Soft jammed materials

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submitted to Tohoku University Press, Sendai, Japan

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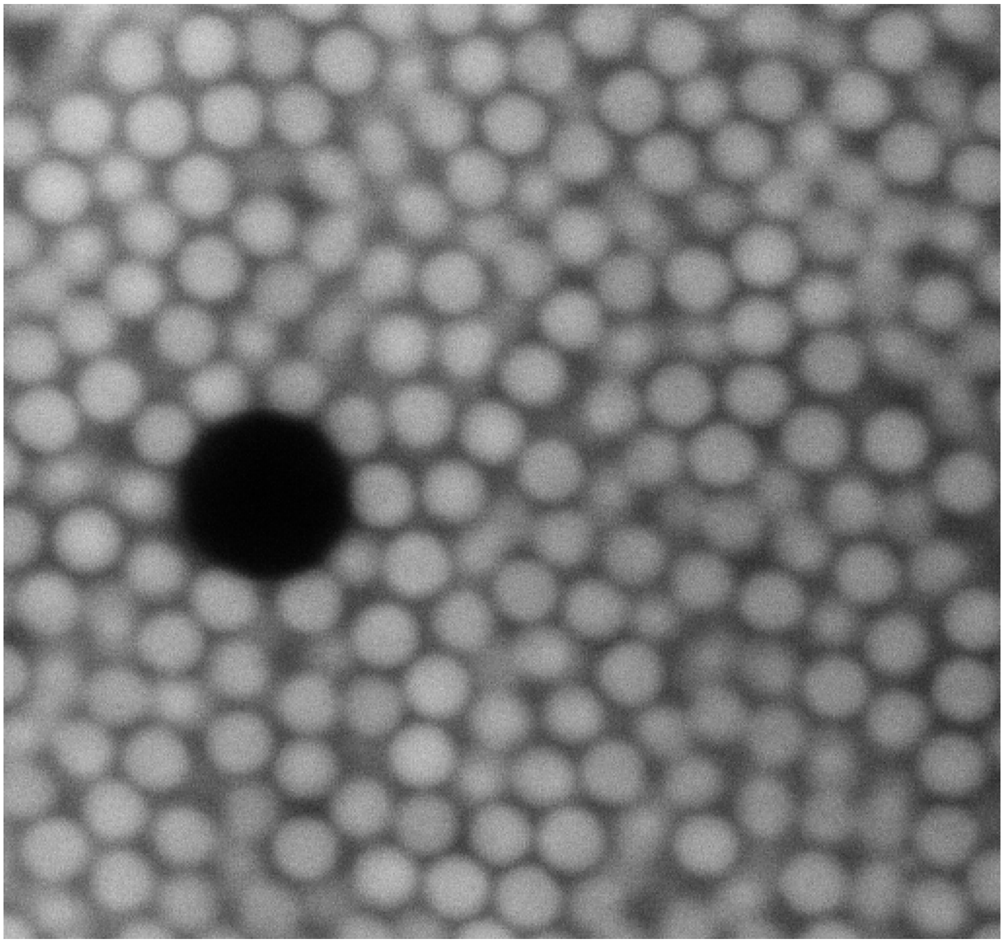

2 μm diameter colloidal particles, with a 5 μm diameter magnetic particle added. Picture taken with a confocal microscopy by P. Habdas and E. R. Weeks.

Author's Preface

Why does mayonnaise act both like a liquid and a solid? What causes shaving cream to flow differently from toothpaste? These types of questions are at the heart of soft condensed matter, the study of materials with both fluid and solid properties (often called "complex fluids"). Moreover, the mechanical properties and ability to flow are in fact the defining features of soft materials, and are key to the practical utility of soft materials. The answers to these questions relate the mesoscopic structure of a complex material to its macroscopic properties (such as its viscoelastic modulus). With the wide variety of mesoscopic structures, it might be expected that the answers would depend strongly on the details of each material, and that the study of such systems would be the study of many special cases. However, recently the analogy of *jamming* suggests the possibility of universal behavior of complex fluids under stress, and in particular, that such systems may behave like granular media. In each case, the material behaves in many ways like a solid. The analogy of jamming depends on the microscopic behavior of such systems, yet there is little experimental evidence to support the analogy apart from macroscopic similarities between these systems.

This review introduces a variety of soft materials, describing both their microscopic structure and their macroscopic flow properties. Features of soft jammed materials are discussed, and open questions for any theory of jamming are proposed.

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February 2007

Acknowledgement

Professor Michio Tokuyama offered me the opportunity to give my lectures at Tohoku University, and also gave me the chance to publish this book that was compiled from the lecture notes. I thank him for his kindness and support during my visit. I thank Gianguido Cianci, Scott Franklin, Vikram Prasad, and Denis Semwogerere for helpful discussions and for reading early drafts of this article. This article grew out of interesting discussions with the above people, and also with Stefan Boettcher, Ted Brzinski, Rachel Courtland, Piotr Habdas, Yoon-Hwae Hwang, Hans König, Andrea Liu, Cory O'Hern, David Schaar, and Michio Tokuyama. I gratefully acknowledge support from the National Science Foundation under Grant No. DMR-0239109.

This book chapter is dedicated to my wife Chrissy, who was very supportive while I traveled to Japan, and then continued to support me when I got back home to write this.

Contents

1. Introduction

1.1 Soft materials

Everybody is familiar with three basic states of matter: solid, liquid, and gas. Yet many materials are hard to classify: shaving cream is a mixture of a liquid and a gas; pastes are a mixture of solids and liquids; foam rubber is a solid with gas bubbles. Some food products have properties of both solids and liquids; consider peanut butter and mayonnaise. These types of materials are known as soft materials, and the study of these systems is the field of "soft condensed matter." These materials are typically composed of mixtures of two or more materials; but the category includes polymers (Silly Putty^{TM}, rubber) and perhaps glass (window glass, for example).

A defining property of soft materials is that they possess both solid and liquid properties; in other words, they are *viscoelastic*. For example, shaving cream is composed of soapy water and air. A pile of shaving cream on a table (Fig. 1.1) holds its shape, unlike a liquid which would spread out into a puddle. The pile can even support a small amount of weight, such as a piece of paper. This is elastic behavior; if a bit more weight is added, the pile deforms slightly, but returns to its original shape when the weight is removed. If too much weight is added – or if the pile is pushed you're your hand – the pile flows in a process that might be informally described as "squooshing" and which more formally we would say is viscous behavior. The pile does not turn to its original shape when the weight is removed, and so the deformation is *plastic* (irreversible).

Fig. 1.1. Image of shaving cream. The shaving cream forms a small pile, with height greater than its width. This would be impossible (in regular gravity) for a regular liquid such as water. (Picture taken by G. Cianci)

This transition from solid-like to liquid-like properties implies that the foam possesses a *yield stress*. If an applied stress is below the yield stress, the foam responds like an elastic solid. If the applied stress is above the yield stress, the foam flows and deforms plastically; it behaves more like a fluid.

Many other soft materials are similar to foam, in being microscopically disordered and macroscopically acting like a solid. To consider just one, consider walking on a beach. Despite the fact that the individual grains are not connected, friction prevents them from flowing very easily, and thus you don’t sink into the sand. Further examples and details of soft materials will be discussed in Secs. 2 and 3.

1.2 Molecular glass

In some ways, glass is similar to these soft materials. The atoms in a window pane are disordered on an atomic scale; a glass is often referred to as an amorphous solid, to reflect this disorder. When a glass-forming liquid is very hot, it flows easily. As the temperature is lowered, the viscosity of the material grows rapidly. For a 20% change of the absolute temperature, the viscosity can rise by 10 or more orders of magnitude. At some point the material flows so slowly that it becomes difficult to measure the viscosity. Loosely speaking, this point can be identified as the glass transition temperature; at temperatures colder than this, glass can essentially be considered a solid.

Glass is the “original” amorphous solid, and has been carefully studied for at least a century to determine how its solid-like properties arise. Crystals are ordered materials and are well understood; their periodic structure allows for powerful analysis techniques to be used to understand their properties, as described in any solid state physics or condensed matter textbook. The disordered packing in a glassy material frustrates this sort of analysis, leaving the glass transition as an as-yet unsolved puzzle (Angell et al. 2000). The glass transition will be discussed further in Sec. 3.5.

1.3 Jamming

So far we have discussed a large variety of materials: glasses, emulsions, pastes, gels, and sand. In some ways these seem superficially similar. In general these all are microscopically disordered, and macroscopically can act like solids. In recent years a conjecture has been put forth that all these materials are *jammed* (Liu & Nagel 1998). The definition of a jammed material is one that is structurally disordered, and possesses a yield stress – in other words, an amorphous solid. The *jamming transition* is then the transition from a liquid state to the jammed state. For example, in a glass, this occurs when the temperature is lowered, and the jamming transition is another name for the glass transition. The key idea of jamming is that all of these transitions from liquid-like to solid-like are due to the same underlying physics. In other words, the similarity between materials such as sand, glass, and foams is not superficial, but due to deeper shared properties of all amorphous solids.

This is a novel idea, and may well be proved to be wrong. These materials have strong differences in their microscopic behavior. For example, molecular glasses have attractive chemical bonds between their atoms, whereas in a sand pile, typically all interactions are repulsive. On the other hand, physicists are optimistic by nature, and the hope is that there is some unifying underlying physics that explains and connects all jammed materials. At the very least, the idea of a common jamming transition suggests many avenues for research, which will lead to a deeper understanding of all these materials, even if ultimately it turns out that they are all quite different in the details of their behavior.

Properties of jammed materials, and the jamming transition, will be described in Sec. 4. Some open questions in the field of jamming are discussed in Sec. 5. The overall intent of this review article is to discuss interesting observations of soft materials, and to use the framework of jamming to compare and contrast the properties of these materials.

1.4 References

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AJ Liu & SR Nagel, “Jamming is just not cool anymore,” *Nature* **396**, 21 (1998).

2. Physics of colloids

There are a variety of soft materials, as mentioned in the introduction – colloidal suspensions, emulsions, foams, gels, and granular materials. I will begin by discussing colloids, as they serve as a simple system for introducing a variety of physics relevant to soft materials.

2.1 Definitions

Colloids are a mixture of small solid particles in a liquid. Examples include toothpaste, peanut butter, paint, blood, and pastes in general. *Colloidal particles* are typically 0.01-10 μm in radius. Even the smallest colloidal particles are usually big enough to be thought of as solid spheres, rather than as large molecules; see Fig. 2.1. For the largest sizes, colloidal particles are still small enough that thermal motion is important for them; the thermal energy scale set by k_BT is relevant for their interactions. (k_B is Boltzmann's constant and $k_BT \approx 4.1 \times 10^{-21}$ J at room temperature.) This is in contrast with granular materials (see Sec 3.4), for which thermal motion is unimportant and friction is crucial. Note the terminology is to refer to the material as a whole as the "colloid" (or colloidal suspension) and the individual particles as "colloidal particles". The liquid commonly used in colloids is water, although physicists often study colloids in organic solvents.

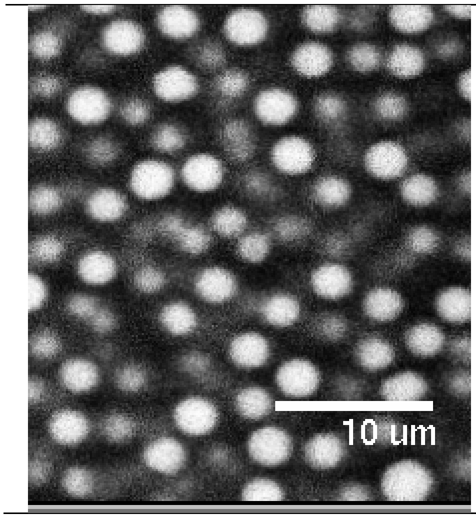

Fig. 2.1. Image of 2.3 μm diameter colloidal PMMA particles, taken with confocal microscopy.

2.2 Brownian motion

In early science classes we learn that temperature is related to the vibrations of atoms. For colloidal particles, this manifests as Brownian motion: under a microscope colloidal particles bounce around in an enthusiastic and random fashion. Biologist Robert Brown observed this in

1827 and thought he was observing tiny creatures swimming. When tiny pieces of inorganic materials were also seen to move in the same way, it was realized that this motion had a physical origin rather than a biological one (Haw 2002). The origin is the random kicks colloidal particles receive from the solvent molecules; these kicks occur in random positions at any moment in time, and thus the particle moves in a completely random direction at any instant; see Fig. 2.2. It is this same motion that gives rise to diffusion of molecules or particles.

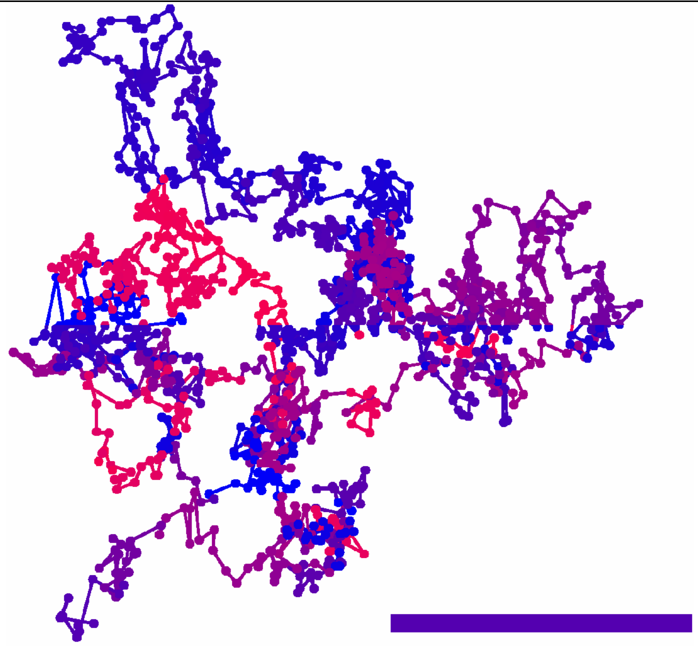

Fig. 2.2. Trajectory of a 2 μm diameter colloidal particle diffusing in water. This shows 24 s of data; the dots mark the particle's position every 1/30 s. The particle starts at the red end of the trajectory and moves to the blue end. The scale bar indicates 0.5 μm.

To characterize this motion of colloidal particles, the mean square displacement of a collection of particles can be calculated. Let's consider the simple case of diffusion in one dimension. Suppose we have *N* particles which move in one dimension, and their positions at time *t* are given as $x_i(t)$, where *i* refers to a particular particle. A particle's displacement for a lag time *Dt* is defined as:

$$\Delta x_i(t,\Delta t) = x_i(t+\Delta t) - x_i(t). \qquad (2.1)$$

The mean (average) displacement is then written as $\langle \Delta x(\Delta t) \rangle$ where the angle brackets indicate an average over all particles *i* and all times *t*. In general, there is no reason for a particle to prefer to move left or right, so the mean displacement is zero for any *Dt*. On the other hand, for normal everyday motion such as for balls, cars, or running giraffes (where random thermal kicks are unimportant), the mean displacement grows linearly with *Dt*. This gives the familiar formula

$$\langle \Delta x \rangle = v \Delta t \qquad (2.2)$$

or distance = velocity × time. In cases where the colloidal particles are in a flowing liquid, one might find that Eqn. (2.2) holds.

For random motion, since $\langle Dx \rangle$ is generally zero, we instead calculate the mean square displacement $\left\langle \Delta x^2(\Delta t) \right\rangle$, which will be nonzero if the particles move. Again, the average is taken over all particles and all times. For a dilute suspension of particles, the mean square displacement grows linearly with the lag time, as:

$$\left\langle \Delta x^2(\Delta t) \right\rangle = 2D\Delta t. \tag{2.3}$$

D is the diffusion constant, and by analogy with Eqn. (2.2), this constant characterizes how fast particles move. You can think of $\sqrt{\left\langle \Delta x^2(\Delta t) \right\rangle}$ as a typical size of a blob of these particles released from some initial point, in other words, "size" $\sim \sqrt{\Delta t}$. Or, you could think of this as the typical distance a particle explores in this amount of time. The motion in *x*, *y*, and *z* is typically independent, so in 3D Eqn. (2.3) becomes:

$$\left\langle \Delta r^2(\Delta t) \right\rangle = \left\langle \Delta x^2 \right\rangle + \left\langle \Delta y^2 \right\rangle + \left\langle \Delta z^2 \right\rangle = 6D\Delta t. \tag{2.4}$$

For particles with trajectories such as the one shown in Fig. 2.2, Eqn. (2.3) can be plotted as shown in Fig. 2.3. On a log-log plot, the data lie along a straight line with slope 1, indicating $\left\langle \Delta x^2 \right\rangle \sim \Delta t$, as Eqn. (2.3) predicts.

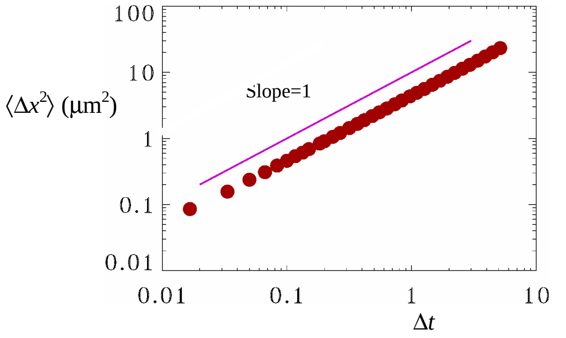

Fig 2.3. Mean square displacement of 2.2 μm diameter colloidal particles.

For simple spherical particles, the diffusion constant *D* in Eqns. (2.3) and (2.4) is defined as:

$$D = \frac{k_B T}{6pha} \tag{2.5}$$

with *h* the viscosity of the liquid the particles diffuse in, and *a* the particle radius. A larger value indicates faster motion, and so Eqns. (2.3) and (2.5) predict that smaller particles diffuse faster. Often these two equations are used together to determine the particle radius *a* by measuring the left-hand side of Eqn. (2.3) to determine *D*. If the particle size *a* is known, then likewise these two equations can be used to determine an unknown viscosity *h* (Gardel et al. 2005; Squires & Brady 2005). Note that in cases where there is an average flow (in other words, Eqn. (2.2) finds a nonzero velocity *v* for the particles), then it is often desirable to calculate

$$\left\langle \left(\Delta x - \left\langle \Delta x \right\rangle \right)^2 \right\rangle = \left\langle \Delta x^2 \right\rangle - \left\langle \Delta x \right\rangle^2 \tag{2.6}$$

which is sometimes known as the variance. The right hand side of this equation can be derived from the left hand side by expanding and noting that $\langle \Delta x \cdot \langle \Delta x \rangle \rangle = \langle \Delta x \rangle \cdot \langle \Delta x \rangle = \langle \Delta x \rangle^2$. The variance will follow the same behavior as Eqn. (2.3).

Equation (2.5) is commonly known as the Stokes-Einstein equation, although it has been recently pointed out that it should more properly be called the Stokes-Einstein-Sutherland equation (Squires & Brady 2005). Using an earlier fluid mechanics result derived by Stokes, in 1905, Einstein and Sutherland independently derived Eqn. (2.5) (Einstein 1905a; Sutherland 1905). At the time Einstein was still working in the patent office in Berne, Switzerland, while Sutherland was a more established scientist working in Australia. The main difference between the two articles published in the same year was the context in which the equation was derived. In Sutherland's article, the equation was used to determine the size of albumin molecules. Einstein's article implied that atoms existed, and that a determination of Avagadro's number was possible (Einstein 1905b). Thus it is not surprising that Einstein's article got more attention, perhaps also due to Einstein's later importance to physics.

2.3 Interactions

Because of their small sizes, colloidal particles have interactions that are much different from larger particles. When the net interactions are repulsive, the colloid is called *stabilized* or *dispersed*. When the net interactions are attractive, the colloid may become a *gel* (see Sec. 3.3). The formation of a gel from an initially dispersed suspension of attractive colloids is called *flocculation*, *aggregation*, or *gelation*; there is no distinction between these terms that I am aware of.

The most important attractive interaction is the *van der Waals force*. This is due to fluctuating electric dipole moments; for details, see (Jones 2002; Larson 1999). While the van der Waals force has a very short range, of the order of 10 nm, it is very strong; the interaction potential is many times $k_B T$. If colloidal particles get close enough, they tend to stick together because of this force, usually irreversibly. This is useful for forming colloidal gels, but otherwise causes problems. For example, I prefer paint to be a moderately low viscosity liquid so that it can be spread on walls, rather than a high viscosity substance like peanut butter.

Thus it is fortuitous that colloidal particles have several possibilities for repulsive interactions. The first is charge stabilization. Often when colloidal particles interact with their solvent, molecules on the surface of the particles disassociate, leaving a charged surface, with counterions then floating in the liquid. These counterions are attracted to the charged surface, forming a layer of opposite charge, so that far away, the colloidal particle appears somewhat neutral. There is a complex interplay between the surface, the counterions, the dielectric constant of the solvent, the temperature, and other factors; see (Jones 2002; Larson 1999) for details. The net result is that when two colloidal particles get sufficiently close, they begin to repel each other due to the Coulomb force. The distance characterizing this interaction is known as the *Debye length*, and is set by the behavior and location of the counterions, and the solvent characteristics. Adding salt to the solvent provides additional ions and counterions, and typically decreases the Debye length.

Typical sizes for the Debye length range from 0.3 nm to 300 nm (Larson 1999, Crocker & Grier 1994). If the Debye length becomes too short, the colloidal particles can sense the van der Waals force and begin to flocculate.

A second important repulsive interaction is *steric stabilization*, which occurs when colloidal particles have a short polymer attached by one end to their surface (perhaps ~50 nm long). If two such particles get close enough, the surface polymers begin to overlap and push against each other. This causes a repulsive interaction, with the range set by the length of the polymer. Thus this length is often set to be larger than the length scale for van der Waals attraction. In some circumstances (changing temperature for example), the chains may shorten, resulting again in flocculation.

For some colloidal particles, steric stabilization is not achieved by permanently grafted polymers, but instead by adding *surfactant molecules*. Surfactant molecules are the molecules which allow soap to create suds. These molecules have a polar head and nonpolar tail. The head likes to be near other polar molecules, like water; the nonpolar tail is *hydrophobic,* preferring not to be near water. For example, these are the molecules that stabilize a foam; the polar head coating the water phase and the hydrophobic tail sticks toward the air; see Sec. 3.2. Thus, for some colloidal particles, the hydrophobic tail coats the particle, and the polar head sticks into water to stabilize the particle. When grafted polymers are used instead, the choice of polymer is often one that mimics the properties of a surfactant, in other words, the part of the polymer that sticks out is hydrophilic, if the solvent surrounding the particle is water.

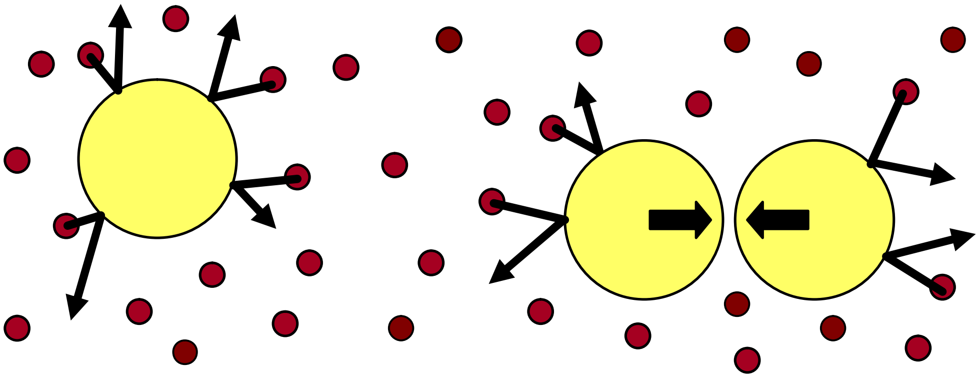

Fig. 2.4. Left: a large particle surrounded by small particles gets kicks from all directions from the nearby small particles. Right: Two large particles close together feel an unbalanced force from the small particles, as the small particles are excluded (depleted) from the space between the large ones. This results in an effective net force between the two large particles – the depletion force.

In some cases, the *depletion force* is used to provide a more controlled attractive force than the van der Waals force. The depletion force comes about when small polymers or particles are added to the fluid. Consider the case of adding small particles (small here means smaller than the original colloidal particles; typically the small particles added are at least ten times smaller in radius than the original particles). A large particle surrounded by small ones gets kicks from the Brownian motion of the small ones. These kicks on average balance out, and there is no net force on the large particle. If two large particles get so close to each other that the small particles can't come between them, then they feel an unbalanced force from the small particles which tends to push them together (Fig. 2.4). This is the depletion force (called this because the small particles are depleted from the region between the large particles.)

Experimentalists love the depletion force because it is easy to tune. The range of this force is set by the size of the small particles. The magnitude of this force is set by the concentration of the small particles – typically it can be a few k_BT. In the case when polymers are used rather than small particles, the range of the attraction is set by the polymer radius of gyration. This radius of gyration depends on the length of the polymer and the solvent conditions; see also (Chen et al. 2003) for the case when the polymer concentration becomes large.

2.4 Gravity and density matching

If you throw rocks into a lake, they sink to the bottom, as the density of rocks is higher than that of water. A similar problem afflicts colloids: in many cases, the density of the colloidal particles is not the same as the solvent. In such cases, colloids can sink to the bottom of the container, or float to the top (if they are less dense than the liquid). This can cause problems, especially if you want to do an experiment where the particle concentration is a control parameter (see Sec. 2.6).

The first relevant bit of physics is to note that Brownian motion tries to homogenize the particle concentration. For example, even a heavy particle near the bottom of a container still gets Brownian kicks in all directions, and has a chance of diffusing upward. The balance between diffusion and gravity is thus important and sets up a density gradient in the container (see Fig. 2.5). As an analogy, consider air: the air is thinner at high altitudes. Like colloidal particles, air has mass and gravity tries to pull the air closer to the Earth; this is balanced by the Brownian motion of the air. Thus we expect that the air's pressure and density decrease as we drive up a mountain, or fly in an airplane. In fact, for air, we expect the density to behave as $r(z) = r_0 \exp(-z/z_0)$ with z_0 known as the scale height; see (Schroeder 1999) for a derivation. For colloids, the density is typically expressed as the nondimensional volume fraction f (the fractional volume of the system taken up by the solid particles), and thus this equation becomes:

$$f(z) = f_0 \exp(-z/z_0). \qquad (2.6)$$

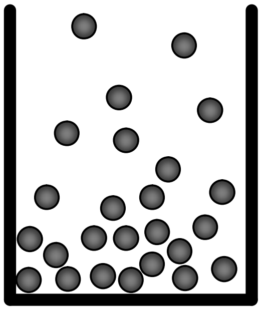

Fig. 2.5. Schematic picture of colloidal particles which have sedimented in a container. Because of Brownian motion, they are not all on the bottom of the container, but have some probability of being anywhere in the container. Higher up in the container, the probability to find particles is exponentially smaller; see Eqn. (2.6).

The scale height z_0 is given by a balance between the thermal energy and the gravitational potential energy. The gravitational potential energy is the buoyant weight times the scale height, so the resulting expression is:

$$z_0 = \frac{k_B T}{W_{buoyant}} = \frac{k_B T}{\left(\Delta\rho\right)\left(\frac{4}{3}\pi a^3\right) g} \qquad (2.7)$$

In this formula, $\Delta\rho$ is the density difference between the particles and solvent, a is the particle radius, and g is the gravitational acceleration.

What is desired is a very large value of z_0. For example, if z_0 is significantly larger than the height of a container, then the colloidal particle volume fraction will be essentially constant throughout the container. (For example, the scale height for the atmosphere is ~ 8500 m, and thus we can approximate the air pressure within a room as constant (Schroeder 1999).) By examining Eqn. (2.7), it is clear there are several ways to increase z_0. The first is to better match the density of the solvent to the density of the particles, thus decreasing $\Delta\rho$. The second is to use smaller particles, which can result in a considerable improvement, as $z_0 \sim a^{-3}$. The third, sometimes used, is to conduct experiments in microgravity (on the space shuttle for example), thus reducing g; see (Cheng 2002) for example.

The second bit of physics relevant for gravitational effects is to consider the sedimentation time. If a bottle of colloids is shaken, how quickly do the particles sediment (assuming for example they are denser than the liquid)? The answer can depend strongly on the volume fraction ϕ, see for example (Segrè 2001). However, a quick idea can be gained by balancing the drag force on particles with their gravitational force:

$$6\pi\eta a v = W_{buoyant} = \left(\Delta\rho\right)\left(\frac{4}{3}\pi a^3\right) g \qquad (2.8)$$

Here, the drag force depends on the solvent viscosity η and particle velocity v, and the buoyant weight is given by the product of the density difference, the (spherical) particle volume, and g. Rearranging, the sedimentation velocity is:

$$v_{sed} = \frac{2}{9}\frac{\Delta\rho\, a^2 g}{\eta}. \qquad (2.9)$$

Smaller particles sediment slower. The sedimentation time can be used in two ways. First, it gives a crude estimate for how long it can take an initially homogeneous colloidal suspension to become stratified, for example, $t \approx z_0 / v_{sed}$. If this time scale is long, then experiments done more quickly can probably avoid serious sedimentation problems. Second, sometimes sedimentation is desired – for example, often colloidal suspensions are centrifuged (thus increasing g) to concentrate them. Thus you could estimate centrifugation times needed for a certain concentration. Alternatively, the time it takes the colloids to move a distance L in a container in a centrifuge can be measured, and then you could work backwards to estimate the density difference $\Delta\rho$ between the colloids and solvent, thus allowing you to use Eqn. (2.7) for the scale height.

2.5 Common colloidal systems

For physicists, there are several important colloidal systems that are widely studied. The ones I will discuss are colloidal PMMA, colloidal silica, colloidal NIPA, and laponite (a clay colloid).

PMMA

The field of physics first became strongly interested in colloids when in 1986, Pusey and van Megen studied the phase behavior of colloidal PMMA particles. PMMA (poly-methyl-methacrylate) is the same polymer that is known as Plexiglas™ on a large scale. These are sterically stabilized to prevent aggregation. They are suspended in an organic solvent mixture, which can be varied to match the density and/or index of refraction of the particles. Often conditions are such that the particles have no net charge, and thus their only interaction is the steric repulsion, which acts at a very short distance compared to the particle size. Thus such particles are very nearly ideal *hard spheres*. They are like billiard balls; they ignore each other at most separations, and the only constraint is that they cannot overlap. Thus they are simple to think about and their behavior is easy to simulate, which is why physicists were fascinated when Pusey and van Megen demonstrated that these colloids behave as hard spheres (1986). These have been widely used by many groups, as discussed in two review articles (Habdas & Weeks 2002; Prasad et al. 2007), although in some cases the particles pick up a slight charge and thus are not quite ideal hard spheres (Royall 2003).

Silica

Silica spheres are also widely used. One reason for this is their relatively easy fabrication (Stober et al. 1968). A second reason is that they are usually suspended in water (or a mixture of water and glycerol), avoiding the smelly and toxic organic solvents that are required by the PMMA system. Because they are in water, repulsion due to charge is the primary mechanism preventing flocculation; adding salt can screen the charges and cause flocculation (which is often irreversible). Silica colloids are hard to density match (their density varies but is larger than 2 g/cm^3), and also it is hard to match their refractive index. This latter constraint makes microscopy difficult.

NIPA

A newer colloidal system is poly-*N*-isopropylacrylamide, sometimes shortened to pNIPAm, but most commonly known as NIPA. I have heard this acronym pronounced with both a hard E and a hard I, in other words, nee-pah and neye-pah. These are hydrogel particles, made from a loose network of cross-linked polymers, soluble in water (Debord & Lyon 2000; Alsayed et al. 2005). At moderately warm temperatures (typically above 30-35° C), water acts as a poor solvent for the polymers, and the NIPA particles shrink in size. (The polymers prefer to be close to each other, rather than close to water molecules.) At moderately cool temperatures (typically around 20-25° C), water acts as a good solvent for the polymers, and the NIPA particles swell so that the polymers can contact as much water as possible. Technically, the mid-point where the polymer is neutral in its preference for water is known as the theta temperature; and NIPA is useful precisely because its theta temperature lies in a range that is easily experimentally accessible. (Note also that often the size of NIPA can be affected by pH as well.)

The size change of NIPA particles is typically at least a factor of two in diameter, and thus a factor of eight in volume. Thus by controlling temperature, you control the volume fraction and thus can control the behavior of the sample in a nice fashion. However, NIPA particles are very soft, which is a key difference from the previously mentioned colloids (PMMA and silica). If NIPA particles are in suspension at a high concentration, and their size is increased, then they can deform each other, and will no longer be spheres. On the other hand, an advantage of NIPA is that they are mostly composed of water: the polymer is a loose network, and so the particles are closely density-matched to water, and also closely match water's index of refraction.

Laponite

Another new colloidal system is laponite. Laponite is a type of clay, and takes the form of a charged disk-like molecule, about 30 nm in diameter and 1 nm in thickness – much smaller than the colloidal silica and PMMA discussed above. If you buy laponite, it comes as a dry powder. When added to water in concentrations of typically 1-4% by weight, laponite forms an elastic material which may be a gel or a glass (Tanaka et al 2005). Macroscopically the material no longer flows. Laponite has gained a lot of attention as it is transparent when added to water, allowing easy study by light scattering or microscopy. (For microscopy, tracer particles need to be added, given the transparency of the material and the small size of the laponite molecules.) However, laponite is difficult to handle experimentally. While it is in water, the behavior of laponite is sensitive to pH, pre-filtering, and the residual water content in the laponite powder prior to mixing with water. Furthermore, laponite samples must be prepared in a pure nitrogen atmosphere to avoid changing its properties due to interaction with carbon dioxide. It is also possible that results may vary depending on the source of the laponite powder. My impression is that people are still learning how to properly handle laponite to give reproducible results, and that you need to take great care to ensure that results from your samples are comparable with those from other groups.

2.6 Phase behavior of monodisperse hard-sphere colloids

For hard-sphere like colloids, such as colloidal PMMA, the main control parameter is the volume fraction f. For low f, for example $f \approx 0.01$, particles diffuse and nicely obey Eqns. (2.3) and (2.5). At higher f particles start to collide and thus they no longer freely diffuse through the sample. This state is more analogous to a liquid, where interactions become more important. Although, for simple hard-sphere colloids, there is no distinction between a gas and a liquid.

Close-packing

The upper limit for the volume fraction is reached at f = 0.74 for monodisperse spheres (all the same size), when the spheres are packed into hexagonal layers, forming a crystal, such as shown in Fig. 2.6. The crystal structure can be hexagonal close packed (**hcp**), face-centered cubic, or random hexagonal close packed; the difference between these structures relates to how the hexagonal layers are stacked (Jones 2002). A different limit is reached at $f \approx 0.64$, known as random close packing (**rcp**). This is a disordered packing where the particles are packed as tightly as possible; nearly every particle touches its neighboring particles. Random packings with $f > 0.64$, or any packing with $f > 0.74$, require deforming the particles.

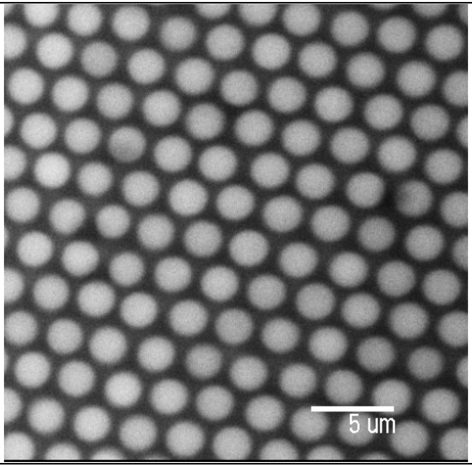

Fig. 2.6. A single layer within a colloidal crystal formed with 2.3 μm diameter PMMA colloids. The scale bar is 5 μm. This sample is at a volume fraction $f \approx 0.6$.

Colloidal crystallization

Interestingly, hard sphere colloids will spontaneously organize into the crystalline phase at a volume fraction $f \approx 0.5$. Counter-intuitively, this transition to an ordered state is due to entropy. Consider two systems at equal volume fractions of 0.64, one random (and thus **rcp**) and the other in a crystalline **hcp** state. The **rcp** system has no room for the particles to move. It has high configurational entropy but low vibrational entropy. The **hcp** system is the opposite; it is in an ordered, low entropy configuration, but the particles have plenty of room to move locally around their lattice sites. After all, they could be packed in as tightly as $f = 0.74$, but the system is only at $f = 0.64$. Thus, the vibrational entropy is higher. In practice, the total entropy of the crystalline system becomes higher than the random system at $f \approx 0.5$. More precisely, the system starts to form crystals at $f \approx 0.494$, and entirely crystallizes at $f \approx 0.545$. In between the system is in coexistence between the liquid-like state at 0.494 and the crystal at 0.545; see Fig. 2.7 for the phase diagram.

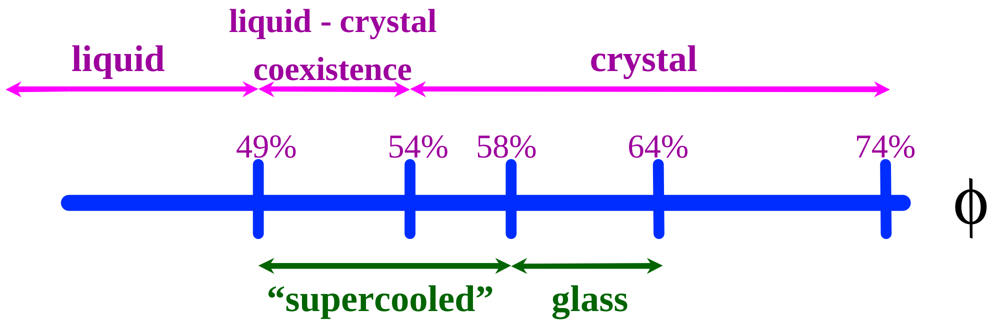

Fig. 2.7. Phase diagram for hard spheres. Note that the metastable glass phase is only present if the system is polydisperse, at least ~5%.

Colloidal glass transition

While crystals may be interesting to study (Gasser et al. 2001; Alsayed et al. 2005), the focus of this article is on jamming, an amorphous state. Clearly **rcp** is a jammed state, but in fact colloids can sometimes form a glass phase if $0.58 < f < 0.64$, and so $f_g \approx 0.58$ is identified as the glass transition, or the jamming transition. Some slight polydispersity (~ 5%) is needed to achieve this glass transition. Polydispersity is the variability of the sizes of the colloidal particles, and is measured by the standard deviation of the distribution of particle sizes divided by their mean size.

The colloidal glass transition is characterized by two main features. First, the sample needs to be amorphous on the microscopic scale – the colloidal crystal state needs to be avoided. This is typically done by centrifugation of the sample, to rapidly increase the volume fraction; or by taking a crystalline state and mixing it rapidly. Because colloidal crystals are fragile, it is easy to break them by stirring or shaking a sample. Second, colloidal glasses are characterized by a lack of diffusive motion of the particles. The particles can diffuse only very short distances before bumping into other particles; long range motion through the sample becomes impossible. Thus, for $f < 0.58$, a sample initially in a disordered state will eventually form crystals, the state which maximizes entropy. A sample with $f > 0.58$ never forms crystals, even though that would be the thermodynamically preferred state. Note that the "supercooled" phase shown in Fig. 2.6 is in analogy with a regular supercooled liquid, in that it will eventually crystallize. To have a colloidal sample in the supercooled phase, it needs to be prepared in an amorphous state, using centrifugation or stirring.

The two properties listed above (amorphous, no diffusive motion) are in some sense defining characteristics of what is meant by a colloidal glass. However, colloidal glasses also possess two other notable characteristics. The viscosity of colloidal glasses is very large, although apparently not infinite, see (Cheng et al. 2002). Macroscopically, they behave much like a paste such as toothpaste: they no longer flow easily, if at all. Finally, they *age*: the system is no longer in thermodynamic equilibrium, and thus the properties of the system change with time (Cianci et al. 2006). Aging will be discussed in Sec. 4.

Remarkably, the colloidal glass transition – the transition to the glassy state as the volume fraction is increased toward 0.58 – agrees in many details with the molecular glass transition. Specifically, the motions of colloidal particles, and their spatial arrangements, are in remarkable agreement with theories of the glass transition. Moreover, many features of traditional glass-forming materials have been seen in colloids. It is for these reasons that colloidal glasses are a popular model system used to study the glass transition.

As mentioned in the introduction (Sec. 1), the colloidal glass state can be thought of as a jammed state. While the idea that all jammed states are similar is yet unproven, certainly a strong case has been made that colloidal glasses and molecular glasses are remarkably close cousins. Although, it is worth mentioning at least one key difference, the viscosity. The viscosity of colloidal samples grows rapidly as the glass transition is approached. However, molecular glasses have a viscosity change of as many as 13 orders of magnitude (Angell et al. 2000), as opposed to 4 orders of magnitude in colloidal glasses (Cheng et al. 2002).

Colloidal glasses share many similarities with other soft materials. Most other soft materials are more polydisperse, and thus it is easier for them to form glasses than to form crystals. These materials will be introduced and discussed in Sec. 3.

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3. Other soft materials

Now that I've introduced colloids, let's discuss other soft systems which resemble colloids to varying degrees.

3.1 Emulsions

Emulsions are similar to colloids, but rather than solid particles in a liquid, they consist of liquid droplets of one liquid, mixed into a second immiscible liquid; for example, oil droplets mixed in water. Surfactant molecules are necessary to stabilize the droplets against *coalescence* which is when two droplets come together and form a single droplet. A cross-section of an emulsion is shown in Fig. 3.1, and a sketch showing a droplet with the surfactants is shown in Fig. 3.2. Mayonnaise is a common example of an emulsion, made with oil droplets in water, stabilized by egg yolks as the surfactant, with extra ingredients added for taste.

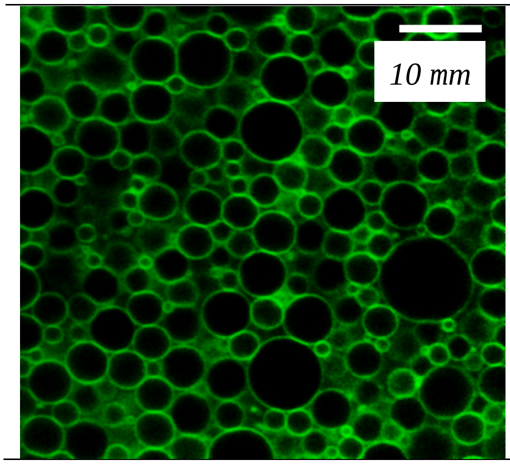

Fig. 3.1. Confocal microscope image of an emulsion. The droplets (dark) are dodecane, a transparent oil. The space between the droplets is filled with a mixture of water and glycerol, designed to match the index of refraction of the dodecane droplets. The droplets are outlined with a fluorescent surfactant. The hazy green patches are free surfactant in solution, or else the tops or bottoms of other droplets. (Picture taken by ER Weeks and C Hollinger.)

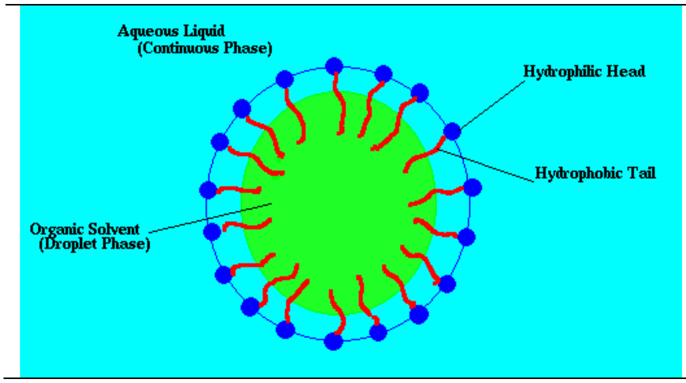

Fig. 3.2. Sketch of an emulsion droplet. Not to scale: typically the surfactants are tiny molecules, whereas the droplet is micron-sized. (Sketch by C Hollinger.)

Making an emulsion is quite easy, especially compared to making colloids. Start with two immiscible liquids such as oil and water. Add surfactant to one of the phases; for example, water with soap mixed in. Then mix the oil and water together; shaking a jar or using a blender works to make a crude emulsion with large droplets. More controlled shearing of the sample can then be used to break the droplets into smaller, less polydisperse droplets; various techniques are described in two good review articles: (Bibette et al 1999, Mason et al 2006).

An important difference between emulsions and colloids is that the emulsion droplets are easily deformable (perhaps a bit like NIPA colloids; see Sec. 2.4). Below random close packing (see Sec. 2.5), the droplets in an emulsion are spherical, due to surface tension. (Think of surface tension as an energy cost: it costs energy to have more surface between oil and water. Given an oil droplet with a certain volume, a spherical shape minimizes the surface tension energy cost for that volume of oil. While surfactant molecules lower this energy cost, it is still preferable to form a sphere.) Above random close packing, the droplets start to deform, and some flat faces between some droplets can be seen (as in Fig. 2.1). Note that this figure shows a moderately polydisperse sample, so random close packing is at a higher volume fraction than for monodisperse particles. I think the sample shown is likely at a volume fraction of ~0.7. Typically the emulsion glass transition is taken to be somewhere close to random close packing. Often the volume fraction for the glass transition is defined experimentally, because emulsions are typically quite polydisperse, and the mathematical value of random close packing may not be known.

Emulsions otherwise are fairly similar to colloidal suspensions, as described in Sec. 3. Sufficiently small droplets undergo Brownian motion, added polymers can cause flocculation by the depletion force, and surfactants stabilize the droplets against coalescence because of steric stabilization (Bibette 1999).

In some cases small colloidal particles stabilize emulsion droplets against coalescence (with a size much smaller than the droplets). These particles work in a similar fashion to the surfactants. Particles are chosen that have a low surface tension with both the droplet phase and the continuous phase (for example, oil and water respectively). Thus they are happy to sit at the surface of the droplets, and lower the surface tension energy cost of having oil and water adjacent to each other; now both the oil and water can touch a particle, rather than touching each other. Such emulsions are called *Pickering emulsions*. Should two droplets come in close contact, the particles sterically stabilize the droplet, similar to the surfactants they replace.

3.2 Foams

Foams are similar to emulsions, except that the liquid droplets are replaced with gas bubbles. Typically the continuous phase is water or a mixture of water and glycerol; foams made with glycerol tend to last longer. A foam with a very high volume fraction of gas is termed a *dry foam*, with perhaps $f_{\text{gas}} \approx 0.99$. A foam with more liquid in it is termed a *wet foam*. Both of these states can be seen in Fig. 3.2. It is clear that in a dry foam, the air bubbles deform from spheres, and take on a much more polyhedral appearance. At the other extreme, if enough liquid is added, the foam eventually becomes a bubbly liquid, and flows quite easily. Thus a requirement to be called a foam might be that the pile of foam should be able to support its own weight, but this is not well-defined. Roughly speaking this would occur at a volume fraction $f_{\text{gas}} \approx 0.7$, in other words, when the foam is jammed.

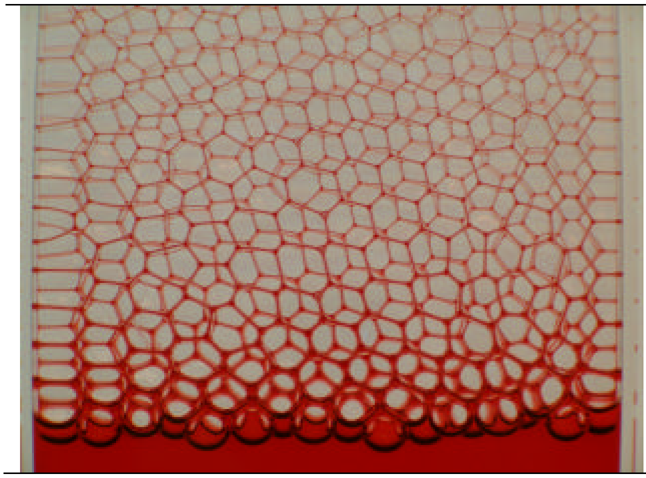

Fig. 3.2. Picture of a foam made with water, soap, and regular air. Red dye is added for easier visualization. At the top the foam has drained and is drier; closer to the bottom it is clear the foam is wetter. (Picture from GC Cianci and ER Weeks.)

Consider a jammed foam, perhaps with $f_{\mathrm{gas}} \approx 0.8$. One route to unjamming the foam is to add more liquid. A second route, though, is to exert a shear force on the foam – perhaps add a weight to the top of the foam; or perhaps slide the foam between your hands; or squeeze the foam through a tube. If a very small force is applied, the foam deforms elastically. However, if a sufficiently large force is applied, the foam flows plastically – the bubbles rearrange and if the force is released, the foam does not return to its original configuration. Similar remarks apply to emulsions (think of mayonnaise).

In fact, at first glance, foams are quite similar to emulsions. After all, the distinction between liquid droplets in an emulsion, and air bubbles in a foam, is really nothing more than a change of density and viscosity of the droplets/bubbles. Fundamentally both the droplets and bubbles are filled with fluids, and the gas/liquid distinction could seem unimportant. To some extent this viewpoint is true.

However, the gaseous nature of foams is important in that gas diffuses through the continuous phase fairly easily. This leads to coarsening: large bubbles grow as gas diffuses to them, from the smaller bubbles, which shrink. This is due to the Laplace pressure, related to the pressure difference between the two sides of a curved surface. Consider a soap bubble floating in the air. The interior of the bubble is at higher pressure than the exterior, and this pressure is needed to prevent the bubble from collapsing. Why would it collapse rather than expanding? The surface tension of the soap film enclosing the bubble, as noted before, can be thought of as an energy cost per amount of surface. For sufficiently high surface tension, the bubble can lower its energy by shrinking its radius slightly, thus increasing the pressure and density inside the bubble. The change in pressure from the exterior to the interior of a spherical bubble is the Laplace pressure, and it is given by $P = s / R$, in terms of the surface tension s and the droplet radius R. Thus, smaller bubbles have higher Laplace pressures. If gas diffuses out of a small bubble into the surrounding liquid, the bubble can shrink, lowering the surface tension energy. However, the gas needs to go somewhere; there is a limit to how much gas can be dissolved in the liquid. Therefore the gas is moved to the larger bubbles, where the Laplace pressure is lower. If a foam is watched over time, the small bubbles shrink and disappear, and the larger bubbles grow. Interestingly, while this leads to a polydisperse distribution of bubble sizes, the distribution has a universal form (Durian et al. 1991). This can be seen as an advantage; independent of preparation method, the distribution is reproducible between different experiments.

Of course, all of this depends on the solubility of the gas in the liquid phase. Experiments are often done using C_2F_6, which has a very low solubility, thus preventing coarsening (Hilgenfeldt et al. 2001).

Foams have one more difficulty: due to gravity; in the foam, in addition to coarsening, the foam changes as the liquid phase drains out of the foam. This process is complex and depends on the local volume fraction of the gas (or liquid, as $f_{\mathrm{gas}} + f_{\mathrm{liquid}} = 1$), and also on the surfactant; see (Koehler et al. 2004) for details.

3.3 Gels

Gels are collections of objects (such as colloidal particles) that are stuck together, thus forming a material which acts like a solid – deforming elastically for weak applied forces. The two main types of gels are colloidal gels, formed with sticky particles, and polymer gels, formed by cross-linking polymer molecules.

Colloidal gels

As discussed in Sec. 2.3, there are two main attractive colloidal interactions: the van der Waals force and the depletion force. If colloids are sufficiently sticky – with an attractive energy larger than k_BT – then they tend to stay together once they come into contact. So, imagine starting with a suspension of infinitely sticky particles that are initially separated from each other. The particles diffuse around and, when they come into contact, they stick and form a small aggregate, which in turn diffuses through the system (although at a slower rate since it is larger). These aggregates can stick to other particles, or to other aggregates. Eventually every particle is stuck into one aggregate, which is as large as the system size. This is the gel. Rather than being all stuck together in a big condensed lump, the colloidal particles tend to form branching structures. The formation process is known as *diffusion limited cluster aggregation*, and the key point is that it is very hard for a diffusing particle to find its way deep into a fractal structure. Rather, it is much more likely to stick at the ends of the branches, as it moves around randomly. Thus, colloidal gels have a tenuous branched structure, as shown in Fig. 3.3.

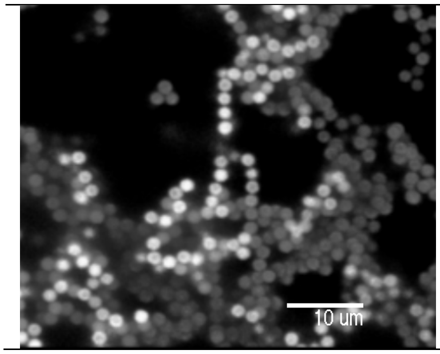

Fig. 3.3. Picture of a colloidal gel formed using the depletion force. The particles are approximately 2 μm in diameter. Picture taken with a confocal microscope, and rendered as a 2D projection of 3D data. (Taken by GC Cianci and ER Weeks.)

The final structure depends on the strength of the attractive forces, and the initial volume fraction. Thus the structures can either be very tenuous (low f, high attraction) or rather bulky (high f, lower attraction); see Figs. 3.3 and 3.4. At the very high end of f, the distinction between a gel and a glass becomes blurred (Dawson 2002). The structure is closely related to the macroscopic strength and properties of the bulk gel, see for example (Dinsmore et al 2006).

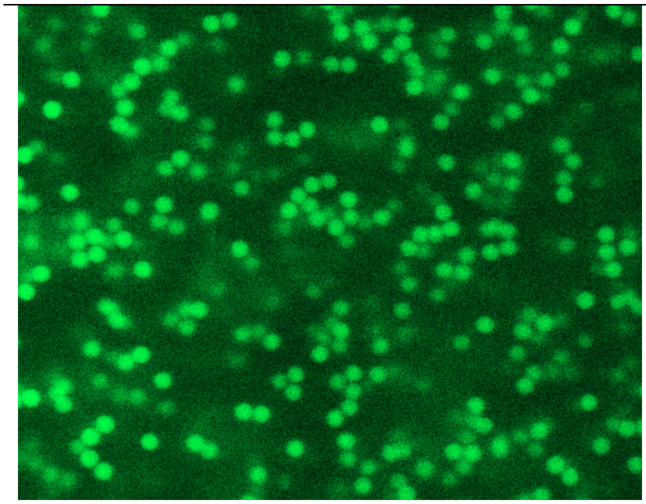

Fig. 3.4. Picture of sticky colloidal particles (2 μm diameter). The depletion force is used to control the attractive interactions. Compared to Fig. 3.3, this is a lower volume fraction system, with weak attractive forces. The system is not a gel, but rather lots of small clusters. (Picture from T Samphel and ER Weeks.)

Certainly for gels with weak attractive forces, bonds between individual particles have some chance of breaking due to thermal fluctuations; you should be cautious about thinking of particles as being permanently stuck together in every gel. On the other hand, aggregates formed due to the van der Waals force are often sufficiently sticky that they are essentially irreversible. In such situations, often *aging* of the gel is seen (Cipelletti et al. 2000). The structure of the gel slowly evolves over time, and likewise the motions of the colloidal particles comprising the gel slow down over time. This is more than just aggregation. Rather, aging still takes place even after a complete gel network is formed spanning the system size. This is often thought to be due to thermal fluctuations of the tendrils of the gel (see Fig. 3.3); occasionally these tendrils contact one another, and stick, and then their fluctuations are reduced and the gel strengthens.

In addition to the volume fraction f and the interaction strength, a third parameter which can control the state of a colloidal gel is the imposed shear. Similar to emulsions and foams, an applied shear stress can tear apart the bonds between particles and effectively “unjam” a colloidal gel.

Polymer gels

Polymer gels are analogous to colloidal gels, except that the things that stick together are now polymer molecules, and what sticks them together are now chemical bonds. Polymers are long molecules; common examples are poly-styrene and poly-methyl-methacrylate. Using tricks from chemistry, these molecules can be induced to bond together, forming *cross-links* which result in a tangled network of molecules. A gel is formed once essentially all polymer molecules are bound together in the network,. This can be at very low polymer weight fraction. Similarly to the colloidal gels, if the chemical bonds linking the polymers together are sufficiently strong, then few polymers are needed to span the system in a tenuous network. JELL-O® gelatin is an example; most of the weight of a solid chunk of JELL-O is due to water, not the added polymer. If you've made JELL-O before, this is obvious: the small amount of powder added (the gelatin) has a tiny mass compared to the amount of dessert produced.

It is important to note a distinction between polymer gels and polymer glasses. Polymer gels are formed due to attractions between the polymers, in other words, the chemical bonds. A polymer glass, on the other hand, is just a pure polymer; there is no solvent. Unlike in a polymer gel, the individual polymer molecules are not necessarily chemical bound together. At a high temperature, a polymer glass flows easily, like any molecular material in a liquid state; this is sometimes termed a *polymer melt*. At lower temperatures, the polymer melt flows more and more slowly. However, it typically cannot form a crystalline state, as the polymer molecules are so hopelessly entangled. Thus, the polymer forms a glass, which is similar in its properties to regular glassy materials (See Sec 3.5). For further details on polymer gels, glasses, and other interesting polymer states (like rubber), see (Larson 1999).

3.4 Granular materials

Sand is the most common *granular material*, which is composed of discrete, large (> 100 μm diameter) solid particles (often called *grains*). Generally the particles only interact by friction forces when they are in contact. Besides sand, other examples include gravel, pharmaceutical pills, and corn kernels. In some situations the fluid around the granular particles is important; typically this fluid is air, but sometimes it is a liquid. Beaches are good places to find wet granular materials. There are several key differences between colloids and granular materials. First is particle size: granular particles are large, at least larger than 10 μm diameter and more typically at least 100 μm in diameter. An important consequence of this is that gravitational forces are much larger than thermal forces (Sec. 2.4). Typically the scale height z_0 is orders of magnitude smaller than the particle size a; see Eqn. (2.7). Thus, Brownian motion is irrelevant for granular particles; particles always will be in a state that minimizes the gravitational potential energy, in a local sense. (That is, the state of lowest gravitational potential energy would have all particles in a flat layer on the floor. A sand pile is in a state that is a local minimum of potential energy, as a function of the particle positions, rather than a global minimum.) A second key difference between colloids and granular materials is friction, which is present between touching granular particles. For a sand pile, this is static friction, and for flowing grains, dynamic friction may be more important. In contrast, colloidal particles do not usually "touch," and if they do, this would then lead to attraction via the van der Waals force (or some other interaction; see Sec. 2.3). Friction, as we think of it for macroscopic materials, does not apply for microscopic colloidal particles.

Due to friction and the lack of thermal motion, granular materials are most often found in the jammed state. For example, as you walk down a beach, you do not sink beneath the sand; rather, the sand supports your weight, due to friction between the grains. A pile of sand maintains a conical shape, rather than slumping into a puddle of sand. However, sand also acts like a fluid in common situations. As you try to walk up a sand dune, you easily push small amounts of sand out of the way, and sometimes your feet trigger small avalanches where a surface layer of sand flows downhill. Sand in a bucket easily pours out, looking somewhat fluid-like in its behavior. In situations of low number density, sometimes sand can even act like a gas. For comprehensive reviews of different behaviors, see (de Gennes 1999, Jaeger et al. 1996, Kakalios 2005).

What, then, controls jamming in granular materials? As with colloids, the volume fraction is an important parameter. However, it is difficult to control this parameter, given gravity and friction. On the one hand, a pile of sand with too low a volume fraction simply collapses. The minimum stable volume fraction appears to be $f_{\mathrm{RLP}} = 0.58$, known as "random loose packing." This is similar to the volume fraction for the colloidal glass transition, although it is not clear if that is just a coincidence (Goldman & Swinney 2006). On the other hand, to set a given volume fraction $f_{\mathrm{RLP}} < f < f_{\mathrm{RCP}}$ (between loose packing and close packing) is tricky because of friction. If you fill a container of sand by pouring sand in, this often results in a volume fraction closer to f_{RLP}, although the details of the initial state depend on how the container is filled. Tapping the sides of the container can compactify the sand and increase the volume fraction, but there is evidence that two states with the same volume fraction are not always equivalent, and that there may be hysteretic effects where the sample preparation history is important (Goldman & Swinney 2006, Nowak et al 1998). This history dependence is due to the under-determined nature of static friction. Recall that the static friction force can take *any* value up to the maximum possible, given by $m_{\mathrm{static}}N$, the static friction coefficient times the normal force between two objects. Thus even two granular samples with the same positions for all of the grains could nonetheless have difference forces acting between the grains and thus be in different states. Probably more importantly, two samples with the same volume fractions may have differently packed grains and so be in different states.

Quicksand is a counterexample to the above concerns. Quicksand is a lower volume fraction suspension of granular particles, where the volume fraction (less than f_{RLP}) is maintained because the particles are nearly density-matched with the liquid (see Sec. 2.3 for the relevant physics). However, such low volume fraction wet granular materials are not frequently studied in the context of jamming. Their flow properties are often studied in engineering literature in the context of slurries.

Shear stress may be a second parameter that controls if a granular sample is jammed. In real life, no material is infinitely rigid; so even a densely packed granular material could flow if the applied stress is large enough to deform the grains. Perhaps more simply, if a container partially full of grains is tilted past a critical angle, the grains will begin to flow. Often this is a surface flow – only the grains at the top of the sample move, those underneath remain motionless. Thus sometimes the "jamming transition" in such a situation is thought to be a function of space, with the flowing grains on top in an unjammed state, and the subsurface grains in a jammed state.

A third parameter that can be relevant is an overall random energy added to the system. Specific examples include shaking the container, and flowing air or liquid at a rapid rate upwards through the container (this situation is termed a *fluidized bed* and is of industrial relevance; see (Goldman & Swinney 2006)). In these sorts of situations, the grains move around somewhat randomly, almost as if they are in thermal motion as discussed in Sec. 2.2 for colloidal particles.

If the energy input is sufficiently large, the system acts like a liquid. An excellent example of this is (Goldman & Swinney 2006) who studied the transition from liquid to jammed state as a function of flow rate in a fluidized bed.

To quantify this added random energy, often the *granular temperature* is used. This is typically thought of as related to the mean square velocity of the particles, or perhaps the mean kinetic energy:

$$k_B T_{granular} = \tfrac{1}{2} m \left\langle v^2 \right\rangle \tag{3.1}$$

where m is the mass of an individual grain. The usefulness of the granular temperature is an ongoing research question, and may depend on what state the system is in (granular gas or granular liquid) (Jaeger et al. 1996; Feitosa & Menon 2002). The idea of a granular temperature is intriguing as it is a nice analogy with regular molecular glasses: by increasing the temperature of a glass or "temperature" of a granular system, the system unjams.

Related to granular systems are possibly snow and soil. Avalanches in snow are similar to avalanches of sand in a sand pile. Soil is usually solid, yet sometimes earthquakes can lead to *soil liquefaction* which can cause houses to collapse. These topics are beyond the scope of this review, but may perhaps be related systems.

3.5 Molecular glasses

While the intention of Sec. 3 is to focus on jammed states of soft materials, it is worth saying a few words about molecular glasses. A main point of the theory of jamming, to be discussed in Sec. 4, is that molecular glasses share similarities with soft glassy materials.

What are the interactions between molecules? Like colloids, there are attractive and repulsive interactions. The attractive interactions are covalent bonds, ionic attractions, hydrogen bonds, and van der Waals forces. Without attractive forces, everything would always stay in a gaseous state; with attractive forces, we have the possibility of liquids and solids. The repulsive interactions are primarily electrostatic in origin: when two atoms get sufficiently close, their electron clouds begin to overlap and the two atoms are held apart. This is similar to steric stabilization in colloids (Sec 2.3).

As noted in Sec. 1, the glass transition is marked by a dramatic increase in the viscosity of a material upon cooling. In some cases, extremely rapid cooling is required, or else the sample will crystallize first. In other cases, slow cooling is possible, as the material seems to have a hard time finding the crystalline state; glycerol is a good example of this. The puzzle, then, is why the sample forms a glass rather than the more thermodynamically stable crystalline state.

While temperature is the traditional way glasses are formed, a second mechanism is to increase the pressure on a material that is otherwise held at constant temperature. It is not completely clear if a glass formed by increasing pressure is the same as one formed by decreasing temperature; see (Win & Menon 2006) for example. The pressure axis is quite similar to the idea of increasing the volume fraction of a colloidal suspension, as pressure modifies the density of a material.

Flow is not traditionally thought of as a way to "unjam" a glass, but more as a question about how a glass responds to shear stress. See (Falk & Langer 1998; Maloney & Lemaitre 2006) for some ideas related to flow in glasses.

As noted above in Sec. 3.3, polymer glasses are closely related to regular molecules glasses. The key difference is that in polymers, the entanglements are an obvious way to prevent crystallization, whereas with molecular glasses it may not be as clear. While polymer glasses and molecular glasses are thought to be due to the same underlying glass transition process, this is not yet completely confirmed. (Likewise, it's not clear if the other jammed states discussed in Sec. 3 are similar to glasses or not.)

In the past 10-15 years, *dynamical heterogeneity* has been widely observed in systems as they approach the glass transition. The idea is that the molecules within a glass have widely varying mobilities close to the transition. Some regions have slow dynamics, while other regions have highly mobile molecules. As the glass transition is approached, the sizes of the mobile regions may grow. It is thought that motion takes place in the mobile regions in a cooperative fashion, that is, in some way the molecules all move simultaneously so that none of them get in each other's way. At this point a wide variety of experiments and computer simulations have seen evidence for this behavior; for a review see (Ediger 2000). Dynamical heterogeneity is interesting as it has been seen in other soft materials such as colloids and foams; and it is also reminiscent of the surface flows in granular materials (see Sec. 4.4).

3.6 Optical microscopy

One feature that makes soft materials attractive for experimental study is that their components are much larger than atoms – polymers are long molecules that contain millions of atoms, colloidal particles range in size from nanometers to microns, foam bubbles are typically tens of microns or larger, and granular materials can be as large as centimeters in a pile of gravel. These large sizes make optical microscopy a powerful tool for studying these materials. Often the individual components of a material can be visualized, sometimes even while the material is being deformed on a macroscopic length scale. Thus microscopy can aid in connecting the microscopic details about the individual components to the macroscopic behavior of the material (Habdas & Weeks 2002; Prasad et al. 2007).

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4. Features of Jamming

The previous section introduced a variety of soft materials, and tried to compare and contrast them. The theory of jamming attempts to unite their common features.

4.1 Definition of jamming

I'll start by quickly summarizing the solid-like states of the soft materials discussed previously, and their control parameters.

Molecular glass	Formed by decreasing T or increasing P (thus increasing density r)
Colloidal glass	Formed by increasing particle volume fraction f
Emulsion glass	Formed by increasing droplet volume fraction f
Colloidal gel	Formed by increasing volume fraction f, or increasing attractive energy U
Polymer gel	Formed by increasing polymer concentration c, or by cross-linking polymers
Foam	Solid-like when bubble volume fraction f is increased
Granular material	Solid-like when volume fraction exceeds f_{RLP} (random loose-packing).

All of the states listed above are solid-like. This means they possess a yield stress, meaning that the materials can deform elastically under a small applied stress. If the applied stress exceeds the yield stress, the materials deform plastically and can start to flow. In general, if the stress is then removed, these materials can equilibrate back into a solid-like state, although the details of this can vary. (For example, as discussed in Sec. 3.4, a granular material can have a solid-like state whose properties depend on the shear history.)

Not only are all of these materials solid-like, but they are *amorphous solids* unlike crystalline solids. There is no long-range order in any of these systems. In a molecular glass, the system might be more stable in a crystalline state, but the molecules are packed randomly and unable to rearrange to form the crystalline state. In some of the other systems, such as foams and emulsions, often they are so polydisperse (comprised of a mixture of many sizes) that a crystalline state is nearly impossible to find.

The idea of *jamming* is that perhaps all of these amorphous solids are solid-like for the same reason; that there is a universal jammed state, and by understanding it, we understand all of these materials simultaneously. Moreover, in each case, there are control parameters that allow the system to be changed from unjammed to jammed. Perhaps there is a universal *jamming transition* that describes how a material changes from unjammed to jammed. The glass transition, then, is a specific case of the more general jamming transition. Loosely speaking, a jammed material is an amorphous solid. More precisely, a jammed material is one with a microscopically disordered structure that can support a finite stress without plastic deformation or flow.

It is important to note, though, that currently jamming is just an idea. It is certainly possible that all of the materials listed in the table are solid-like for unrelated reasons. Another possibility is that there are several different jamming transitions; some materials may share a common transition, but perhaps ultimately there will be found that there are distinct categories of these transitions, with sharp differences between categories. Why, then, has jamming become a very popular idea? The hope is that by comparing and contrasting these different systems, we may learn more about each of them. Ideas from one type of material may provide insight into another material. Individually each of these amorphous solids provides many puzzles, but perhaps considering them as a group, the puzzles might provide a collection of clues that leads to more understanding. The remainder of Sec. 4 will discuss these clues and puzzles.

One important idea of jamming is that the control parameters for the materials mentioned in the table can be unified by one "phase diagram." Figure 4.1 shows the first such proposed diagram; the control parameters are temperature T, inverse density $1/r$, and applied load. The states which lie within the curved surface, close to the origin, are jammed. The plane formed by T and $1/r$ is the regular glass transition, where the inverse density represents the influence of the more normal glass transition parameter P (pressure). At high T or low density, you have liquids; by lowering T or increasing density (decreasing $1/r$), a glass is formed. For colloids, emulsions, foams, and granular materials, the inverse density is equivalent to inverse volume fraction. (That is, the key idea is the amount of particles or droplets, rather than the physical density.) The truly novel idea is the third axis, the applied load. If the load is above the yield stress, the materials unjam and flow. Thus, all jammed states are formed by crossing the jamming transition surface (Fig. 4.1), and the continuity of the surface thus implies that there is a universal jamming transition and a universal jammed state, with perhaps differences that vary smoothly as a function of the parameters.

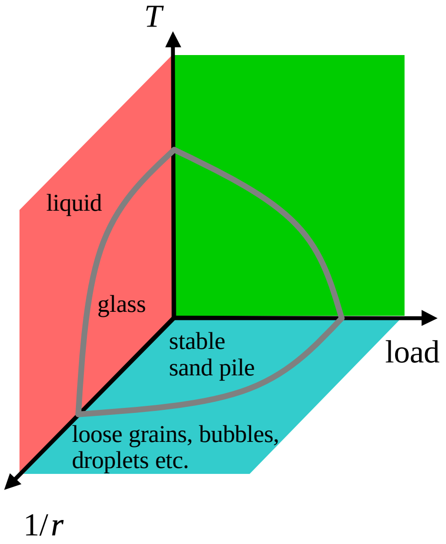

Fig. 4.1. Sketch of original jamming phase diagram (after Liu & Nagel, 1998). Jammed states lie within the curved surface, close to the origin. Unjammed states are outside. The red T – $1/r$ plane is the one normally used for molecular glasses, and thus traditional liquids and glasses lie in this plane.

This jamming phase diagram is the one most often shown at conferences. However, upon further thought, it has been replaced by a revised phase diagram, shown in Fig. 4.2. The three axes are the same: temperature, inverse density (now written as inverse volume fraction), and load (now in terms of the applied stress S). What has changed is the curvature, and the addition of point *J*. The curvature reflects the idea that a material can be kept in a jammed state with sufficiently high density even if the temperature is raised dramatically; and likewise at sufficiently low temperature and high density, a material remains jammed even with a very high applied stress. (The curvature was suggested by experiments (Trappe et al. 2001) and is obvious in hindsight.) The point *J* reflects that below a certain volume fraction, likely f_{RLP}, particles no longer touch each other and thus the system cannot be jammed at all. This is particularly clear in the case of granular materials, which are considered to be at $T = 0$ (see Sec. 3.4), and which unjam below random loose packing. For further discussion of point *J*, see (O'Hern et al. 2003) and other work by those authors.

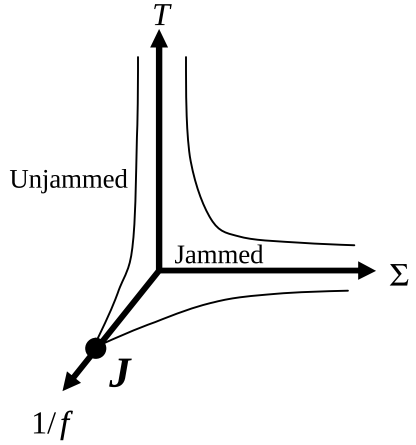

Fig. 4.2. Revised phase diagram (after O'Hern et al. 2003). Again, the jammed states are the ones near the origin, underneath the curved surface. Note that in some cases, the temperature axis *T* is replaced with $k_B T/U$, using the characteristic interaction energy *U* controlling particle interactions. Point *J* is a special point for granular systems. See text for details.

A further revision of Fig. 4.2 is possibly, by replacing the temperature axis *T* with $k_B T/U$. This could be used to consider sticky colloidal particles, for example, where *U* is the characteristic energy for the attractive interaction potential. Thus, increasing stickiness (increasing *U*) can lead to jamming, or for constant *U*, jamming can be induced by decreasing *T*. The conceptual idea is that thermal energy $k_B T$ provides a chance for colloidal particles to escape the interaction potential. Using $k_B T/U$ for the phase diagram axis also has the advantage of being nondimensional, like the density axis $1/f$. In some cases, the stress axis Σ is also nondimensionalized using information about the system.

The next sections will discuss common features of jammed systems. These are the pieces of evidence that jamming is indeed universal.

4.2 Amorphous solids

As noted in Sec. 4.1, the definition of a jammed system is an amorphous solid – microscopic disorder, existence of a macroscopic yield stress. Thus this cannot be said to be a common feature so much as the defining feature! Yet one important point to make is that to define a material as a solid can be a matter of time scales.

For example, consider molten glass. As noted earlier (Sec. 1), at high temperatures, glassy materials are liquids and flow quite easily. As the temperature is decreased, the viscosity of the material grows dramatically, by many orders of magnitude. One somewhat arbitrary definition of the glass transition temperature is the temperature at which the viscosity is 10^{13} times greater than water. This is set by human time scales; were one to try to measure a larger viscosity, it would take more time than one would probably want to spend. This then raises the question of whether the viscosity of a glass, far below the glass transition temperature, is truly infinite; or merely larger than we are able to see, even if we wait a long time.

Is it possible to observe flowing glass by waiting a long time, perhaps centuries? It is often stated that in very old cathedrals, the glass in the windows is thicker at the bottom. This seems to be true; but it is because of the particular techniques used to make glass panes long ago (Walker 2007). The techniques resulted in wedge-shaped pieces of glass, and the people who set the panes into the windows typically put the thicker side down; random orientations would have resulted in odd views through the windows due to refraction. It is estimated that for glasses to flow enough to account for the observed thickness variations, you would have to wait longer than the age of the universe (Walker 2007).

It is worth noting, however, that even solid materials flow if one waits long enough. However, flow in solids is due to defects in their crystalline structure, and the movement of these defects. This is a much different mechanism than flow in a liquid. Are glasses similar? That is, one could imagine that glasses might flow if you wait long enough, but by a qualitatively different mechanism than how they flow when they are liquids. The glass transition temperature would then be where the mechanism changes. I think this is probably unlikely; the viscosity changes smoothly as a function of temperature, and so even if a sufficiently cold glass changes its flow mechanism, it does not really explain the huge, smooth viscosity growth seen near the normally-identified glass transition.

The main point, then, is that it is possible that a jammed state only appears jammed because we haven't waited long enough. One possible answer to this concern would be if we found that the viscosity truly diverges, for example, having a temperature dependence such as $h \sim \left(T - T_g\right)^{-g}$. (This is definitely not the behavior of real glasses, but illustrates what I mean by a divergent behavior.) Another answer is that for some jammed materials, time is not a factor. Granular materials are a good example of this; static friction holds the grains in place, and prevents a sand pile from “melting” into a sand puddle.

4.3 Non-ergodicity

Related to the idea of jammed materials resisting flow, is the idea that the particles (or molecules) comprising the jammed material no longer can rearrange. More technically, a jammed material is *non-ergodic*, a term which means that some microscopic configurations of the material are unreachable.

Recall the distinction between microstates and macrostates, from thermal physics (Schroeder 1999). Consider a cup of water. The macrostate of the water is described by the water's temperature, density, volume, and pressure. The microstate of the water is described by giving the position and velocity of every molecule of H_2O in the cup. While we often care about the macrostate of the water – for example, we avoid drinking water that is at too high of a temperature – we do not care about the microstate. Furthermore, there are very many microstates that all correspond to the same macrostate, within our ability to measure the macrostate. Due to microscopic motion, the system is changing its microstate continually; but always in a way that is compatible with the observable macrostate. The idea of ergodicity, then, is that if one waits long enough, all possible microstates are seen (that are consistent with the macrostate). No microstate is impossible.

Now consider a sand pile. The macrostate could be described by the height and shape of the pile, and the density of the pile (perhaps described by the volume fraction occupied by the grains). Many possible microstates are consistent with the same macrostate; you typically don't care where each grain is, but only with the overall shape of the pile. However, an unperturbed sand pile will sit there indefinitely with no change in the microstate; no grain will move. Thus the sand pile is *non-ergodic*.

This idea, then, is related to sample flow. With an infinitesimal applied stress, in an ergodic sample, the particles (or molecules) eventually rearrange in such a way to relieve the stress. This will happen simply because the sample continually varies its microstate, and finds a microstate that is at a lower energy because the stress has been relieved. For a non-ergodic sample, this may not happen, and thus the stress is never relieved – the sample does not flow.

Related to this non-ergodicity are two additional features. First, the diffusion constant D for particle motion (or molecule motion) goes to zero (see Eqn. 2.3). Second, the relaxation time scale t goes to infinity. This time scale is the time scale for stress to relax, for example. Both of these observations ($D \to 0, t \to \infty$) depend on our patience and ability to measure them, as discussed above for the viscosity.

While it seems that all jammed materials are non-ergodic, it is worth noting that non-ergodicity is not a defining feature of a jammed state (Prasad et al. 2003).

4.4 Spatially heterogeneous dynamics

A common feature of unjammed materials which are close to their jamming transition is *spatially heterogeneous dynamics*. Figure 4.3 shows a good example of this. Some particles in this image are moving very little, whereas others move large distances in the same time. The ones with larger motion are typically adjacent to each other, and for example several "strings" of moving particles can be seen, as well as some regions where clumps of particles are all highly mobile. In colloidal "liquid" samples near the colloidal glass transition, this motion is also temporally heterogeneous. As the transition is approached by increasing the volume fraction, the motion involves larger groups of particles, but also becomes more intermittent (Weeks et al. 2000, Kegel et al. 2000). This was first directly seen in computer simulations, which especially focused on the string-like motion (Donati et al. 1998).

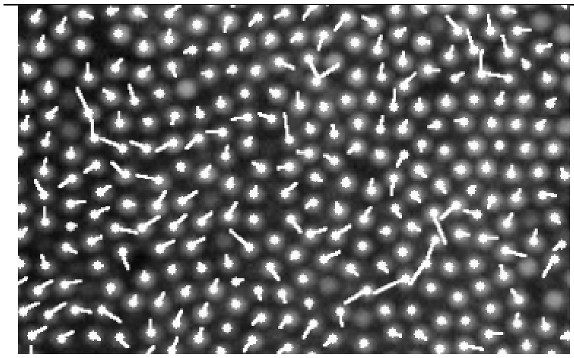

Fig. 4.3. Microscope image of a dense colloidal liquid, with superimposed displacement vectors on the particles. This is a 2D image of a 3D sample, and some particles may move perpendicular to the plane and thus not have displacement vectors on them. The particles are 2.2 μm in diameter. The sample is at $f \approx 0.5$, and the image is taken near the coverslip, thus resulting in much of the motion being in the plane of the image.

The idea of spatially heterogeneous motion was first proposed for glasses by Adam and Gibbs (1965). They thought that perhaps, near the glass transition, liquids would relax stress by the action of "cooperatively rearranging regions." Within a region, all of the molecules move in some cooperative fashion, and the motion of each region is unrelated to the other regions. Figure 4.3 gives a better idea of what this might mean; here the cooperation seems to be that particles are mobile when they move in similar directions to their neighbors. Over time, every particle in a given sample will have a chance to move in this fashion; no particle is special, and the sample remains ergodic. There is now a large amount of evidence for spatially heterogeneous motion in molecular materials close to the glass transition; for a review, see (Ediger 2000).

Spatially heterogeneous dynamics are also seen in other systems near the jamming transition, although the character of this in some cases seems qualitatively different. For example, with the flow of sand, in many situations the motion of sand grains is restricted to the surface of the material. Avalanches are a good example. Thus the heterogeneous dynamics are not throughout the sample, as with colloids and glass-formers, but are located at the boundary. Sheared foams appear more similar to colloids. Rearrangements in foams are often due to four bubbles exchanging positions: two move apart, two move together, which is termed a "T1" event. For more on the details of foam flow, see (Kraynik 1988).

Currently it is unclear if spatially heterogeneous dynamics are a feature of the jamming transition; or if they are a possible explanation. One criticism of this as an explanation is that it focuses on the moving particles, whereas a jammed state is thought of as due to stationary particles (Conrad et al. 2006). On the other hand, the idea of jamming is related to the loss of a sample's ability to flow, and it seems suggestive that the mechanism of flow changes near the jamming transition (in other words, flow proceeds by means of these cooperatively rearranging regions).

4.5 Force chains and percolation

This next idea comes from granular materials, in particular, experiments done with soft photoelastic disks such as those pictures in Fig. 4.4. Photoelastic disks can rotate polarized light if the disks are compressed. Thus, by viewing the disks between crossed polarizers, the image is dark where the disks are uncompressed, and lights up where disks are compressed. In this way *force chains* are visible: chains of particles that all experience large forces. In Fig. 4.4, the gravity points downward, and the disks are being compressed from above by the weight of a piece of metal with scalloped edges. The weight of this metal is being supported by these force chains; thus some disks bear most of the weight, whereas many others are almost irrelevant to bearing this weight. This is in contrast to a liquid, for example, where the pressure varies smoothly in space.

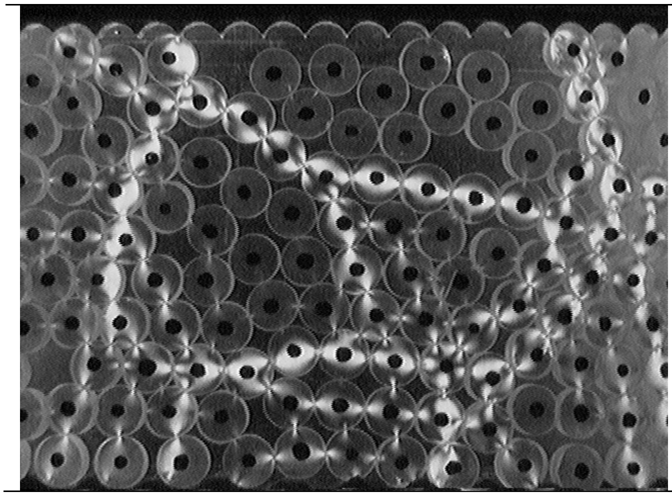

Fig. 4.4. Photoelastic disks, viewed between cross-polarizers. They are confined to a thin channel so that they are a two-dimensional system, and they are compressed between the top and bottom of the image. The bright particles are experiencing large forces. (Picture from SV Franklin & ER Weeks.)

Force chains have been carefully investigated using these photoelastic disks, most notably by the group of Bob Behringer (for example, Geng et al. 2001). There is also evidence that they exist in three-dimensional systems (Liu et al. 1995). One observation is that the force chains seem to be most evident – and most spatially heterogeneous – close to the jamming transition volume fraction (or, for 2D systems, the area fraction). This makes sense. Below the jamming volume fraction, grains (or disks) do not need to touch each other, and no forces are felt. Well above the jamming transition, all grains are deformed and feel strong forces; the forces are much more homogeneously distributed.

Recently, force chains have been investigated in emulsions by two groups (Brujic et al. 2003; Zhou et al. 2006). The deformation of droplets was observed using confocal microscopy, and the forces could then be determined. This has allowed for a more careful understanding of force chains in 3D.

Force chains are a powerful idea in granular physics, and almost all experiments related to dense granular materials invoke force chains as an explanation for their observations (Losert et al. 2000; Albert et al. 2000). It is less clear if force chains are relevant for other jammed systems. Certainly if they apply to emulsions, they ought to apply in foams, which are quite similar (Secs. 3.1 and 3.2). For colloids, it seems more difficult, as the particles do not touch in many situations. For gels, while force chains are not obvious, certainly the particles are arranged into branching chains.

This brings us to the idea of percolation. In a granular material, ultimately the force chains come to an end when they exert forces on the boundaries (and the boundaries in turn exert forces on them, by Newton's 3rd Law). In a gel, the tendrils of the gel extend to the boundaries of the material. Perhaps in an amorphous material, these apparently random connections are constrained by having to end on the boundaries – in other words, to span the system. This seems related to the problem of percolation, as illustrated in Fig. 4.5. In percolation, each site of a lattice is on or off, with probability p to be on. Above a critical value of p, a connected chain of "on" sites will span the system, connecting from one side of the lattice to the other, as shown in the middle picture of Fig. 4.5. The critical value of p is defined in the limit of an infinitely large lattice.

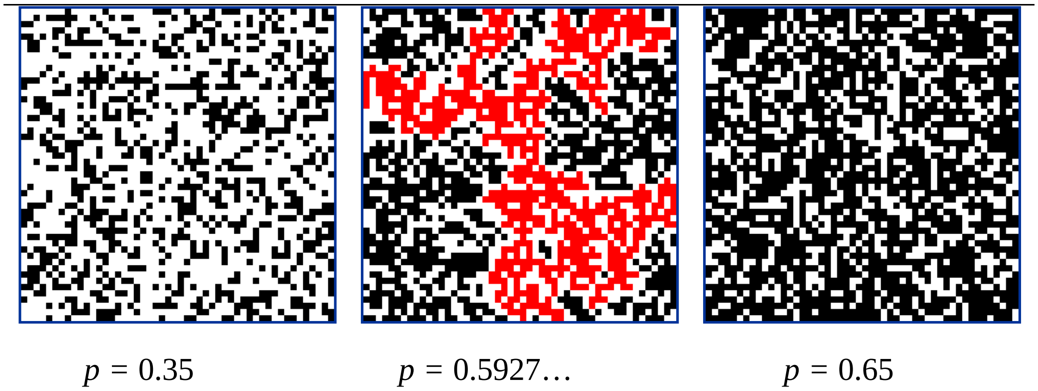

Fig. 4.5. Percolation in a 100 × 100 grid. Sites are on (black) randomly with probability p, given below each picture. In the middle picture, the density of on sites is high enough that a connected chain of them connects the four boundaries, as shown in red.

While the percolation picture looks suggestive, it is not clear that it applies to jammed systems, where there are spatial correlations for physical reasons. In a percolation simulation, each lattice site is independent. The probability of a site being "on" is unconnected to the state of neighboring sites. This is not true in force chains, by Newton's 3rd Law. A particle in the interior of a sample that feels a strong force must necessarily be supported on at least two sides by other particles, which it then exerts forces on. Likewise, in a colloidal gel, particles diffuse around freely until they touch another particle. The volume fraction for gelation is not set by a universal threshold, as for percolation, but by the attractive forces between particles. As noted in Sec. 3.3, for very sticky particles, they can form a gel at low volume fractions, which will have a much more tenuous appearance than Fig. 4.5. For the colloidal glass transition, perhaps the entire sample becomes glassy simultaneously; although see (Conrad et al. 2006) for the possibility of percolating immobile regions.

4.6 Aging

Once a material is jammed, it is out of equilibrium (non-ergodic). In many cases, its properties then change as a function of time; this is known as *aging*. In general, properties such as the relaxation time scale will be a simple function of the *age* of the sample, defined as the time since the sample was put into the jammed state. Data from an aging colloidal glass are shown in Fig. 4.6. The initial time is set by stirring the sample at very high strains; the ending of the stirring sets $t_{\mathrm{age}} = 0$. At early ages (less than one minute), the mean square displacement rises rapidly, and it takes a time scale of about 60 s to see motion of about $\langle \Delta x^2 \rangle \approx 0.1\, mm^2$. At later ages, it takes much longer to observe the same amount of motion.

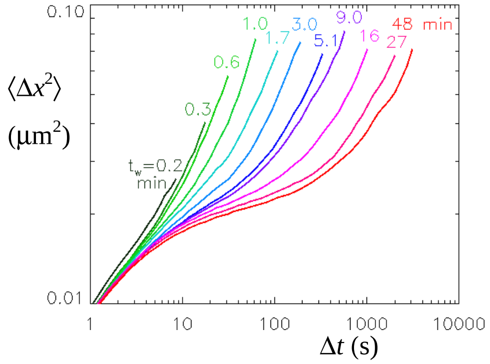

Fig. 4.6. Mean square displacements from an aging colloidal glass. The age of each curve is indicated (in minutes). Data from (Courtland & Weeks 2003).

Aging is also well known in the context of molecular glasses (Angell et al. 2000). The key idea of aging is that the system is trying to minimize its free energy. By slightly changing the positions of the molecules, the system can find a slightly better free energy, perhaps by decreasing the potential energy, or increasing the system's entropy. However, over time, the system is in a fairly good local free energy minimum, and finding configurations with lower values of free energy becomes progressively more difficult. Thus changes in the configuration occur less frequently – which would be measurable as slowing of molecular motion, such as shown in Fig. 4.6 for colloidal particles. Thus aging is connected to the non-ergodicity of the sample: an ergodic system explores configurations at a steady rate, as all microstates are equally probable and easy to reach, whereas an aging system is always slowing down its exploration.

Less obvious is how aging occurs in a granular system. As noted earlier, a sand pile will not change at all if left by itself, as it is held motionless by static friction, and does not have sufficiently thermal energy to explore other configurations. To force any change, the system needs an external stimulus, an idea used by clever experiments (Nowak 1998). Figure 4.7 shows the idea; a container of sand is vibrated, perhaps crudely by striking it with a hammer, or shaking the container vertically in a controlled fashion. The height of the sand pile is measured after each "tap". The sample gradually compactifies, with the overall volume fraction growing roughly logarithmically with the number of applied taps. After many taps (perhaps 10^4 – 10^5), the sample approaches a steady state, which depends on the amplitude of the taps (Nowak et al. 1998). This logarithmic growth appears quite similar to aging in molecular glasses and colloidal glasses, although clearly the origin differs (external perturbations for sand, thermal motions for glasses). Note that in granular systems, this slow increase of the volume fraction is not monotonic; individual taps can result in a decrease of the volume fraction. However, the average trend is clear.

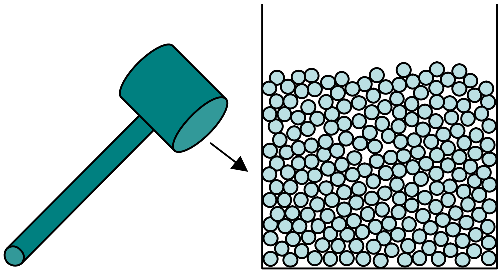

Fig. 4.7. Sketch of granular aging. A column filled with sand is given a series of taps. Often this is done by vertically shaking the container, but even crude taps with a hammer can result in similar granular aging.

As described in Sec. 3.2, foams coarsen over time, with the average bubble size always increasing. This too resembles aging, but is not due to thermal motion of bubbles, or externally driven motion either. Rather, it is due to diffusion of gas through the bubbles. It is not clear if these three types of aging (glasses, granular materials, foams) are really the same phenomenon or merely superficially similar.

4.7 Shear history and high-strain behavior

All of these samples have interesting behaviors at high strains, in some cases requiring high shear rates as well. Consider a material between two parallel plates, which are moved in opposite directions; this is a simple example of *shear*. Recall that *strain* is a measure of how far the plates are moved, and *stress* is related to the force required to move the plates; for more careful definitions, see (Larson 1999; Jones 2002) for example.

Foams and emulsions are composed of bubbles and droplets, respectively. At high shear rates, these components can rupture irreversibly. In fact, this is the technique needed to produce smaller droplets in an emulsion (Mason 2006). This changes the system irreversibly; often the properties of a foam or emulsion with smaller sizes are quite different (Mason 2006).

A gel sheared at high strain can have its bonds broken. If the shearing is stopped, these bonds have a chance to reform, but probably will make different connections than the original gel. Most likely the structure, and perhaps the subsequent properties of the gel, depend on the shear history.

For colloidal glasses, shear can be used to influence the aging. As noted in Sec. 4.6, high shear is used to initialize the age of a colloidal glass (Courtland & Weeks 2003). Lower amounts of shear can be used to "over-age" a sample; see for example (Bonn et al. 2004).

In granular media, as already noted, a sample's characteristics can depend on the shear history. Aging provides a simple example of this (Nowak et al. 1998), although see also (Losert et al. 2000).

4.8 Summary

At this point I have listed several common traits:

Trait	Relation to jamming
Amorphous solid	Defines jammed state
Non-ergodic	Property of jammed state
Spatially heterogeneous dyanamics	As jammed state approached
Force chains & percolation	Both jammed and unjammed samples close to the transition
Aging	Property of jammed state
Dependence on shear history	Property of jammed state

Note that several of these relate to the jammed states, and two relate to unjammed materials close to the jamming transition. This table is a collection of suggestive similarities between different materials; but as noted in Sec. 4.1, these similarities do not prove that all jammed materials are the same, or that there is a universal jamming transition. At the very least, they identify behaviors that we would like to explain. I would hope that any theory of the jamming transition, or even a theory of the jamming transition in a specific system, would help explain the behaviors discussed in this section.

While Sec. 4 has tried to argue that all jammed materials share universal behaviors, and that the idea of a generic jamming transition is plausible, Sec. 5 will discuss problems with the idea of jamming.

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5. Open Questions about Jamming

The previous section described common features of jammed systems. This section poses several questions that theories of jamming may try to address, and points out complications that were neglected in Sec. 4. Note that one interesting question, that of time scales, was raised in Sec. 4.2.

5.1 Are attractive and repulsive systems the same?

Some jammed systems have attractive interactions: glasses have chemical bonds, colloidal gels have sticky particles. Some jammed systems have only repulsive interactions: colloidal glasses, emulsion glasses, granular particles. (Of course, at short range, both molecules in glasses and particles in colloidal gels have repulsive interactions. Nonetheless, they seem to jam because of attractive interactions; this is most clear for gels.) Is jamming the same in attractive and repulsive systems?

The jamming phase diagram is shown again in Fig. 5.1 (similar to Fig. 4.2). The particle interaction is quantified by *U* which is the characteristic energy scale for the interaction potential. This could be the depth of the potential well for an attractive depletion interaction (Sec. 2.3) for example. It is less clear what *U* might be for a repulsive interaction; for ideal hard spheres (Sec. 2.6) the interaction energy is zero. Note though that this phase diagram makes no attempt to distinguish between attractive and repulsive interactions, and *U* is always considered a positive number.

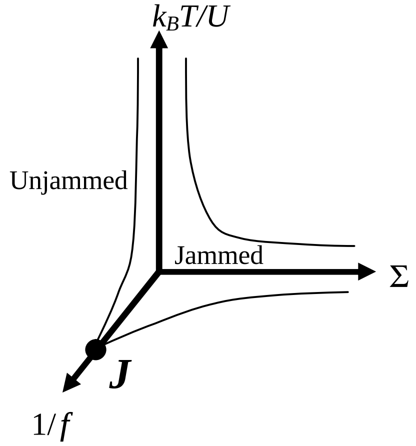

Fig. 5.1. Revised phase diagram (after O'Hern et al. 2003). The jammed states are the ones near the origin, underneath the curved surface. The temperature axis has been nondimensionalized using *U*, the characteristic energy scale for particle interactions.

How should the phase diagram be modified, then? One bit of intriguing evidence that both attractive and repulsive systems can be the same has come about through the study of slightly sticky colloidal particles. Near the colloidal glass transition, the phase diagram can look like Fig. 5.2 (Dawson 2002). For $U = 0$, the horizontal axis is just the regular hard sphere glass transition (the same as shown in Fig. 2.7, with $f_g = 0.58$). This then is a purely *repulsive glass*. If the particles become slightly sticky, that is, if U becomes nonzero, this doesn't change the glassy state significantly. As U is increased further, at some point appears a different glassy state, and this is termed an *attractive glass*. At the coexistence line between the attractive and repulsive glasses, the two states look different. But, evidence indicates that by adjusting the parameters to follow a path in phase space around the point A_3 in the phase diagram (Fig. 5.2), you could smoothly vary the system between these two states, and thus they are similar, just as liquids and gases are both really just fluids at different densities.

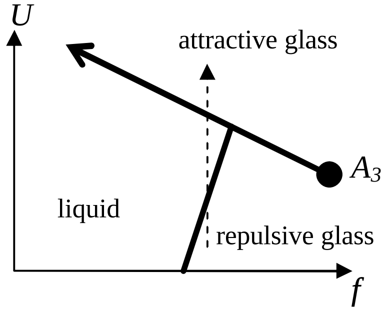

Fig. 5.2. Sketch of glass transition phase diagram for sticky colloids (after Dawson 2002). The point A_3 is a singularity which terminates the coexistence curve between the attractive and repulsive glass states. See text for discussion of dashed arrow.

Figure 5.2 does raise a question. Imagine a system at constant volume fraction where the interaction energy is raised from $U = 0$. The system can start as a repulsive glass, enter the liquid part of the phase diagram, and then enter the attractive glass region – all at constant f (following the dashed arrow shown in Fig. 5.2, for example). It seems counterintuitive that adding attractive forces between particles could unjam the system! This seems to be only possible if the attractive interaction is very short range, 3% of the particle diameter or shorter (Dawson 2002). What is happening here? I am not completely sure. One explanation is that if particles stick together in clumps for short periods of time, it could locally increase the volume fraction, thus decreasing the volume fraction nearby, allowing the less dense region to rearrange in a liquid-like fashion. Certainly near f_g, small changes in volume fraction have a large influence. By further increasing the attractive forces, the particles stick together for a longer period, and thus start forming system-spanning chains that support stress and give the sample solid-like properties.

So, Fig. 5.2 presents a possible answer, that attractive and repulsive jammed systems may be smoothly changed from one to another (by moving around the A_3 point); but that the phase diagram (Fig 5.1) may have an extra wrinkle in it, with the coexistence line.

5.2 Is fragility required?

The term jamming was used in an article by Cates et al. (1998). This article was then reviewed by Liu and Nagel (1998), who introduced the jamming phase diagram (Fig. 4.1). However, the term jamming means different things in these two articles. While Liu and Nagel discuss jamming as defined in Sec. 4.1, in the article by Cates, jamming refers to structures induced by the applied stress, as suggested by Fig. 5.3. For example, the left picture in Fig. 5.3 shows a colloidal suspension between two plates which shear the suspension. This induces a chain of particles which oppose this shear; should the plates stop moving, Brownian motion quickly breaks up the chains. In other words, the colloidal suspension is *not* jammed unless the plates are moving. This is known as shear thickening. Shear thickening is seen when mixing corn starch and water. If the mixture is stirred slowly, it is easy to stir. If stirred rapidly, the effective viscosity rises dramatically, and it acts much more like a solid (Larson 1999, Jones 2002).

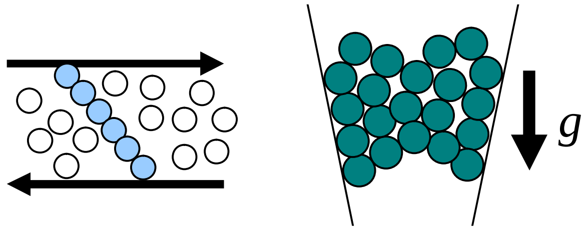

Fig. 5.3. Jamming induced by external forcing. Left: particles in a colloidal suspension, between two plates moving in opposite directions. Shaded particles form a chain opposing the motion. Right: Sand falling through a hopper, with an arch formed supporting the sand.

Related to this is the idea of *fragility*, in that the chain of particles is fragile to some applied forces. In particular, the chain supports large forces along its length; but would be easily broken by a small force applied perpendicular to its length. Likewise, the arch shown supporting the other grains in the right picture of Fig. 5.3 could be easily broken by small horizontal forces. In fact, jamming such as shown in that sketch often occurs with grains flowing out of hoppers, and this sort of jamming is broken by hitting the hopper, thus disrupting the arches.

This type of jamming is distinct from the picture that has thus far been presented in this article. Cates states that "...I would prefer to use [the term jamming] only for systems that arrest because of an applied stress." (Cates 2003). But, the viewpoint taken by this article and by (Liu & Nagel 1998) and other authors is that jamming can describe states at rest, such as sand piles and colloidal glasses. It is important to be aware that "jamming" may have multiple meanings, and you should be careful when reading different articles.

One way to integrate these two ideas might be to modify the phase diagram. Figure 5.1 indicates that upon lowering the applied stress, a system could pass through the jamming transition and then become jammed, and stay jammed as the stress is lowered to zero. However, it is possible for some systems that at sufficiently low stress, there could be reentrant behavior, and the system could unjam. ("Reentrant" means that as the stress is monotonically decreased, the system reenters the unjammed part of phase space. This is different from most phase transitions, which happen only once as a parameter such as temperature or pressure is varied.) This might make sense for systems with volume fractions below f_{RLP}, for example.

5.3 Can jammed and unjammed phases coexist?

Often when systems are sheared, shear bands form (Lauridsen et al. 2004; Losert et al. 2000). That is, most of the strain occurs over a narrow band of the material, known as the *shear band*. The rest of the material remains relatively unstrained. This is another common feature of jammed systems, although it seems far from universal behavior, so thus was not mentioned in Sec. 4.

The implication of shear bands is that in some materials, there could be both jammed and unjammed regions in the material at the same time. Thus when the shear is applied, the shear band represents unjammed, fluid-like material, whereas the unstrained material is still jammed. Shear bands thus could be spontaneous phase separation between these two states, if this picture is correct. This would then be a further feature to be explained by jamming theories. I am unsure if macroscopic phase separation is possible in situations without shear, although in some gels there might be microscopic phase separation between a connected backbone of particles, and some freely diffusing clusters of other particles.

5.4 Is there hysteresis near the jamming transition?

The phase diagram (Fig. 5.1) presents a simple surface for the jamming transition. However, clearly the picture is often more complex.

For the molecular glass transition, the glass transition temperature usually depends on the temperature quench rate (Angell et al. 2000). That is, some materials will crystallize if the temperature is slowly lowered. By rapidly lowering the temperature, a glass is formed at some temperature T_{g1}. If the quench rate is further increased, often the glass forms at a higher temperature T_{g2}. Furthermore, the properties of a glass can depend on further thermal history, such as annealing at different temperatures (Angell et al. 2000). Aging, as discussed in Sec. 4.6, further changes the state of a glass. This frustrates the idea of a simple phase diagram such as Fig. 5.1 correctly capturing the state of a jammed system.

Granular materials likewise can have hysteretic behavior (Losert et al. 2000; Nowak et al. 1998). In particular, often the shear history of a granular system sets up force chains (Sec. 4.5), and thus the system has anisotropic responses to subsequent shear (similar to the discussion in Sec 5.3).

While I am unaware of direct hysteretic effects in sheared foams, foams do coarsen with time, as discussed in Secs. 3.2 and 4.6. Thus the state of a coarsening foam depends on time and again is not determined only by the parameters in the phase diagram.

5.5 What is missing from the jamming phase diagram?

Some imperfections of the phase diagram have already been mentioned in this section: a distinction between attraction and repulsion, and possible reentrant behavior with shearing. There are other parameters which could be added to the phase diagram as new axes.

Polydispersity is an interesting one. Hard sphere systems with a wide range of sizes of the spheres have a jamming transition at higher volume fractions than monodisperse spheres. And, in nature, polydisperse systems are much more common. While sometimes binary systems are studied (mixtures of two particle sizes), the polydisperse case is much less commonly studied by physicists. When it is studied, it is often to prevent crystallization, especially for simulations of the glass transition (see for example Donati et al. 1998; Doliwa & Heuer 2000). Thus clearly the influence on jamming may be nontrivial, allowing systems to jam that might not jam if they were monodisperse, and varying the transition density for others.

Shape is another often overlooked parameter. Some recent work has studied jamming in granular rods (Stokely et al. 2003; Desmond & Franklin 2006), see Fig. 5.4 for example. In these systems, rods can entangle with each other, somewhat like entangled polymers. Because of this, rods can jam at much lower volume fractions than spheres (Desmond & Franklin 2006). Recent work has also studied the packing properties of M&M's™ (Man et al. 2005). Molecular shape also can influence properties of molecular glasses (Angell et al. 2000).

Fig. 5.4. Image of acrylic rods in a narrow tumbler. The rods are 2.5 cm long and have an aspect ratio (length/width) of 16. The tumbler is four rod diameters across, so the experiment is quasi-two-dimensional. The pile shows a complicated surface profile and large voids throughout. This snapshot is during the collapse of a large void in the center; the resulting motion occupies a large portion of the pile (blurry moving rods at upper right). Image from Gallagher & Franklin 2005 (unpublished).

Often in this article, reference has been made to attractive or repulsive forces, characterized by a typical energy scale *U*. However, the reality is that the interaction between pairs of particles separated by a distance *r* is given by a function *U(r)*. The shape of this potential function is important and for example has a strong influence on the qualitative shape of the phase diagram shown in Fig. 5.2 (Dawson 2002).

Dimensionality might also play a role in the jamming transition. For example, crystallization is very hard to avoid in a two-dimensional system of monodisperse hard disks, whereas it is somewhat easier to avoid in a three-dimensional system; a rapid "density quench" (increasing density faster than the sample can crystallize) is not as necessary in three dimensions.

In summary, this section is meant to raise questions for jamming theories, and to illustrate that jamming is trying to unify a diverse set of systems with rather complex behavior. But, certainly the simplistic phase diagram (Fig. 5.1) may be reasonably correct, even if there are other cuts through phase space that could be considered.

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6. Summary

A wide variety of systems are considered in Secs. 2 and 3. These include glasses, colloidal suspensions, emulsions, foams, gels, and sand piles. To this list could be potentially added bubble rafts (where a layer of bubbles floats on the surface of water); shear thickening (as discussed in Sec. 5.3); and perhaps even traffic jams of automobiles. The relevant physics varies widely. As noted in Sec. 5.1, some systems are dominated by repulsive interactions between the constituents, whereas others have attractive interactions. Details that may be relevant include chemical bonds, friction, and Brownian motion – but it is hard to imagine a system where all three of these are relevant for the system properties. Also, for systems such as colloidal suspensions, emulsions, and foams, the viscosity of the continuous liquid phase might be important, as well as the compressibility of the colloidal particles (or the viscosity and compressibility of the droplets and bubbles).

These systems all possess an apparent jamming transition. Simply put, they all can be in a state which is microscopically disordered, and which macroscopically can support weight with only elastic deformation. These two features (microscopic disorder, elastic response) are the defining characteristics of a jammed state. Other common behaviors were discussed in Sec. 4, and include non-ergodicity, dynamical heterogeneity, and aging. It is unclear how important these other features are. It is possible they will be key ideas for explaining how jamming occurs, but it is also possible that these behaviors are merely things that need to be explained. It is also possible that they will be seen to be qualitatively different in different systems, and thus merely superficially similar behaviors. If they are really system-specific, they would then not be amenable to a common theoretical explanation.

Finally, as noted in Sec. 5, there are many open questions that are worthy of further experimentation and theoretical explanation. For experiments and simulations, it is always important to consider time scales, especially as behavior slows down near the jamming transition. More importantly, the popular phase diagrams (Figs. 4.1, 4.2, and 5.1) are suggestive, but should not constrain one's thinking. Many details may be missing, such as an attractive/repulsive distinction, hysteresis near the transition, and other parameters such as polydispersity and shape. Ideally physicists searching for universal behavior of jammed systems will be able to show that these details are all part of a comprehensive phase diagram.

As an experimentalist, I will also be happy if jamming is not a universal phenomenon; if the jammed systems are all distinct entities. By learning enough to confirm the distinctions between these different systems, we will learn a lot of interesting physics. All of the systems mentioned in this review article are interesting in their own right, and if the idea of jamming merely motivates cross-fertilization of ideas between different areas, that is already a large success.