Local Structure Analysis in a Colloidal Glass Former[a] and Crystalline Multi-Layers[b]: Advantage of Experimental Study[c,1]

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Summary

Light microscopy in a binary two-dimensional (2D) colloidal glass former allows us to analyze nearest neighbor configurations via the time-dependent particle coordinates of tracked colloids. By special tilings, the so-called elementary triangles (ET), we could describe the static near-zone 2D packing with a low number of locally density-optimized characteristic forms. Those triangles arrange themselves in regions, termed as crystallite clusters (CC). Different CCs group together with some structurally frustrated transition zones in-between, with which the liquid-like 2D structure is explained. Additionally, by a novel microscopy method including Fourier filtering, we could investigate the local particle arrangements of crystalline colloidal multi-layers. Therein, different regions of crystalline layer configurations become visible in the microscope image by different colors. On the other hand, regions of the same configurations show up in each case by the same, i.e. characteristic color codes. Since the color code are locally resolved we suggest an experiment, with which the different CCs (and their dynamics) should become directly visible in another 2D colloidal glass former by colored regions.

1. Introduction

The fundamentals of the glass transition are yet not completely understood [2]. Why does the viscosity of supercooled liquids dramatically increase approaching the glass transition temperature? Why is the glass transition temperature dependent on the cooling process? Why does no clear change in the local particle arrangements occur at the glass transition temperature? Why do relaxation processes in glasses age? Those questions are amongst others still under discussion.

Nevertheless, the glass transition is described by a dynamic process, at which the liquid-like particle arrangements freeze, and glasses are solids without long-range order. Current mean-fields theories [3, 4] are able to describe the main features of the temperature dependent dynamics in supercooled liquids, e.g. the three different time regions of such mean-square displacements. For short-time dynamics the particles diffuse like free ones. In the intermediate time zone the particles are captured by their surrounded neighbors for a while, which is called cage-effect, until in the long-time region structural relaxations allow the particles to escape their vicinity. For decreasing temperatures, such cages become stronger and remain longer stable, as the system solidifies at the glass transition temperature due to stiff cages. However, the mean-field theories cannot demonstrate, which kind of local re-

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a. The local particle arrangements and the dynamics of a 2D binary colloidal glass former were analyzed depending on particle interaction strength. The author made these investigations during his doctoral theses and as Research Associate in 1997–2003 at the University of Konstanz, Germany, at the chair of Prof. G. Maret. Special thanks to Prof. G. Maret for his support and Dr. K. Zahn for his cooperation.

b. The crystal-packing of air-dried multi-layers of monodisperse colloids was investigated in 1/2004–6/2005 at the University of Mainz, Germany, in the group of Prof. T. Palberg. The author thanks Prof. T. Palberg for his support, Dr. R. Biehl for his preliminary work, J. Marques Hueso for samples, and A. Barreira Fontecha and H.J. Schöpe for discussions.

c. The investigations of local particle arrangements and dynamics in the 2D glass former have been presented at more than 20 conferences and workshops. Unfortunately, the dynamical part is only published in the doctoral theses [1] up to now.

laxations really occur. For example for the long-time relaxations, heterogeneous dynamics or hopping processes can only be assumed.

For the understanding of relaxation processes in supercooled liquids, it is necessary to point out the close relation between local particle arrangements and local particle relaxations. Indeed, the local structure rules the local dynamics. This statement is immediately obvious for the cage-effect because the neighbors construct the cage for the central particle. Unfortunately, it is not easy to get these local information.

Experiments are often not able to measure the local particle configurations and the local relaxation processes, e.g. scattering experiments. Light microscopy of colloidal suspensions is an exception. The particles can be directly observed and their relaxation processes are so slowly that time-dependent particle coordinates can be contained. Colloidal suspensions consist of a huge number of interacting particles and allow to investigate local relaxations in liquids, supercooled liquids and glasses. Individual time-dependent particle coordinates of a three dimensional (3D) colloidal glass former can be investigated by confocal microscopy [5].

In one-component colloidal suspensions a particle polydispersity of more than 10% is typically used to suppress crystallization. Thus, the shape of the cages varies and it is difficult to relate local free volume to the local relaxation dynamics.

Time-dependent particle coordinates of supercooled liquids are directly available by numerical simulations, for example in 2D [6]. But, such systems often consist of a low number of particles, need special defined boundary conditions, and are restricted in computing time. Therefore, local relaxation processes of strongly supercooled liquids or aging of the glass state cannot be simulated.

Even if the time-dependent coordinates of well-defined particles would be available in supercooled liquids, dynamic properties of single particle (mean-square displacements) or of pairs (dynamic structure factor) are typically calculated. These functions are not useful for analyzing the cages together with the local dynamics at the same time since the relation between nearest particle arrangements and local relaxations are lost. Therefore, the dynamics of triangles of nearest neighboring particles are necessary in two dimensions (2D) and of tetrahedra in 3D.

In the first part of this paper, a 2D binary colloidal glass former is presented. The two kinds of colloids are well-defined. In this suspension, crystallization is suppressed because of very slow particle velocities and time-dependent coordinates are available from normal to strongly supercooled liquids. The nearest neighboring particle configurations could be characterized by only four different local density-optimized triangles, the so-called 'elementary triangles' (ET). Since tiling mismatches come up for random distributions of both kinds of colloids, regions of 'structural frustration', i.e. of local non-density optimized package, additionally occur. The liquid-like local structure is finally based on conglomerations of the four different ETs beneath structural frustrated regions [7, 1].

In the second part of this paper, a new fast method is introduced for analyzing the crystalline packing of thin multi-layers of monodisperse colloids. Illuminating the sample with white light parallel to the direction of the confinement, rainbow-like spread Bragg-peaks arise. However, the intensities of different wavelengths vary because the interference conditions depend on crystal structure, layer number, and stacking sequence. Using a variable aperture stop in the back focal plane of the microscope objective - the Fourier space of the sample - all Bragg peaks can be rejected. In this case, differently colored regions appear in the image of the sample, which are related to varying layer packing, because different spectra of the scattered Bragg peaks are filtered out from the incoming white light. However, regions of the same color belong to the same local layer packing. Although the particles are no longer resolved in the image because of the small aperture stop, Fourier filtering shows depth-sensitive packing information by special color codes [8].

In the last section a new experiment is suggested, in which the time-dependent particle arrangements of a binary 2D colloidal glass former are studied by the above introduced Fourier filtering microscopy. We expect that the different elementary triangles are visible by various, but characteristic color codes and structural frustrated regions are differently dyed as well. Thus, time-dependent changes of the local particle arrangements, i.e. of the cages, should be able to be detected by local changes of color.

2. Binary Colloidal Glass Former in 2D

2.1 Experiment

In a binary suspension of superparamagnetic

PMMA (polymethyl methacrylate) spheres, the colloids were confined to 2D due to gravity lying on a completely flat adjusted water-air interface of hanging droplet geometry. The big (b) colloids of diameter 4.7μm had a nearly 10 times greater magnetic susceptibility $\chi_b = 6.2 \cdot 10^{-11}\mathrm{Am}^2/\mathrm{T}$ than the small (s) ones of diameter 2.8μm with $\chi_s = 6.6 \cdot 10^{-12}\mathrm{Am}^2/\mathrm{T}$, concerning small external magnetic fields B. In the suspension, the thermally fluctuating colloids interact with their induced magnetic moments, tuneable by B applied perpendicular to the water-air interface. Time-dependent particle coordinates were determined by video-microscopy in real time.

During an experiment the room temperature, T, the number area density, ρ, and the ratio, ξ, of the number N_s of small particles to the number $(N_b + N_s)$ of all colloids remain constant. Hence, only B controls the strength of the particle repulsion by the parallel aligned induced magnetic moments. Other in-plane particle interaction potentials can be neglected. The system is characterized by an interaction parameter, Γ, that is proportional to the magnetic energy E_m divided by k_BT. Thus, Γ corresponds to an inverse system temperature:

$$\Gamma(B) = \pi^{3/2}\frac{E_m}{k_BT} = \frac{\mu_0}{4\pi}\frac{B^2(\rho\pi)^{3/2}}{k_BT}\left(\xi\cdot\chi_s + (1-\xi)\cdot\chi_b\right)^2. \quad (1)$$

A more detailed description of the experiment can be looked up in [9]. Why the 2D system is a glass formers is explained in [10].

Even though the experiment is difficult to carry out, the 2D confined system is a very effective model glass former for the analyzes of liquid-like structures since the time-dependent particle positions can be easily observed. Investigating the nearest neighbor arrangements of only two well-defined types of colloids in 2D, lead to a narrow number of different three particle compositions. The repulsive potential between induced magnetic moments is known and leads to an energy-landscape with a well for each particle. The highest dividend derives from the access to the time-dependent particle coordinates allowing us to investigate local particle configurations from short-time up to long-time relaxation processes for normal to strongly supercooled liquids [1, 10].

2.2 Elementary Triangles and Triangles of Nearest Neighboring Particles

In a first approach the liquid-like local structure of a 2D binary mixture can be described by the different cages around central particles. In a 2D simulation of soft discs [11] the cages are characterized by their central big or small particle and the number of surrounding big and small discs. Next neighbors are distinguished by pair-distances, which are comparable with the first maximum of the appropriate radial pair-distribution function. The authors consider 31 different cages. For their cage analysis a huge statistic of different configurations is necessary for getting reliable results.

But, is it necessary to handle so many cage configurations? Do those cages describe the smallest units, which characterize the local liquid-like structure? Doubts arise since each particle of the cage is also a central particle of its own cage. These cages are interconnected. The shape of the cage around a central particle can be quite diverse even though of the same numbers of small and big next particles for varying alignments of the surrounding discs. One should also expect different cage dynamics for different the next but one vicinities of the central particle. These comments are illustrated in Fig. 1 for particle configurations of a 2D binary colloidal strongly supercooled liquid.

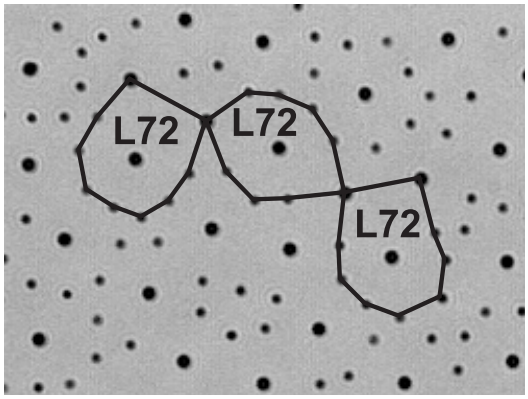

Fig.1 A cut-out of an image of a 2D binary strongly supercooled liquid with $\Gamma = 411$ and $B = 7.00mT$. L72: cage notation of [11] for a big central disc and 7 small and 2 big next particles. The alignment of small and big surrounding particles as well as the cage shape in the middle L72 is different to those of the two others. In spite of the same alignment of the surrounding colloids for the right and the left marked cages, the cage shape deviates since the next but one particle vicinity manipulates the considered cages as well.

The author of this paper analyzed the liquid-like structure of the binary 2D colloidal glass former by

triangles of nearest neighboring particles (TNNP) using a specially developed triangulation [1, 13]. These TNNPs cover the 2D system without overlap. Investigating the geometric properties of the TNNPs [1, 7] each three-particle combination of small and big particles prefers one special triangular shape. These triangles are isosceles and belong to a locally density-optimized packing. That is why the author calls them 'elementary triangles' (ET) [7]. ETs can also be found by 3-point correlation functions [1, 12, 13].

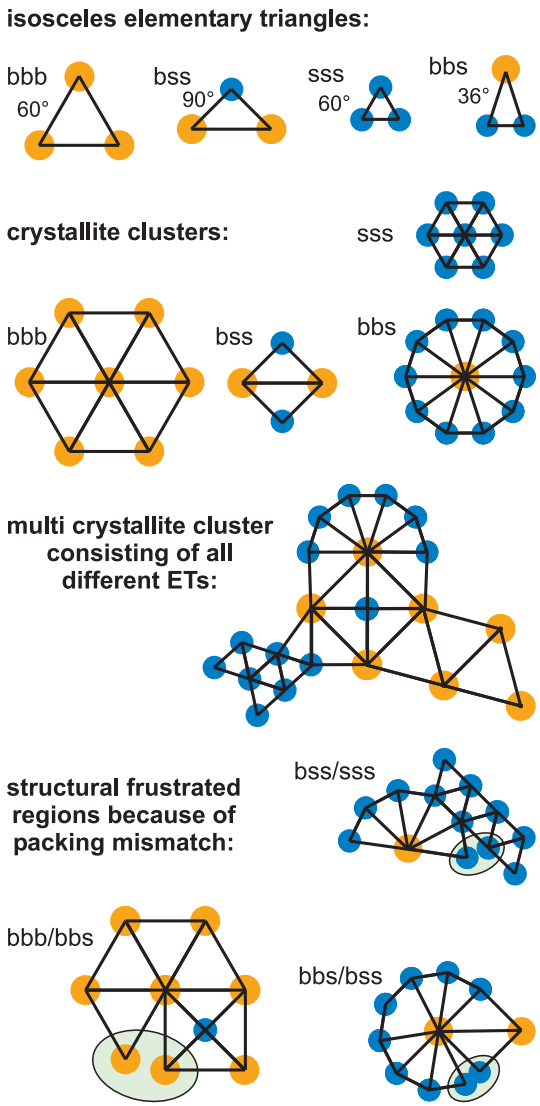

Fig.2 ETs of all 3-particle combinations and examples for the different CCs as well as for one MCC are presented. Additionally, structurally frustrated regions are shown, which come up because of packing mismatch. However, the number of small colloids around a big one slightly differs in the experiment depending on the magnetic field B [7, 18].

The ETs are equilateral for 3-particle combinations *bbb* and *sss*, *bss* ETs form rectangular triangles and *bss* ETs have a 36^o angle at the big particle. ETs can conglomerate to local density-optimized clusters. Such of only one kind are called 'crystallite clusters' (CC) and such of different kinds 'multi crystallite clusters' (MCC). A schematic illustration of the different clustered ET combinations are shown in Fig. 2.

Since the small and big colloids are randomly distributed, the 4 different ETs occur in the monolayer everywhere at the same time. Because the different ETs cannot cover the monolayer completely packing mismatch exists visible in structurally frustrated regions as demonstrated in Fig. 2 and [7] as well. These considerations are general. There is no restriction to 2D - in 3D tetrahedrons should be investigated -, binary mixtures or special triangular shapes.

The important sticking point of these local structural considerations is the ansatz that no longer particles but triangles are in the center of interest. This kind of analysis is unusual because experiments and theory typically examine particle properties, e.g. radial correlation functions, static and dynamic structure factors or mean-square displacements. Assimilable functions can be introduced for triangles. Continuative studies of local structure triangular relaxations are investigated in [1] and will be published elsewhere. In this paper, TNNPs are only used for considering the statical amorphous structures.

Some interesting earlier publications have to be mentioned here as well [14, 15, 16]. These papers also consider tiling models for studying melting and liquid structure in 2D. However, in this proceeding it is not possible to go into details, to work on or to group with similar ones.

3. Multi-Layers of Thin Colloidal Crystals

3.1 Air-Dried Colloidal Multi-Layers

In a one-component suspension of about 1% packing fraction, polystyrene (PS) spheres of a diameter of 590nm and a polydispersity of less than 6% were mixed with distilled water (PS590; Batch No. PS-F-3390 Mycroparticles, Berlin, Germany). The suspension was deionized, filtered, and dropped on top of a cleaned glass substrate with a hydrophilic surface. When the water was evaporated the remaining colloidal particles are densely packed and form crystalline multi-layers, however, with a lot of defects.

The local ordering of the colloidal multi-layers

was investigated by microscopy illuminating the sample with parallel white light. The image could be shifted from real to Fourier space by inserting a Bertrand-lens into the optical path. The additional lens maps the back focal plane of the microscope objective, i.e. the Bragg peaks of the ordered structures. An example of the real and Fourier space image of one sample is shown in Fig. 3.

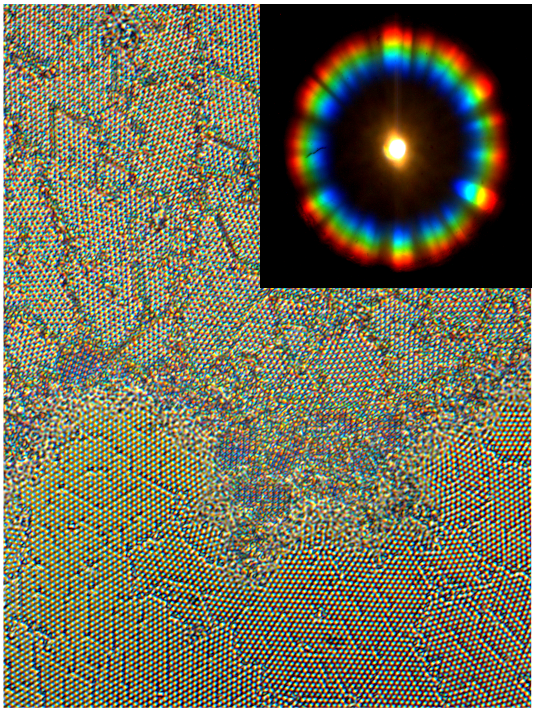

Fig.3 The large photo shows a real space image of air-dried colloidal multi-layers with completely open numeric aperture stop (N.A.=1.4). The particles at the surface are visible as single spheres. The inlay presents the scattering pattern of the sample. The Bragg peaks are rainbow-like split up and only of lowest order. The signals of different structures overlap leading to a ring-like scattering pattern. The central spot comes from the unscattered light.

In the back focal plane of the objective, an additional variable numerical aperture stop (N.A.) allowed to adjust the microscopic resolution. With completely open N.A. (= 1.4), the colloids are visible as single particles. In the scattering pattern, the rainbow-like split Bragg peaks of first order are rotation-symmetrically grouped around the central unscattered beam (see Fig. 3). For the minimized N.A. (= 0.7), all Bragg peaks are just blocked. The colloids cannot be distinguished as single particles and regions of characteristic colors come up, as presented in Fig. 4.

More details about the experiment and theoretical considerations about scattering theory in thin multi-layers can be found in [8]. In the following only the conclusions are summarized for getting quickly to the point how these method can help for the analysis of liquid-like 2D structures of a binary mixture as well.

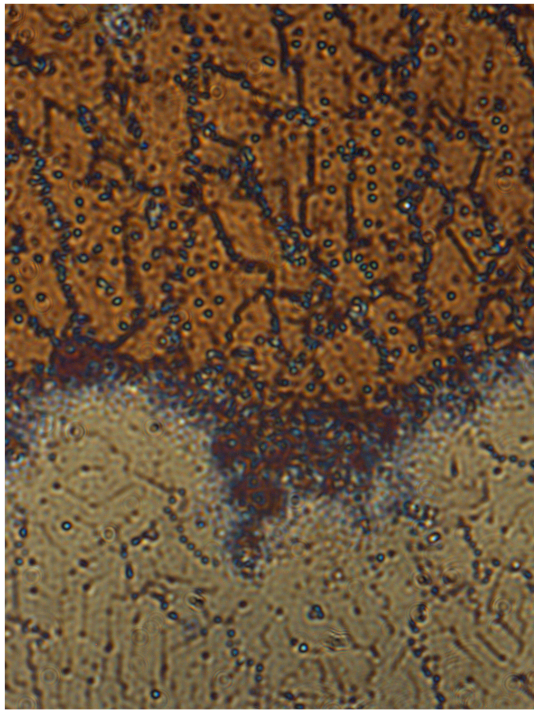

Fig.4 For minimized numeric aperture stop (N.A.=0.7), differently colored regions appear in the image of the sample, which is presented in Fig. 3, while single particles cannot be resolved anymore. The grey region at the bottom belongs to hexagonally packed mono-layer and the brown region at the top to a hexagonally packed bi-layer. In the small rim in-between, i.e. inside the rubiginous transition zone, the colloids form a square structure.

3.2 Characteristic Color Codes

In the air-dried samples, the colloids lie in densely packed layers on top of the planar glass substrate. Typically, mono-layer, bi-layer up to approximately six layers form because of the low packing fraction of colloids in the suspension. Inside of regions with the same number of layers, the particles are hexagonally packed. In the transition zones between regions, which layer numbers differ by one, a square structure occur. These crystal structures are alike with those observed in wedge cell geometry, in which, however, more distinguishable crystal structure can be detected. In the transition regions between mono- and bi-layer can also be found e.g. a rhomboedric and a bucking phase [17].

For a mono-layer, six Bragg peaks of the hexago-

nal packing are spread like a rainbow, since in 2D each wavelength fulfills the scattering conditions, but under another scattering angle (see Fig. 5). The scattering conditions change for increasing number of layers, because the system becomes less 2D confined. But, also for the same number of layers, the wavelength dependent signals of the Bragg peaks differ, if the stacking sequence varies. Thus, the wavelength or scattering angle dependent intensities of the Bragg peaks are characteristic for the special packing of ordered thin multi-layers, described by the crystal structure, the layer number, and the stacking sequence. All of these magnitudes affect the scattering conditions.

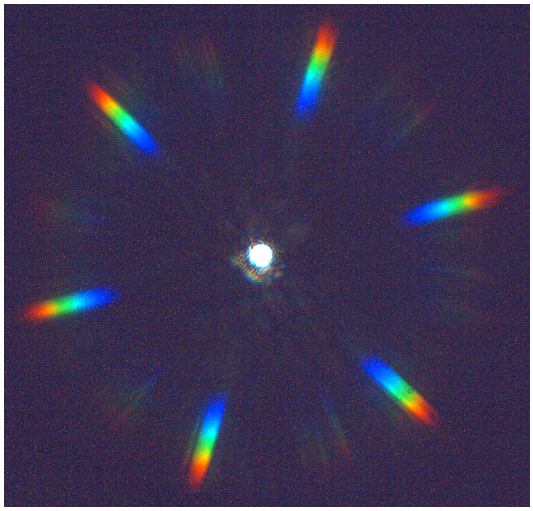

Fig.5 Six Bragg peaks of first order for a hexagonally packed mono-layer. The scattering pattern lies rotation-symmetrically grouped around the central unscattered beam and are rainbow-like spread because of the 2D confinement.

The principal axis of the microscope showed in the same direction than the perpendicular of the colloidal multi-layers. That's why the Bragg peaks are rotation-symmetrically grouped around the central unscattered beam. When the N.A. is minimized and all Bragg peaks are blocked, the spectra of their scattered light is missing in the image of the sample, i.e. different spectra of the scattered Bragg peaks are filtered out from the incoming white light. Regions of the same color belong to the same local layer packing and crystal structure and regions of different color are differently build up.

Grain boundaries, dislocations or other kinds of defects inside the multi-layers disturb the scattering conditions so that these regions are visible by locally changed colors as demonstrated in Fig. 4. Thus, the quality of the crystalline packing can immediately be detected although single particles cannot be resolved.

Fourier filtering is a fast and very useful analysis method of the packing inside thin multi-layers with high local resolution. Even though the transition region is a small rim, the color is always equal and explicitly defined as shown in Fig. 4.

Although the particles at the surface are no longer resolved in the image because of the small N.A. (see Fig. 4), one gets qualitative depth-sensitive information about the crystal structure at a glance. But, only if local crystal packing is first identified, so that the different colors can be correlated to the structure, one is locally able to indicate the crystal structure, layer number, and stacking sequence indeed.

4. Local Liquid-Like Structure and Dynamics Visible by Dyed Regions

In [18], the author showed that in air-dried 2D colloidal mono-layer of two components form the same ET-like structures as observed in the 2. section since the drying process is so fast that no crystallization occur. Because the local crystal structure for the different ETs (or the CCs) and the lattice constant vary among each other, their Bragg peaks differ as well.

That's why we would like to suggest a novel experiment, in which a binary 2D colloidal glass former is investigated by the novel experimental method of Fourier filtering. Therein, local density-optimized regions as a whole, especially the various crystallite clusters, should become visible by dyed regions. E.g. no triangulation is necessary and only CC and no longer ETs are considered. We expect that also the structurally frustrated regions in-between will be distinguishable. Thus, local colors would give the information of micro-structure in glass forming systems.

Additionally, it would be nice to observe the dynamics inside the mono-layer of a 2D colloidal glass former, investigating changes of the colored regions time-dependently. Therefore, a binary colloidal glass forming suspension must be studied.

5. Outlook

Supercooled liquids and glasses show universal features in many various atomic, molecular or macromolecular systems by rather different interactions [19].

Perhaps, the understanding of these peculiarities in one single model system would help to recognize the connectivity to other systems – and, maybe, the essential properties of glass formers at all. A colloidal 2D binary mixture, which does not crystallize, is at least a good candidate for these kinds of studies.

Acknowledgments

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