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Abstract. The mode-coupling theory of the liquid–glass transition is applied to the hard-sphere system. The critical exponents and amplitudes characterising the slow relaxation of density fluctuations in the vicinity of the transition are calculated. Particular attention is devoted to the description of the frozen correlations in the glass and to the critical amplitudes describing the β-relaxation process. The latter appears to be quite local, involving only rearrangements extending over a few interatomic distances.

1. Introduction

The recently developed mode-coupling theories of the glass transition [1, 2] have provided a rather detailed picture of the dynamics of supercooled liquids near a certain crossover temperature T_c, or crossover density n_c. In the original version of this theory, to which we shall restrict ourselves in this paper, T_c or n_c mark a bifurcation singularity: for temperatures T greater than T_c or densities n smaller than n_c the dynamics exhibits the features of a strongly coupled liquid. For $T < T_c$ or $n > n_c$, the density fluctuations exhibit the non-ergodicity characteristic of an ideal glass [3]. The main difference between the idealised picture and reality is the neglect of activated hopping processes, which will finally restore ergodicity for sufficiently long times also for $T < T_c$. In spite of this shortcoming one can hope that the predictions of the theory for mesoscopic times have some relevance for the experiment. For a summary of the present status of the theory with references to the original papers the reader can consult reference [4].

According to the above-mentioned theory, there is a certain region of the spectra or of the time axis, the so-called β regime, where the correlation functions exhibit some sort of universality, to be specified below. All spectra in this region, for example, are proportional to each other. The proportionality coefficient or critical amplitude specifies, for example, the spatial variations of the correlations. The common time dependance is determined by an exponential parameter λ, which also gives the exponent for the power-law divergence of the transport coefficients [5]. In this paper we want to discuss the above-mentioned quantities for the hard-sphere system which is considered as an example for a simple fluid. The critical amplitude for the density fluctuations will provide a description of the β motion in space. The values for the critical exponents

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might be of interest for a future molecular dynamics analysis of the self-blocking of the motion in the dense system.

2. Basic equations

The mode-coupling theory focuses on the correlator formed with density fluctuations ρ_q for wavevector q: $\phi(q, t) = \langle \rho_q^*(t)\rho_q \rangle / S_q$. Here S_q denotes the structure factor. Function $F(q, t) = S_q\phi(q, t)$ is the coherent intermediate scattering law, its Fourier transform with respect to the time t being the dynamical structure factor $S(q, \omega)$, the relevant quantity for neutron scattering experiments. In the ergodic liquid state the correlation functions approach zero in the long-time limit: $F(q, t \to \infty) = 0$. Within the ideal glass state there is spontaneous arrest of the fluctuations: the perturbed system does not return to the thermodynamic equilibrium state, fluctuations approach a non-trivial long time limit, specified by the glass form factor f_q

$$F(q, t \to \infty) = S_q f_q = F_q. \tag{1}$$

The form factor has to be evaluated from the following non-linear equation [2]:

$$f_q/(1 - f_q) = \mathcal{F}_q(f_k) \tag{2}$$

$$\mathcal{F}_q(f_k) = \tfrac{1}{2}S_q n q^2 \int d^3k/(2\pi)^3 V(q, k)V(q, q - k)f_k f_{q-k}. \tag{3}$$

The vertex function $V(q, k)$ can be expressed in terms of the two- and three-point direct correlation functions of the fluid $c(k)$ and $c(q, k)$, respectively [6]

$$V(q, k) = [kqc(k) + (q - k) \cdot qc(q - k) + q^2c(k, q - k)][S_q S_{q-k}/q]. \tag{4}$$

Notice that the temperature T enters the equation for f_q only indirectly via the various static distribution functions. For a hard-sphere system, T is irrelevant and so we will restrict ourselves to a discussion of the dependence of the results on density n only. Equation (2) is solved most conveniently by the iteration procedure $f_q^{n+1}/(1 - f_q^{n+1}) = \mathcal{F}_q(f_k^n), n = 0, 1, \ldots$ [2]. The convergence of this iteration is ruled by the spectrum of the stability matrix, defined by

$$C_{qk} = \partial\mathcal{F}_q/\partial f_k(1 - f_k)^2. \tag{5}$$

This is a Frobenius matrix (i.e. $C_{qk} \geq 0$). Its maximum eigenvalue E_0 is non-degenerate. Imposing the conventions for the right and left eigenvectors $e_k, \hat{e}_q$

$$\sum_q \hat{e}_q e_q = 1 \qquad \sum_q \hat{e}_q(1 - f_q)e_q^2 = 1 \tag{6}$$

the latter are determined uniquely and obey $e_q > 0, \hat{e}_q > 0$. For $n > n_c$ the iteration above defines a stable fixed point f_q, since $0 < E_0 < 1$. The transition point is characterised by E_0 approaching unity from below according to the formula

$$(1 - E_0)^2 = A_0\varepsilon + O(\varepsilon^2) \qquad A_0 > 0. \tag{7}$$

Here

$$\varepsilon = (n - n_c)/n_c \tag{8}$$

is the separation parameter. A plot of $(1 - E_0)^2$ versus n thus yields the precise value of

the critical density n_c. The form factor and eigenvector at the critical point, f_q^c and e_q^c enter the critical amplitude h_q

$$h_q = (1 - f_q^c)^2 e_q^c. \tag{9}$$

This amplitude determines the critical variation of the form factor near n_c, up to some constant $A_1 > 0$

$$f_q = f_q^c + A_1 h_q \sqrt{\varepsilon} + O(\varepsilon) \qquad \varepsilon \to +0. \tag{10}$$

This formula is of experimental relevance, since f_q is measurable in principle as the Debye–Waller factor of the system. F_q is the area under the so-called α peak of the structural relaxation. For $\varepsilon > 0$ this peak area is predicted to agree with F_q^c up to corrections of order ε. Neutron scattering experiments have verified the critical ε dependence to some extent [7–9]. Therefore we expect equation (10) to be of interest also for future molecular dynamics work.

From the eigenvectors and the form factor at the transition one can evaluate the exponent parameter by

$$\lambda = \tfrac{1}{2} \sum_{q,k,p} \hat{e}_q^c (\partial^2 \mathscr{F}_q / \partial f_k \partial f_p) h_k h_p. \tag{11}$$

This number determines the master functions $f_\pm(\hat{t})$ of the β-relaxation region. Here the correlators read

$$\phi_q(t) = f_q^c + h_q \sqrt{|\varepsilon|} f_\pm(t\omega_\varepsilon) \qquad \varepsilon \to \pm 0. \tag{12}$$

From λ one obtains two critical exponents $0 < a < \tfrac{1}{2}$, $0 < b \le 1$ by: $\Gamma(1 - a)^2 / \Gamma(1 - 2a) = \lambda = \Gamma(1 - b)^2 / \Gamma(1 + 2b)$. The first exponent determines the β-relaxation scale $\omega_\varepsilon = A_2 |\varepsilon|^{1/2a}$. It enters also the critical correlations, which are expected for times exceeding the microscopic scale t_0 but being smaller than $1/\omega_\varepsilon$

$$\phi_q(t) - f_q^c = h(q)(t_0/t)^a \qquad t_0 \ll t \ll \omega_\varepsilon^{-1}. \tag{13}$$

Let us emphasise that all correlation functions are predicted to be given by a formula like equation (12) within the β region. They all agree in the part $f_\pm$ and differ in the respective values f_q^c and h_q. The β region extends from t_0 to the time scale τ of the α-relaxation process. One gets

$$\tau = \tau_0 |\varepsilon|^{-\gamma} \qquad \gamma = 1/2a + 1/2b \qquad \varepsilon \to 0 -. \tag{14}$$

All α resonances exhibit the same critical increase at n_c; they merely differ in the factor τ_0, which varies regularly with n. In particular the diffusivity D, related to the low-frequency current spectrum [6] is predicted to decrease like

$$D \propto (n_c - n)^\gamma \qquad n \to n_c - 0. \tag{15}$$

Proofs of the preceding statements can be found in reference [5].

3. Results

The vertex (4) has been determined with the Verlet–Weis approximation [6] for the structure factor and the convolution approximation for $c(k, q)$ (i.e. $c(k, q) \equiv 0$). The physical control parameter n shall be converted as usual into the packing fraction $\eta = \pi n \sigma^3 / 6$ with σ denoting the sphere diameter. The critical value was then found to be
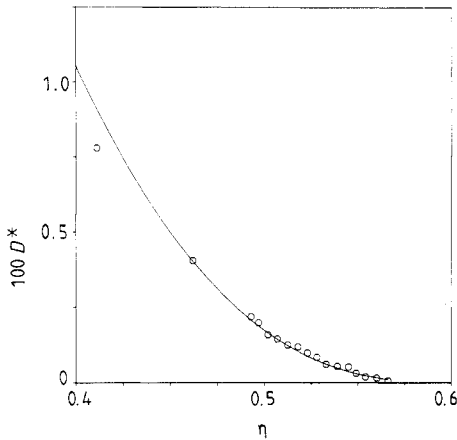
Figure 1. Reduced diffusivity $D^* = D(m/\sigma^2 k_B T)^{1/2}$ of a hard-sphere system as a function of packing fraction η. Open circles are molecular dynamics data [13]. The full curve is the power law $D^* = 0.716(0.60 - \eta)^{2.58}$.

$\eta_c^{VW} = 0.525$, confirming the calculations of Bengtzelius [10]. This value is somewhat larger than the one from the Percus–Yevick approximation $\eta_c^{PY} = 0.517$ [2]. We have also improved the latter work by eliminating the convolution approximation in favour of a recently proposed approximation [11] for the triplet correlations. This modification shifted η_c^{PY} to 0.510. The intensitiveness of η_c can be traced back to the small value of $c(\boldsymbol{q}, \boldsymbol{k})$ for triplets of wavevectors of length q_0. The latter value denotes the position of the structure factor peak. The mentioned triplets are the most relevant configurations for the determination of the critical point. So $\eta_c^{MC} = 0.52 \pm 0.01$ is the expected value on the basis of equation (3). Improving the theory, couplings to pair modes enter which consist of current and of density fluctuations. They yield a leading contribution to hopping and eliminate the transition. Approximating the density fluctuations by their static part, however, the transition remains present, but is shifted to larger η [12]. In this sense the result η_c^{MC} should be considered as a lower bound for the actual critical value. Indeed, the value for η_c, obtained by molecular dynamics [13] is about 10% larger than our estimate. The size and direction of the discrepancy between the mode-coupling calculation and computer simulation is of the same kind as reported by Bengtzelius [10] for Lennard-Jones models.

For the exponent parameter $\lambda = 0.758$ is found, somewhat larger than the value 0.741 obtained for a Lennard-Jones system [14]. From λ one predicts the relevant exponents for the hard-sphere model

$$a = 0.301 \qquad b = 0.545 \qquad \gamma = 2.58. \tag{16}$$

In figure 1 the simulation results for the diffusivity [13] are compared with the mode-coupling prediction $D = D_0(\eta_c - \eta)^{2.58}$, where the two unknown constants D_0 and η_c are used as fitted parameters. The full curve shows the result for

$$\eta_c = 0.60 \tag{17}$$

which then appears as the prediction for the true critical packing fraction for the hard-sphere system. There is reasonable agreement between the data and the theoretical picture. But this agreement should not be considered as a test of the evaluated exponent
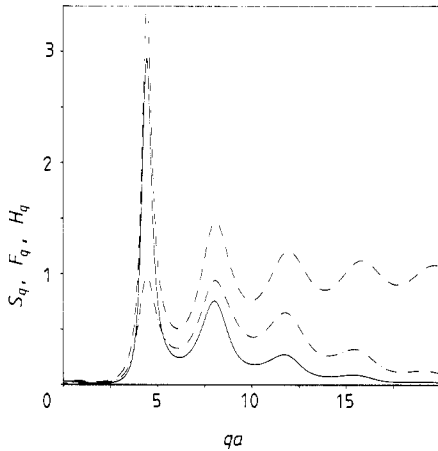
Figure 2. Structure factor S_q (broken curve), glass form factor $F_q = S_q f_q$ (full curve), and critical amplitude $H_q = S_q h_q$ (chain curve) of the hard-sphere system at the critical packing fraction $\eta^c = 0.5252$ as function of wavevector q. $a = (3/4\pi n_c)^{1/3}$ is the averaged interparticle distance.

γ. Since the available data for D extend only over about one decade, an unbiased fit to a power law (15) cannot determine γ to better than about 25%.

Figure 2 displays the structure factor S_q, the form factor $F_q = S_q f_q$ and the critical amplitude $H_q = S_q h_q$ at the transition point. The relevance of these quantities for a realistic system is obvious from the preceding discussion of equation (10). One can hope that these curves reflect reality in as far as a hard-sphere system can be considered as a qualitative model for a real system. The behaviour of S_q, the total scattering cross section, is well understood [6]. The intensity F_q of the quasi-elastic line oscillates in phase with S_q, but it decreases for large wavevectors. The amplitude H_q, the derivative of the Debye–Waller factor with respect to the square root of the separation parameter, oscillates in phase with S_q as well. The magnitude H_{q_0} at the position of the structure factor peak is as large, as the magnitude at the position of the second peak $q_1 \simeq 1.8\, q_0$. This peculiarity is important if one wants to measure the β-relaxation dynamics, equation (12), in particular the critical decay, equation (13); be it by neutron scattering or by molecular dynamics done for $F(q, t) = S_q \phi_q(t)$. As far as scattering intensity is concerned, measurement at q_0 or q_1 are equivalent. However, because of the DeGennes narrowing effect [6] the averaged spectrum is squeezed to lower frequencies at q_0 than at q_1. Therefore the separation of the β spectrum from the microscopic excitation band is better at q_1 than at q_0. The validity of the asymptotic formula (13) sets in at an earlier time for q_1 than for q_0. The α-peak intensity is considerably larger at q_0 than at q_1. Therefore the disturbance of the β spectrum by the α process is stronger at q_0 than at q_1. So there are two arguments in favour of testing β relaxation at q_1 and not at q_0.

In figure 3 the Fourier back-transform of the mentioned three quantities are shown. The pair correlation $g(r)$ is zero within the hard-curve diameter σ and then exhibits the usual shell structure of a densely packed system [6]. $F(r)$ is the averaged spatial distribution of the particle pairs, which are frozen on a timescale shorter than τ. Beyond the second nearest neighbour $F(r) = g(r)$ and the deviations at the second nearest neighbour distance are very small. In any case the oscillations of $F(r)$ follow those of $g(r)$. This result is in qualitative agreement with molecular dynamics data, obtained for
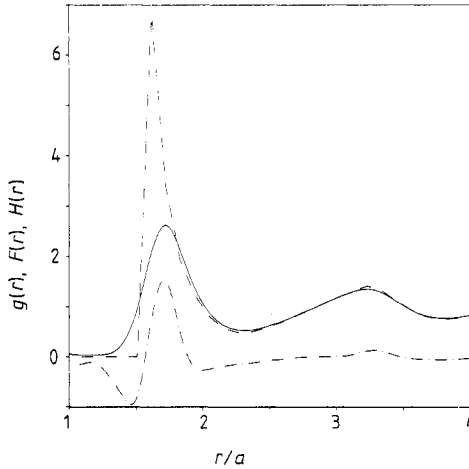
Figure 3. Pair correlation function $g(r)$ (broken curve), and Fourier back-transforms of the form factor $F(r)$ (full curve) and critical amplitude $H(r)$ (chain curve); density and a as in figure 2.

a binary soft-sphere system within the glass phase [15]. The main differences between $F(r)$ and $g(r)$ occur for r smaller than twice the averaged interparticle distance $a = (3/4\pi n)^{1/3}$. For $r \sim 1.7a$, $F(r)$ is considerably smaller than $g(r)$ and this is compensated for by $F(r)$ being non-zero for $r < \sigma$. The critical amplitude $H(r)$ exhibits sign changes. It is rather large but negative for $r \lesssim \sigma$ and it is large and positive at the next neighbour position. The oscillations are repeated with a much smaller amplitude at the next nearest neighbour shell. For $r > 4a$, the amplitude $H(r)$ for the β dynamics is practically zero. Obviously, a molecular dynamics test of the β process in ordinary space is done best by studying density fluctuations on a distance $r \sim 1.4\sigma$.

4. Conclusions

The results for the spatial variation of the form factor $F(r)$ and critical amplitude $H(r)$ are non-trivial, and allow a physical interpretation of some aspects of the dynamics described by the mode-coupling theory. The correlator $F(r, t) = \langle \rho(r, t)\rho(0, 0) \rangle$ describes the evolution of a density perturbation $\delta\rho(r, t)$, created at time $t = 0$ and position $r = 0$ by an adiabatically switched on potential [6]. At $t = 0$ one has $F(r, t = 0) = g(r) + \delta(r)$, i.e. the fluctuation established by the requirements of equilibrium thermodynamics. On the microscopic time scale t_0, $\delta\rho(r, t)$ will be rather complicated, involving, for example, emission of sound waves and building up of a backflow pattern. We are not concerned here with this complex behaviour, but rather with the motion which occurs on a longer time scale in supercooled liquids or glasses and is described by equation (12)

$$\langle \delta\rho(r, t) \rangle = F(r) + H(r)\sqrt{|\varepsilon|}f_{\pm}(\omega_{\varepsilon} t) \qquad t_0 \ll t \ll \tau. \tag{18}$$

The time-dependent part in this equation is known from previous work [4]: $f_{\pm}(\hat{t})$ decreases monotonically. From figure 3 it is seen that $\delta\rho(r, t)$ decreases strongly at the
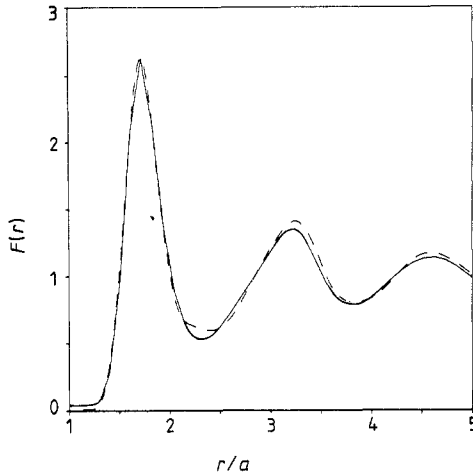
Figure 4. Comparison of the mode-coupling prediction (full curve) with the 'random packing' description (broken curve, equation (19)) for the glass form factor $F(r)$.

nearest-neighbour shell, this decrease being accompanied by an increase for $r < \sigma$. The whole motion follows the power law (13) at the beginning of the β process. This motion has a weak analogue for the second-neighbours shell, but there is no motion whatsoever for $r > 4a$. This means that the whole β dynamics involves only a particle and its nearest (and to a lesser extent next nearest) neighbours. Outside this volume the medium is at rest: the initial disturbances have already vanished, leaving $g(r)$ unchanged, while the α-relaxation process, which will yield a full relaxation in the liquid, has not yet started. Within the sphere $r < 4a$ all fluctuations move in phase or out of phase depending on the sign of $H(r)$, but there is no flow from one point of space to another. In this sense the β relaxation is a localised excitation of the system. We believe that this characterisation of the β relaxation as a strictly local phenomenon is consistent with the original ideas of Goldstein [16] and Johari [17].

A final remark concerns the interpretation of the quantity $F(r)$: this quantity characterises the frozen correlations in the glassy phase; let us suppose that the ideal glass can be described as a frozen, irregular lattice, as is usually assumed in structural models for glasses such as random packings [18]. Each particle has then a well defined equilibrium position $R_i = \langle r_i \rangle$. The probability distribution of the particle position around its lattice site is given by $\langle \delta(r_i - r) \rangle = \varphi(r - R_i)$, where φ is typically a Gaussian (whose width gives the Lindemann ratio). Assuming the displacements from equilibrium positions to be uncorrelated for $t = 0$ and $t = \infty$ one gets from the definition of $F(r, t)$:

$$F(|r - s|, t = \infty) = F_s(|r - s|) + \int dR \, dR' \, \varphi(r - R)g_L(R - R')\varphi(s - R') \tag{19}$$

with

$$F_s(|r - s|) = \rho^{-1} \int dR \, \varphi(r - R)\varphi(s - R)$$

and where $g_L(R - R')$ is the site–site pair correlation function of the lattice. Choosing for φ a Gaussian with a width $\langle r^2 \rangle^{1/2} = 0.11\sigma$ (which is reasonable for the transition point [2]) and taking g_L from the random packing simulation of [18], the broken curve

presented in figure 4 is obtained. The results for this simulation and for the mode-coupling prediction are very similar; the mode-coupling prediction appears thus to be consistent with other descriptions of the glass.

Acknowledgments

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