The geometry of empty space is the key to arresting dynamics

2004 J. Phys.: Condens. Matter 16 S4841

(http://iopscience.iop.org/0953-8984/16/42/003)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S4841–S4848 PII: S0953-8984(04)79702-7

The geometry of empty space is the key to arresting dynamics

Aonghus Lawlor, Paolo De Gregorio and K A Dawson

Department of Chemistry, University College Dublin, Irish Centre for Colloid Science and Biomaterials, Belfield, Dublin 4, Republic of Ireland

Received 19 April 2004, in final form 31 August 2004
Published 8 October 2004
Online at stacks.iop.org/JPhysCM/16/S4841
doi:10.1088/0953-8984/16/42/003

Abstract
We present the concept of dynamically available volume as a suitable order parameter for dynamical arrest. We show that dynamical arrest can be understood as a de-percolation transition of a vacancy network or available space. Beyond the arrest transition we find that droplets of available space are disconnected and the dynamics is frozen. This connection of the dynamics to the underlying geometrical structure of empty space provides us with a rich framework for studying the arrest transition.

(Some figures in this article are in colour only in the electronic version)

It is a central observation in Nature that, for some appropriate choice of experimental conditions such as temperature, density, and more complex experimentally determined external parameters, the molecules or particles (or other objects in the system) essentially stop moving[1] in a reproducible manner, even though the thermodynamic potentials are not minimized. The phenomenon has been termed dynamical arrest, and the outcome, the arrested state of matter [1, 2]. Such phenomena are ubiquitous, constituting a much larger class of behaviour in Nature than that described by the statistical theory of Boltzmann [3].

Examples in practice have been termed gelation [4–11], 'solidification', glassification [12–17], jamming [18, 19], and the ergodic–non-ergodic transition. Furthermore, they are observed in diverse systems, from simple atomic substances ('glassification') to particle and colloidal dispersions (aggregation, or particle gelation) to polymers and proteins. The view has recently arisen that these are all manifestations of the same phenomenon, and may admit a common theoretical description. The present paper represents a possible conceptual framework for such a theory [1, 2].

[1] In practice it is considered that many systems do not completely stop moving, but that there is a sharp and reproducible phenomenon in which the nature of the dynamics changes so profoundly that, beyond this 'arrest', such large scale motions as remain occur on a profoundly different timescale.

There is, in fact, currently only one microscopic theory that purports to describe glassy systems, mode-coupling theory (MCT) [20, 21]. Attempts have been made to relate this to mean-field scenarios (such as that of the p-spin model) but to date the qualitative, and in some cases quantitative, successes [4–11] of MCT have not been rationalized. This should remain an aim of any conceptual development in the overall theory of dynamical arrest.

We may also remark that, despite many successes in the broader field of glass theory [12–17], both in practical and conceptual terms, the arena has lacked a concept of 'order parameter' that is directly related to the physical state, and properties of the system. Such concepts were central to the mastering of critical phenomena, because they strip away the non-essential details occurring at the transformation, leaving only those features that drive it, and ultimately exposing its underlying simplifications [22].

Other, older, pictures of arrest or vitrification may provide hints. These emphasize the importance of 'free' volume in determining the phenomenon of dynamical arrest [23, 24]. However, the concept of 'free' volume has had different meanings for different authors, perhaps because there was little microscopic basis for the early research, and different semi-phenomenological laws are often fitted equally well by experimental data. Nevertheless, a strong opinion has endured that it is the unfilled rather than the filled space on which one should focus in describing these systems. We shall here propose that empty space is indeed key to understanding arrest, but that the type ('usable' by a dynamics step) and geometry of that empty space enter in a crucial manner.

We have chosen to divide empty space into two types: volume that is and is not dynamically available to the system on the short timescale and small length scale, these being set by some microscopic cut-offs upon which the arrest is not crucially dependent. The first type of empty space we name dynamically accessible volume (DAV) and the second, vacancy volume [1]. Where exchange is possible between different regions of DAV they are considered connected. These ideas are readily expressed in lattice models of dynamical arrest, where empty sites that are accessible to at least one particle in the next move (DAV) are named holes, all other empty sites being termed vacancies. Holes arise from quite different local particle arrangements for different models, but their definition as carriers of transport is general.

It is the central proposition of this paper that it is the geometrical arrangement of these two types of empty space (hole and vacancy) that determines the nature, and laws, of arrest. The geometry of these entities determines the type of connectivity of phase space, and we shall see that using the language of DAV, there are only a few classes which can be understood relatively easily. In particular, we find new features arising when de-percolation transitions in holes and vacancy space arise. The centrality of the percolation transition renders many features of dynamical slowing universal, a point that has been missed in previous conceptions of dynamical arrest.

Our ideas are not dependent on any particular model or system, but to illustrate our points we choose two models of different conceptual types, the Kob–Andersen (KA) [25] kinetic model and the Biroli–Mezard (BM) 'landscape' model [26], both of which are known to describe dynamical arrest. There are numerous other models that we expect to behave in a similar manner to what we describe here [3, 27, 28]. In the KA case, particles are prohibited from moving out of a site if it is 'caged' by more than c particles, or into a site if, after moving there, it is similarly caged. In the Biroli–Mezard model an (infinite) energy cost is assigned to particles that are surrounded by more than c nearest neighbours. In this paper, apart from the use of larger system sizes, and much longer times, facilitated by some technical developments, single-particle diffusion constants are determined from the two types of model in the standard manner and, where applicable, are consistent with those given by the earlier

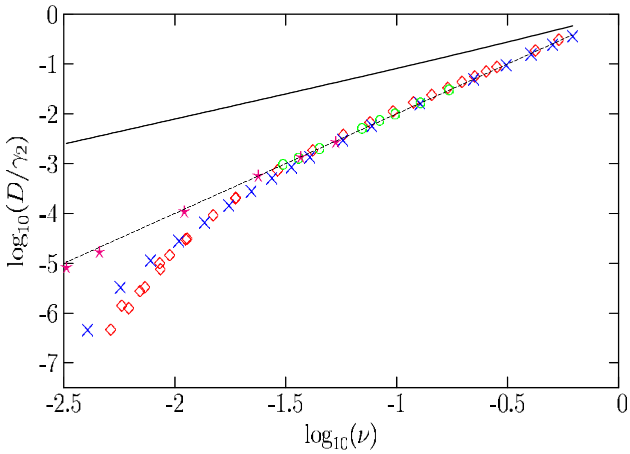


Figure 1. A universal scaling plot ($D \propto \nu^2$) for the KA sc (◊), KA fcc (×), BM_{13} (O), and EM_{13} (★) cases. The dashed line has a slope of 2.0. We also plot the lattice gas result as a solid line ($D \propto \nu$).

authors[2]. We also calculate the mean hole density ν, either exactly as in the KA model, or numerically in the BM model from simple equilibrium methods.

We have earlier reported that, over an extended range of near-arrest densities, the single-particle diffusion constants of such models are quadratic in the hole density [1], leading to an idea that there is an extended regime of 'universality' in such models. In figure 1 we plot data in the form $\log(D/\gamma)$ versus $\log(\nu)$ where ν is the bulk hole density and γ is a non-universal constant. The slope of the line is exactly 2.0 for the BM model and also for the 'extended model', EM [1], while in the KA models it deviates from 2.0 at very high density.

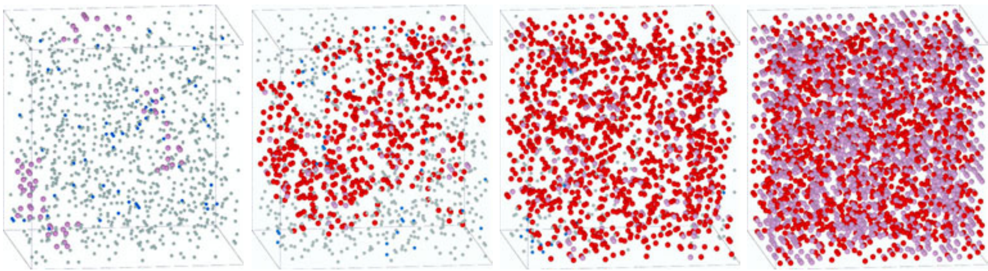
We have previously been able to understand the simple quadratic hole dependence [1] on the basis that most single holes are readily trapped, because of the restrictive constraints on particle motion. In contrast, in the lattice gas model there is a linear dependence of diffusion on hole density.

Two holes are able to cooperatively move together, although they often need the presence of excess vacancies with which they can exchange identity. This point is well illustrated in the BM model (see figure 1) where the arrest occurs only around $\rho = 0.56$, vacancies are always in excess, and the quadratic behaviour continues to vanishingly small hole densities. There, arrest appears to occur due to simple exhaustion of the DAV.

We have also noted that, for some models, as the density is increased yet further, there is a fraction of 'rattlers' (that is, particles that move in a limited manner) present without contributing to the diffusion. We observe that the KA model, unlike the BM model, exhibits an apparent deviation from the quadratic behaviour (see figure 1) at highest densities (higher than have been studied before). For lower particle densities in the KA model, such as those previously studied, there has been sufficient vacancy density on which hole pairs can form and move, leading to sustained motion.

Now we are able to understand the deviation and, for the first time, identify the origin of the arrest phenomena observed by means of simulation in such models. The answer, remarkably,

[2] As the density increases the simulation time needed to accurately determine the diffusion constant also increases. Our determination of the diffusion constant is based on simulation times at least an order of magnitude longer than the crossover time. Our results agree with the previous results at all densities except the highest, where we find slightly lower (and more accurate) diffusion constants due to our longer simulation times (10^{10} MCS as compared to 10^7 MCS).



(a) ρ = 0.87 (b) ρ = 0.85 (c) ρ = 0.82 (c) ρ = 0.65

Figure 2. Sample configurations from the fully arrested state (a) to the fully connected state (d) (corresponding to the locations indicated on figure 3). In the fully connected state (d) the percolating vacancy network is made up of all holes (dark/red) and vacancies (light/pink) in the system. This vacancy cluster facilitates diffusive particle motion. On approach to arrest the vacancy network de-percolates and in (c) the last percolating cluster is shown—the disconnected vacancies are the smaller/blue objects. In (a), there is no percolating vacancy network, but some large vacancy droplets are visible. These droplets are isolated from each other so that particles on the droplets cannot diffuse and the state is arrested.

is connected to the geometry of the dynamically accessible volume. The evolution of the geometry of the holes and vacancy volumes for the SC lattice is illustrated in figure 2.

Thus, for the simple cubic and fcc examples above, the last extended hole cluster spanning the whole system de-percolates[3], leaving droplets of holes, some of which are isolated from any extended network of vacancies, and therefore are unable to contribute to diffusion in a direct manner (figure 2). The locations of these hole de-percolation transitions, as calculated by conventional percolation theory, correspond to the deviation from the simple quadratic law, and we find that only those holes occupying a vacancy percolation cluster remain carriers of transport. Beyond this point some holes become isolated, there being insufficient holes or vacancies in their vicinity to ensure free extended motion. However, if we recalculate the hole density on the extended vacancy network (all such holes being able to contribute to diffusion) then we find, once more (see the red lines in figures 3 and 4), simple characteristic behaviour. The quadratic dependence on holes extends to higher particle density[4]. We may then write, in great generality for such models,

$$D = \gamma_2 \nu_{\mathrm{p}}^2 \tag{1}$$

where the coefficient γ_2 is a non-universal coefficient, and ν_{p} is the density of holes on the system-spanning network of vacancies. Here, particles that are or are not associated with connected DAV undergo an enormous and spontaneous separation of timescales, equivalent

[3] When we refer to de-percolation we mean that, as the particle density increases, the vacancy and hole densities decrease. On the lattice it is trivial to study the classical percolation transitions of holes and vacancies using whatever definition of connectivity is desired. Here we define holes and vacancies to be connected if they are diagonally related, for it is essentially diagonal relationships of holes that lead to assisted or correlation multi-hole motion. We find that (for the system sizes studied, $L = 50$–120), the percolation transitions of these entities are consistent with random percolation exponents. The percolation transitions for both are marked on the appropriate figures, for system sizes studied in the dynamics. On increase of particle density the hole de-percolation transition occurs first, leading to some disconnected hole droplets, not attached to the infinite vacancy cluster. Then follows the vacancy de-percolation transition, at which point even hole droplets inside vacancy droplets are no longer able to move through the system on computational timescales.

[4] Naturally, in simulation studies, we cannot claim any truly asymptotic dependences. Nevertheless we believe that we are interpreting those effects that dominate previous simulations, and probably much of the experimental observation so far.

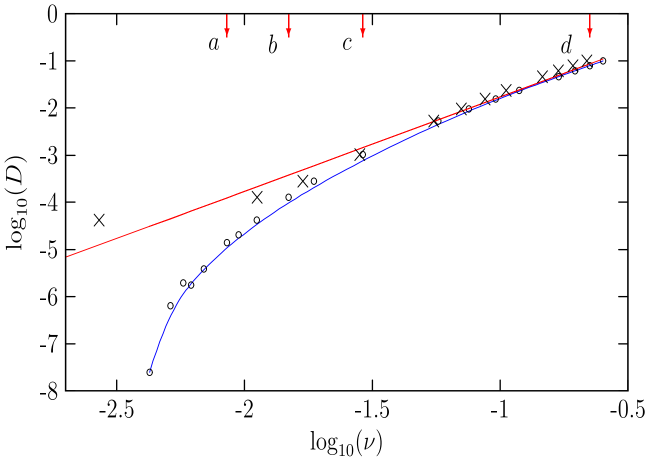


Figure 3. $\log(D)$ against $\log(\nu)$ for the sc Kob–Andersen $L = 50$ (3D) case. The (○) points, calculated for the total hole density ν, show a clear deviation from the quadratic law (red line). However, when we plot the connected hole density ν_p we find agreement with the quadratic law (×).

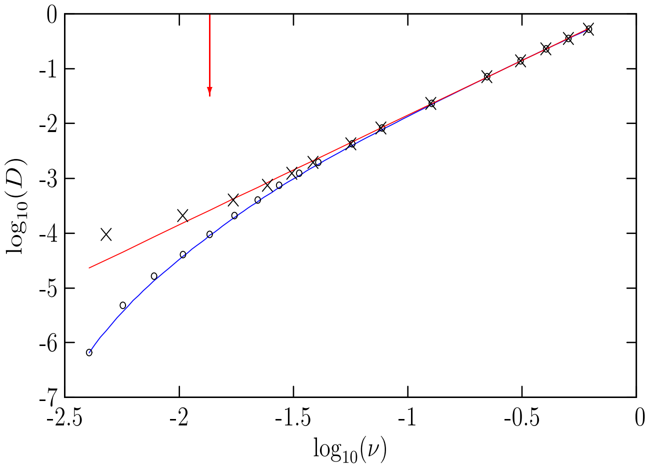


Figure 4. $\log(D)$ against $\log(\nu)$ for the fcc Kob–Andersen $L = 64$ case. The (○) points represent the total hole density ν and the (×) points represent the agreement of the connected hole density ν_p with the quadratic law (red line). The arrow indicates the de-percolation transition of the second-neighbour vacancy cluster.

to a sort of DAV micro-phase separation. In the extreme case, the DAV-poor regions undergo complete arrest, and effectively take no further part on any timescale, while in others the separation is large, but finite. Unlike the BM model, the KA model has no hard local density constraint, thus allowing particle configurations to sustain a vacancy de-percolation (see figure 5), leading to a complete quenching of the percolative transport mechanism. We then find a remarkable 'critical' point of the transport at which holes travel on the last remaining ('critical') vacancy percolation cluster, yielding a universal sub-diffusive law,

$$r = \alpha t^{\beta}. \tag{2}$$

Here β is expected to reflect both fractal (mass) and spectral (elasticity) dimensions. We estimate values of $\beta = 0.4$, and, within our numerical accuracy, the exponents are the same for the two different lattice types. This scenario has, in different manifestations, been contemplated before, but until now has not been established for arrest [29–31][5].

[5] We find that this sub-diffusive behaviour grows from the short timescale, ultimately extending over the measurable time regime as the size of (finite) correlated clusters grows (the infinite cluster ultimately dominating away from de-percolation). Thus, diffusion constants vanish because moving particles are forced to remain longer (and travel further) on fractal pathways, these dominating completely at the de-percolation point to produce an exponent β, less than unity, and hence a vanishing diffusion constant.

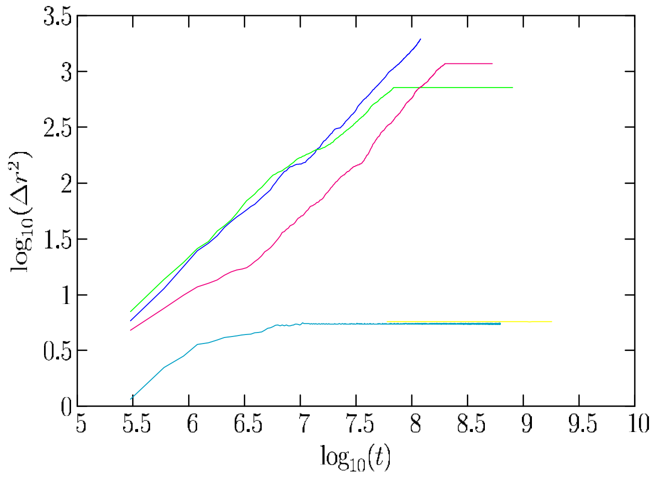


Figure 5. A sample mean square displacement for the simple cubic KA case at $\rho = 0.884$, $L = 20$. Each run is for a different random initial condition. For early times the mean square displacement scales with time as $\langle r^2(t)\rangle \propto t^{2\beta}$ where $\beta = 0.4$.

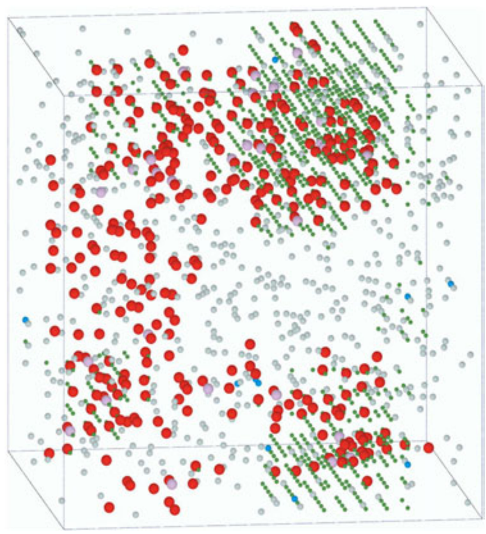


Figure 6. A sample arrested configuration—the disconnected vacancy droplets are visible (larger spheres). The particles which were mobile during the course of the simulation move only within the droplets and are shown as the small dark (green) particles.

Beyond this, vacancy de-percolation occurs, and this type of diffusive motion is quenched. In figure 6 we illustrate the point visually by showing a configuration just beyond vacancy de-percolation in which there are large but isolated clusters of vacancies (inside which there remain ample holes) and some isolated hole droplets where motion is negligible. Holes living on extended vacancy clusters continue to move, but ultimately travel only a typical diameter of the vacancy cluster, leading to saturation of the mean square distance travelled. This is shown in figure 5, where the diffusion is quenched after very large times, the asymptotic mean square distance travelled being consistent with the hole-populated vacancy size, as determined by a cluster counting algorithm[6].

Thus the phenomenon of de-percolation or disjoining of dynamically available volumes is the origin of the observed dynamical arrest, and, originating in a universal geometrical phenomenon, the laws possess many elements of universality. We believe that this is the

[6] Vacancy cluster counting methods such as those used in percolation studies are used. From the known largest cluster size and the numbers of particles moving within them, we calculate the predicted asymptotic mean square distance travelled and the result is in agreement with simulations (see figure 5).

origin of many of the precipitous changes of dynamical behaviour and rheological behaviour observed in Nature.

In some models, holes on vacancy droplets (these droplets become smaller as density increases) can still provide some residual large scale motion, on a much longer timescale (indeed these are expected for some models [32, 33, 1]), but such contributions are not observable in the simulations here. Such mechanisms would lead to diffusion constants smaller than anything observed in any simulations. However, one can explore the processes implied by this geometry. Thus, particles can move into holes on the interface between a region of immobilized particles and the vacancy cluster, and be transported to another part of that cluster. Thereby the low particle density of the vacancy cluster is preserved, while the whole cluster moves. Consequently particles can move across extended regions of space, and contribute to a new diffusion regime.

We may sum up the slowed dynamics scenarios present in models, and possibly in Nature (figure 2), as comprising (a) percolating DAV, (b) holes moving on the infinite vacancy network—which may be exhausted, leading to a form of arrest (cf the BM model), (c) holes moving on the critical vacancy cluster, (d) holes moving within vacancy droplets (constituting the arrested—or nearly so—state). We note carefully that the most general model of dynamical arrest will possess two independent degrees of freedom (hole and vacancy density) and the geometries of these portions of empty space may be independently varied. Since this has not been understood previously, existing models vary only the particle density, and the hole and vacancy densities then vary in an ill-controlled and dependent manner. In the interpretation of experiments in the field, this has been one source of confusion, because one is looking at different regimes, some where existing theory works, others where it does not. This has until now represented a major impediment to the development of a coherent and universal view of dynamical arrest.

From a purely theoretical point of view, the picture that we offer holds great promise for interpreting existing theory, and further rapid development of the field. Thus, crucially, the order parameter consists of excitations that are highly diluted, albeit sometimes with a complex geometry. The phenomena are also driven, in an unexpected manner, from the long length scale, where universality is to be expected. Together these observations hint towards a tractable theory where weak coupling tools, properly framed, may master the processes.

As the systems become denser, we can expect some highly cooperative dynamical processes to survive the second-neighbour vacancy de-percolation transition. These processes can move along vacancy structures which are connected in a highly non-trivial manner. In this high density regime, diffusion is still possible, but the connected available space is now described by ideas from bootstrap percolation [34].

We may expect most elements of our description to survive into a continuum description, and into Nature, though much remains to be established there. In particular, we believe that elements of the story may already have been observed but not yet interpreted. Thus, it is well known that there exist ‘dynamical heterogeneities’ in glassy and other near-arrested systems [35–37]. It has been understood that there is a length associated with more and less densely compacted parts of the system, to which one has sometimes associated some loose concept of ‘slow’ and ‘fast’ particles. We believe that these low density domains are closely connected to our domains of hole and vacancy networks, noting that it is indeed only in the vicinity of these domains that particles (‘holes’) can move, and appear to be ‘fast’. The ‘strings’ of fast particles may be close to the percolating vacancy network outlined here, implying a degree of universality not yet sought.

However, the implications of this identification are profound in a more general sense, for it relates experimentally observable phenomena to the basis of future theoretical descriptions, with the bridge being the geometrical concepts outlined there. We could therefore expect there to be a concept of vacancy space upon which DAV travels, the picture adjusting as density is increased. If this is confirmed, then it is essentially the geometry of these dynamical heterogeneities that is the key to describing a rich set of dynamical behaviours for near-arrested systems, and we expect any encompassing theory of dynamical arrest to accommodate a concept of geometry.

References

[1] Lawlor A *et al* 2002 *Phys. Rev. Lett.* **89** 245503
[2] Dawson K A 2002 *Curr. Opin. Colloid. Interface Sci.* **7** 218
[3] Barrat A, Kurchan J, Loreto V and Sellitto M 2001 *Phys. Rev.* E **63** 051301
[4] Dawson K *et al* 2001 *Phys. Rev.* E **63** 011401
[5] Bergenholtz J and Fuchs M 1999 *Phys. Rev.* E **59** 5706
[6] Bergenholtz J, Fuchs M and Voigtmann T H 2000 *J. Phys.: Condens. Matter* **12** 6575
[7] Foffi G, Zaccarelli E, Sciortino F, Tartaglia P and Dawson K A 2000 *J. Stat. Phys.* **100** 363
[8] Pham K N *et al* 2002 *Science* **296** 104
[9] Foffi G *et al* 2001 *Phys. Rev.* E **65** 031407
[10] Foffi G *et al* 2002 *Phys. Rev.* E **65** 050802
[11] Zaccarelli E *et al* 2002 *Phys. Rev.* E **66** 041402
[12] Angell C A 1985 *Relaxation in Complex Systems* (*National Technical Information Series*) ed K Ngai and G Wright (Springfield, VA: US Department of Commerce)
[13] Debenedetti P G 1996 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
[14] Mezard M and Parisi G 2000 *J. Phys.: Condens. Matter* **12** 6655
[15] Martinez L M and Angell C A 2001 *Nature* **4410** 663
[16] Debenedetti P G and Stillinger F H 2001 *Nature* **410** 259
[17] Angelani L *et al* 2000 *Phys. Rev. Lett.* **85** 5356
[18] Liu A J and Nagel S R 1998 *Nature* **396** 21
[19] Trappe V, Prasad V, Cipelletti L, Segre P N and Weitz D A 2001 *Nature* **411** 772
[20] Götze W 1990 *J. Phys.: Condens. Matter* **2** SA202
[21] Götze W 1991 *Freezing and Glass Transition* ed J P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland) p 287
[22] Wilson K G and Kogut J 1974 *Rev. Mod. Phys.* **45** 76
[23] Cohen M H and Turnbull D 1959 *J. Chem. Phys.* **31** 1164
[24] Cohen M H and Grest G S 1979 *Phys. Rev.* B **20** 1077
[25] Kob W and Andersen H C 1993 *Phys. Rev.* E **48** 4364
[26] Biroli G and Mezard M 2002 *Phys. Rev. Lett.* **88** 025501
[27] Weigt M and Hartmann A K 2003 *Europhys. Lett.* **64** 533
[28] Ciamarra M P, Tarzia M, de Candia A and Coniglio A 2003 *Phys. Rev. Lett.* **67** 057105
[29] Lemke N and Campbell I A 1996 *Physica* A **230** 554
[30] Jund P, Jullien R and Campbell I 2001 *Phys. Rev.* E **63** 036131
[31] Gefen Y and Alexander S 1983 *Phys. Rev. Lett.* **50** 77
[32] Jäckle J and Krönig A 1994 *J. Phys.: Condens. Matter* **6** 7633
[33] Krönig A and Jäckle J 1994 *J. Phys.: Condens. Matter* **6** 7655
[34] De Gregorio P, Lawlor A, Bradley P and Dawson K A 2004 *Phys. Rev. Lett.* **93** 025501
[35] Donati C *et al* 1998 *Phys. Rev. Lett.* **80** 2338
[36] Glotzer S C 2000 *J. Non-Cryst. Solids* **274** 342
[37] Weeks E R, Crocker J C, Levitt A C, Schofield A and Weitz D A 2000 *Science* **287** 627