathbf{x}-\mathbf{x}_1)]\times C(\mathbf{x}-\mathbf{x}')\sum_{i=1}^{N}n_G(\mathbf{x}'-\mathbf{x}_i)\ . \tag{3.19}$$

Notice that the self interaction term

$$n_G(\mathbf{x}-\mathbf{x}_1-\delta\mathbf{x}_1)C(\mathbf{x}-\mathbf{x}')n_G(\mathbf{x}'-\mathbf{x}_1-\delta\mathbf{x}_1)$$

does not contribute to ΔF_{int} (it can be seen to vanish by a change of integration variables). Next expand ΔF_{int} in powers of $\delta\mathbf{x}_1$:

$$\begin{aligned}\frac{\Delta F_{\text{int}}}{N}&=-\frac{1}{N}\int d\mathbf{x}\int d\mathbf{x}'\,\nabla n_G(\mathbf{x}-\mathbf{x}_1)\cdot\delta\mathbf{x}_1C(\mathbf{x}-\mathbf{x}')\sum_{i=2}^{N}n_G(\mathbf{x}'-\mathbf{x}_i)\\&\quad-\frac{1}{2N}\int d\mathbf{x}\int d\mathbf{x}'\,\nabla\nabla n_G(\mathbf{x}-\mathbf{x}_i):\delta\mathbf{x}_1\delta\mathbf{x}_1C(\mathbf{x}-\mathbf{x}')\sum_{i=2}^{N}n_G(\mathbf{x}'-\mathbf{x}_i)+\cdots\\&\simeq\tfrac{1}{2}\underline{K}:\delta\mathbf{x}_1\,\delta\mathbf{x}_1+\cdots\ .\end{aligned} \tag{3.20}$$

Here we have used that the term proportional to $\delta \mathbf{x}_1$ vanishes since the initial lattice was assumed to be a minimum of the free energy. Physically, the spring constant K given by Eq. (3.20) should be related to the variational parameter α in Eq. (3.12) by $\alpha_K = K/2$, where α_K denotes the value for α determined via the response argument given above. From this and Eqs. (3.20) and (3.14), and using the isotropic glassy state, one obtains

$$\alpha_K = \tfrac{1}{6} \int \frac{d\mathbf{q}}{(2\pi)^3} q^2 C(q) n_0 h_0(q) \exp(-q^2/2\alpha) \ . \tag{3.21}$$

This spring constant differs somewhat from the one obtained from the variational argument by a self-interaction term. This discrepancy seems to be inherent in the use of the Einstein oscillator trial function and will occur for periodic crystals and for different routes to elastic constants. It is not unusual for two different routes to thermodynamic properties to give different results when using approximate free-energy functionals.

The dynamical spring constant from density-functional theory agrees with the result of the naive mode-coupling theory *if* one approximates $h_0(q)$ by $h(q)$, the liquid-state correlation function. In the DFT, the state into which the liquid freezes is determined by $h_0(q)$.[40] For the glass transition problem considered here, $h_0(q)$ is determined by the aperiodic or amorphous distribution of the $\{\mathbf{x}_i\}$. In the MCT a search for an amorphous lattice is ensured by using a liquid state $h(q)$. Physically the replacement of $h_0(q)$ by $h(q)$ in the DFT for the glass transition is a reasonable approximation. Technically this replacement seems necessary to establish the connection between the static and dynamical approaches in describing the glass transition. In what follows we will assume that this approximation is not a crucial one.

IV. EXACT EQUIVALENCE FOR THE $d \to \infty$ MODEL

In this section we examine the hard-sphere model and show that if the differences between $S_0(q)$ and $S(q)$, or $h_0(q)$ and $h(q)$, are neglected then the spring constants given in Sec. III become identical in the $d \to \infty$ limit. The basic idea is that the static DFT is clearly a mean-field theory (MFT) and, in general, MFT become exact in the limit of high dimensionality. In the dynamic approach, vertex corrections are neglected in the naive MCT. One would expect these corrections also to be negligible in the $d \to \infty$ limit.

We are also motivated by the recent work of Frisch *et al.*[25,26] on the $d \to \infty$ hard-sphere gas. They have argued that the equilibrium statistical mechanics of hard hyperspheres in d dimensions becomes exceptionally simple for a range of densities in the $d \to \infty$ limit. Using their results we can construct an exact (at least in perturbation theory) DFT to describe the hard-sphere fluid-glass transition.

To proceed we first define the equilibrium statistical mechanics of the hard hypersphere gas by the Mayer function f_{12} for two spheres at $\mathbf{x}_1$ and $\mathbf{x}_2$ in a d-dimensional space,

$$f_{12} = -\Theta(\sigma - |\mathbf{x}_1 - \mathbf{x}_2|) \ . \tag{4.1}$$

Here σ is the hard hypersphere diameter and $\Theta(x)=1$ for $x>0$ and is zero otherwise. The ordering scheme used for $d \to \infty$ is most easily illustrated with an example: The first few terms of the virial expansion of the pressure p in the liquid phase, as $d \to \infty$, are

$$\frac{p}{n_0 k_B T} = 1 + \frac{n^*}{2} \left[1 + n^* \frac{8\Gamma(\frac{1}{4})}{3\pi^{1/2} d^{1/4}} \left[\frac{2}{e} \right]^{d/2} \right] + O(n_0^3) \ , \tag{4.2a}$$

and

$$n^* = \frac{n_0 \sigma^d \pi^{d/2}}{\Gamma(1+d/2)} \ , \tag{4.2b}$$

and Γ denotes a gamma function. An important fact follows from Eq. (4.2). If the second virial term, $\sim n^*$, is finite or only algebraically large for $d \to \infty$, then the third virial term vanishes exponentially fast in the $d \to \infty$ limit. It is not very difficult to show that for these densities all higher-order terms also vanish exponentially fast. Further, we show below that a phase transition occurs in this system in the density range where the first two terms in Eq. (4.2a) give exactly the liquid-state pressure in the $d \to \infty$. The exactness of the first two terms in Eq. (4.2a) has been emphasized previously.[25,26] Technically one notices that all loop diagrams in the virial expansion vanish in the $d \to \infty$ limit if the second virial coefficient is finite or algebraically large.

In general all equilibrium quantities and equilibrium correlation functions can be calculated in a loop expansion (only tree diagrams survive in the $d \to \infty$ limit). Of particular interest is the liquid-state direct correlation function[28] C_{12} given in the $d \to \infty$ limit by

$$n_0 C_{12} = n_0 f_{12} \ . \tag{4.3a}$$

The Fourier transform of this function is given by

$$\begin{aligned} n_0 C(q) &= \int d(\mathbf{x}_1 - \mathbf{x}_2) e^{-i\mathbf{q}\cdot(\mathbf{x}_1 - \mathbf{x}_2)} n_0 C_{12} \\ &= -n^* \Gamma(1+d/2) 2^{d/2} \frac{J_{d/2}(q\sigma)}{(q\sigma)^{d/2}} \ . \end{aligned} \tag{4.3b}$$

The free energy for an inhomogeneous system can also be computed by expanding around the uniform liquid:

$$\begin{aligned} F = {} & \int d\mathbf{x}_1 \, n(\mathbf{x}_1)[\ln n(\mathbf{x}_1) - 1] \\ & - \tfrac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, n(\mathbf{x}_1) C_{12} n(\mathbf{x}_2) \ . \end{aligned} \tag{4.4}$$

Equation (4.4) is the usual starting point (cf. Sec. II) for the application of DFT to describe phase transitions in liquid-state physics. However, in previous applications, Eq. (4.4) has been an approximate starting point since higher-order direct correlation functions are neglected. The important point here is that Eq. (4.4) is exact in the $d \to \infty$ limit.

We next show that Eq. (4.4) leads to a glass transition in the density range where it gives exactly the liquid-state free energy. We first use the variational approach given in Sec. III B 1. Define an aperiodic density in d dimensions by

$$n(\mathbf{x})=\left[\frac{\alpha}{\pi}\right]^{d/2}\sum_{i=1}^{N}e^{-\alpha(\mathbf{x}-\mathbf{x}_i)^2}\;. \tag{4.5}$$

We argue below that an aperiodic free-energy minimum is only possible if $\alpha\sigma^2 \sim O(d^2)$, i.e., α is large in a $d \rightarrow \infty$ aperiodic solid. With this we can use the approximations given in Sec. III B 1 to obtain an equation analogous to Eq. (3.17). Replacing $S_0(q)$ by $S(q)$ yields

$$\alpha=\frac{1}{2d}\int\frac{d\mathbf{q}}{(2\pi)^d}q^2e^{-q^2/2\alpha}C(q)S(q)\;. \tag{4.6}$$

We next solve Eq. (4.6) for $d \rightarrow \infty$. First note that $C(q \rightarrow 0)<0$ while $\alpha>0$ for a stable solid. This is only possible if the large q [$q\sigma>d/2$, cf. Eq. (4.3b)] regions in Eq. (4.6) dominate the small q regions. This follows, since for $q\sigma>d/2$, $C(q)$ can be greater than zero. From Eq. (4.6) we see that this is only possible if $\alpha\sigma^2 \sim O(d^2)$. Next insert Eqs. (4.3c) and (4.3b) in Eq. (4.6). From straightforward asymptotic analysis the following conclusions may be made.

(i) For small n^*, Eq. (4.6) does not possess a solution.

(ii) For $n^* \sim O(d)$ and $\alpha\sigma^2 \sim O(n^{*2}) \sim O(d^2)$, Eq. (4.6) does have a solution. This implies the existence of a metastable aperiodic or glassy solid.

(iii) The self-part of $S(q)$ in Eq. (4.6) leads to vanishingly small contributions. As a consequence, Eq. (4.6) can be replaced by

$$\alpha=\frac{n_0}{2d}\int\frac{d\mathbf{q}}{(2\pi)^d}q^2e^{-q^2/2\alpha}C(q)h(q)\;. \tag{4.6$'$}$$

The equivalence of Eqs. (4.6) and (4.6′) is the major result of this section. The conclusion is that all of the spring constants calculated in Sec. III become identical in the $d \rightarrow \infty$ limit. Physically this is because the self-term is less important when there are a large number of neighbors. We also note that since the large q regions in Eq. (4.6) are dominant, the Vineyard approximation used in Sec. III A is "exact" for $d \rightarrow \infty$. As a consequence, the naive MCT used here is in principle identical (for $d \rightarrow \infty$) to the MCT given elsewhere.[1-6]

Under the conditions listed above, the solution of Eqs. (4.6) is

$$\alpha\sigma^2=\frac{n^{*2}}{8\pi}\exp(-d^2/4\alpha\sigma^2)\;, \tag{4.7}$$

with n^* at *least* of $O(d)$. The conclusion is that for $n^* \sim O(d)$ a metastable aperiodic solid is possible. Explicit values for $\alpha\sigma^2=\alpha^*$ and n^* where Eq. (4.7) first has a nontrivial solution can be easily obtained from this equation. Denoting these critical values by α_c^* and n_c^*, one finds

$$\begin{aligned}\alpha_c^*&=\frac{d^2}{4}\;,\\ n_c^*&=d\sqrt{2\pi e}\;.\end{aligned} \tag{4.8}$$

Finally, one can compare this transition density with the Roger's bounds for close packed hard hypersphere lattices in d dimensions.[42] For $d \rightarrow \infty$, the maximum packing fraction satisfies the approximate bounds,

$$\frac{d}{2^d}<\frac{n^*}{2^d}<\frac{d}{2^{d/2}}\;. \tag{4.9}$$

From Eq. (4.9) and the arguments given above, it follows that the glass transition occurs just inside the lower bound for maximum crystalline packing in $d \rightarrow \infty$ dimensions.

V. DISCUSSION AND SPECULATIONS ON THE STRUCTURE GLASS TRANSITION

The theories discussed in this paper are clearly not completely correct treatment of the structural glass transition. Our goal has been to show their connections to each other and to highlight their similarities with older treatments of spin glasses. In this section we would like first to contrast the results of present structural glass theories with those of the spin glass. Following this we will use our analogy along with our current understanding of spin glasses to speculate on the nature of the glass transition in real systems. These speculations may be of some value in both designing more complete theories and in making appropriate comparisons with experiment of the current theories.

Both the dynamic and static approaches to the glass transition predict sharp transitions. This is similar to the situation in early spin-glass theories. Laboratory glass transitions are not mathematically sharp. However, when account is taken of the difference in temperature scales they are not dramatically less sharp than those in laboratory spin glasses.

The present structural glass theories differ from the early spin-glass theories in having a discontinuity in properties at the transition. They are, in some respects, first order. The mean-square displacement has a finite maximum value. Because of the close connection of the density-functional theory of aperiodic crystals with that of ordinary freezing this behavior is almost to be expected. It is somewhat more unexpected in the dynamic theory. More sophisticated mode-coupling theories do have a more complex behavior.[1-6,43] In these theories the infinite mean-square displacement is discontinuous but on the fluid side of the transition a continuous slowing down does occur.

In making the comparison with spin glasses it should be pointed out that the continuous nature of the transition in Ising spin glasses is tied to the underlying symmetry of the model. Spin models without this symmetry, such as Potts glasses with more than three components or spin models with p-spin interactions ($p>2$) do not exhibit continuous transitions but again appear to be first order in mean-field theory.[16-20] It should be noted that Monte Carlo calculations of random Potts systems do exhibit slow relaxations. Thus our comparison of mean-field theories may indicate that it is the Potts glass and structural glasses which should be considered as being in the same class.

The more modern spin-glass ideas allow us to construct a scenario for the structural glasses. The crucial realization of the modern spin-glass theories is that one must take into account the multiplicity of states into which the spin system can condense and the relationships between them. In sophisticated equilibrium theories this multiplicity is manifested by replica symmetry breaking.[44] In sophisticated dynamical theories the multiplicity is manifested in a breakdown of the fluctuation-dissipation theorem so that averaging over different macroscopic time scales must be taken into account.[45] Further progress on the structural glass problem will require coming to grips with the multiplicity problem. Again the analogy with Potts glasses may be useful. The replica based mean-field theory of the Potts glass due to Gross *et al.*[19] has many suggestive features. Here the order parameter is discontinuous, just as for the structural glass but there is no latent heat for the transition. This effect comes from the singular behavior of the distribution of the valleys: The number of valleys that overlap and have a nonzero (and discontinuous at T_c) Edwards-Anderson order parameter is of measure zero at the glass transition temperature.[20] For the infinite range Potts glass model the heat capacity is discontinuous which is not precisely the case for structural glasses, which show rather an extremely rapid change from the heat capacity of the liquid to that of the glass. Another suggestive feature of the Potts glass is the appearance of lower-temperature transitions.[19] This again often happens in structural glasses.[46]

On the basis of the aperiodic crystal picture it is clear that multiple minima of the free-energy functional exist. Many different random close packings have been constructed and different ones can sometimes be distorted into each other. Stillinger and Weber's[39] studies of energy (as opposed to free energy) minima also show many states. The crucial question is the height of the free-energy barriers between these states.[47] In the mean-field spin glasses these barriers are macroscopically large. It is unclear whether the barriers are macroscopic in the finite range spin glass. It is likely that in the structural glass some of the barriers, at least, are very large but not necessarily macroscopic. Thus interconversion between the states will be a slow process giving rise to the observed hysteretic phenomena at glass transitions. A reasonable guess is that the simple mean-field theories signal the existence of such states and that the sharp transition is smoothed out by the transitions between these states.[47] In the glassy region transport would also occur by these activated transitions. Thus the mean-field-theory transition point should probably not be identified with the so-called ideal glass transition temperature (which enters into the Vogel-Fulcher relation) but rather with a temperature near to the laboratory glass transition at which a change of slope in the Arrhenius plot of the transport properties occurs. This assignment seems most reasonable even bearing in mind the dependence of that transition point on a laboratory time scale. How to consistently include these transitions in a real microscopic theory on both sides of the transition is far from clear at the moment.

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