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Colloidal arrest by capillary forces

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Abstract

Three situations are compared in which capillary forces, arising at a solid–fluid–fluid contact line, can lead to an arrested state. In the first, an isotropic fluid that enters a biphasic isotropic/nematic coexistence is arrested in its phase separation by the presence of colloids. In the second, colloids coating an interface between two fluids can inhibit the Rayleigh–Plateau instability. In the third case, capillary stresses acting at the surface of a droplet of dense colloidal suspension, surrounded by air, can explain the observed bistability between a fluid droplet and a jammed ‘granule’. Common features between these problems are emphasized.

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

1. Introduction

Colloidal suspensions generally involve solid particles in a single solvent. Sometimes, however, one must consider solid particles in the presence of an interface between two solvents, or between a solvent and air. A classical example of the two-solvent case is the physics of so-called ‘Pickering emulsions’ where spherical emulsion droplets of oil can be stabilized in water (or vice versa) by coating them with particles whose wetting properties favour interfacial adsorption. (This is the case for neutral wetting, where the relevant contact angle is 90° ; see below.) Important recent work on Pickering emulsions is reviewed in [1]. In the present paper, three situations are compared where interfacial forces lead to states of arrest. In all these cases, the system is trapped by high barriers in a metastable state, which is not that of lowest free energy.

There is a basic reason why capillary forces and colloids combine to create high barriers. Colloids are large compared to molecules, yet interfacial tensions between immiscible fluids, or between a fluid and a solid, are generally of order $k_B T / \ell^2$, where ℓ is a molecular length. Thus the change in interfacial energy ΔU in moving a colloid of radius a from one solvent to another (or out of its solvent and into air) obeys

$$\Delta U / k_B T \simeq (a / \ell)^2$$

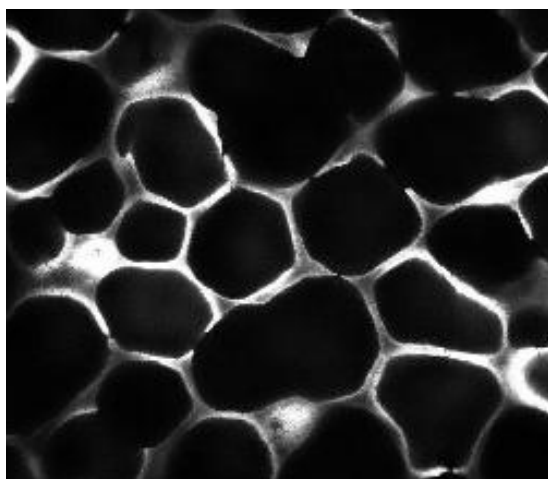


Figure 1. Nematic–colloid composite. The colloidal regions occupy the domain walls between nematic droplets. The microstructure observed depends on quench rate and volume fraction. Image courtesy of Cleaver, from [3].

which, even for colloids a few nanometres in radius, is a very large ratio. Hence any local minima in free energy created by capillary forces on the scale of a colloid are likely to be deep compared to $k_B T$, and arrest of metastable states is very efficient.

An extremely simple example is the case of a single spherical colloid at an interface between two solvents. Suppose the two solid–liquid interfacial tensions are identical (perfectly neutral wetting); this means the surface energy of the colloid is exactly the same whether it is in the bulk of either fluid, or placed symmetrically at the interface between these. However, in the latter case, the *fluid–fluid* interfacial energy is reduced by $\sigma\pi a^2$, where σ is the tension of the fluid–fluid interface, and πa^2 is the area of the disc of that interface covered up by placing the colloid on it. For the reasons given above, $\Delta U = \sigma\pi a^2/k_B T$ is typically very large, so that adsorption of a neutrally wetting colloid to the liquid–liquid interface between two solvents is effectively irreversible by Brownian motion [1].

The situations discussed below are slightly more complex; in all of them, capillary forces create states of colloidal arrest that thermal motion cannot overcome.

2. Nematic–colloid composites

Consider a thermotropic nematogen above its isotropic/nematic transition. It is often possible to suspend colloids in such a nematogen. However, when quenched below the nematic transition, colloids tend to be expelled by precipitation. This is because the nematic director has to obey an anchoring condition at the colloidal surface (typically, it must be normal to the surface); this is not compatible with a uniform state of nematic order and hence a high price in nematic elastic energy must be paid by each colloid. This can be reduced by aggregation or precipitation.

In certain systems, however, colloids remain macroscopically trapped in the nematic phase, but aggregate mesoscopically during the phase transformation into exotic foamlike structures (figure 1), imparting mechanical rigidity to the overall material so as to create a composite soft solid with rapidly switchable nematic activity [2].

As understood until quite recently, this problem appears to have little connection with the issue of capillary forces. Specifically, it was argued [2] that nematic droplets nucleate early in the quench and that, as these droplets grow, the colloids would be excluded from them and therefore gathered into the domain walls, where the anchoring energy, perhaps combined with simple van der Waals forces, would sequester them. However, recently an improved

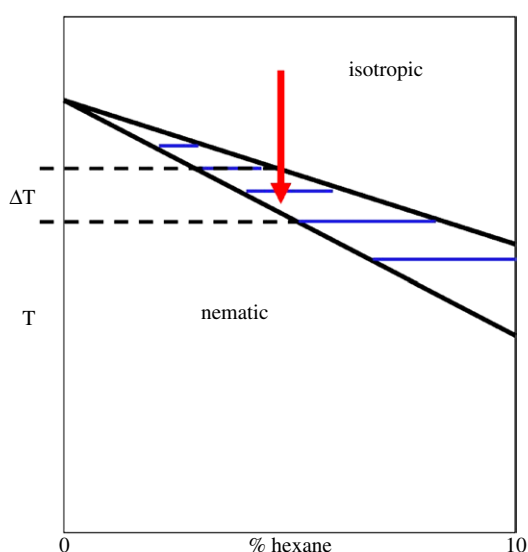


Figure 2. Schematic phase diagram of nematic/hexane mixture, showing finite miscibility gap over temperature range ΔT for nonzero hexane content.

understanding of the kinetics of formation of the nematic foam has emerged [4, 5] in which interfacial effects play a greater role than anticipated. It was found experimentally that if the colloidal particles, which are prepared in hexane, are totally dried out before being mixed with the nematogen, no solid composite is formed on quenching into the nematic phase [4].

Careful further experiments [4, 5] have shown that the presence of hexane drastically reduces the rate of growth of the nematic droplets. Indeed, the presence of a second solvent, even at the level of a few per cent, creates at the isotropic/nematic transition a miscibility gap spanning a finite temperature range (figure 2). This means that, given some initial density of nuclei for the nematic droplets (and ignoring colloids for the moment), their growth rate is determined directly by the rate of change of temperature. For example, if one reduces the temperature to the point where the system is midway along a tie-line (figure 2) then the nematic droplets will have grown to fill half the volume. If the temperature is now held constant for a period, no further growth occurs; if temperature ramp-down is later resumed, the growth of droplets resumes at a rate fixed by dT/dt . This is very different from the situation without a second solvent (on the extreme left-hand axis of the plot): here the isotropic/nematic transition is abrupt with temperature and—ignoring possible temperature inhomogeneity within the sample—the growth rate of nematic droplets is governed not by the quench rate, but by the intrinsic dynamics of the nonconserved nematic order parameter.

Turning now to the colloids, an interesting paper by West *et al* [6] calculates the critical interfacial velocity below which a moving interface between nematic and isotropic phases will sweep up a colloidal particle, and above which the particle will be left behind. This directly involves interfacial physics: the question is whether the anchoring energy, which tries to expel the colloid from the nematic, exerts a strong enough tension at the solid–isotropic–nematic contact line to overcome colloidal inertia. The result of [6] is that the critical velocity obeys $v^* \sim W(K\rho)^{-1/2}$ with W an anchoring tension (of order 10^{-6} J m^{-2}), K a representative nematic elastic constant (of order $10^{-11} \text{ J m}^{-1}$) and ρ the density of a colloid (of order 10^3 kg m^{-3}). This gives v^* in the range of millimetres per second; it is independent of particle size over a wide range. This calculation does not take direct account of the presence of a second solvent; this might increase the isotropic–nematic tension and so increase v^* .

Only for interfacial velocities $v < v^*$ will colloidal particles be swept before the growing nematic droplets to create the foamlike texture. It is observed [5] that in the absence of hexane the intrinsic growth rate v of the droplets is at least millimetres per second, whereas with hexane present, for the reasons given above, it can be far less, and moreover can be directly controlled via the quench rate. Thus, a key role of hexane is to modify the interfacial velocity v so that the sweep-up of the colloidal particles becomes possible, leading finally to the arrested structure [4]. The issue of sweep-up is closely analogous to one involving the capillary detachment of particles from a fluid–fluid interface by an external force such as gravity. That problem is simulated in [7], and we describe related simulations in section 3.

For colloid–nematic composites, several interesting issues remain to be fully resolved, particularly concerning the state of nematic order and/or nematogen/hexane phase separation in and around the colloidal regions at temperatures well below the transition. It is not clear whether capillary forces arising from any continuing microphase separation between nematogen and hexane, in the neighbourhood of the colloids, plays a role in maintaining the structure. However this does seem probable, at least in a finite temperature interval below the bulk miscibility gap for the nematogen–hexane mixture.

3. Colloids in binary solvents

We now turn to our second problem. This involves the physics of neutrally wetting colloids at interfaces between two solvents; the case of a single colloid was discussed in the introduction. We have initiated studies of this physics by lattice Boltzmann simulation, and algorithmic details, as well as some preliminary results, have already appeared [7, 8]. We do not repeat details of the methodology here, but present new simulation results for a very specific geometry.

We address the time evolution of a long cylinder of one fluid within another. It is well known that such a cylinder is unstable with respect to a peristaltic, Rayleigh–Plateau instability, whereby the cylinder can continuously decrease its interfacial area by a sinusoidal variation in radius along the axial direction. The fastest growing wavelength is $\Lambda_m = 9.02R$ with R the cylinder radius; all wavelengths $\Lambda > 2R$ are unstable [9]. Any such perturbation, whether arising from slight thermal noise or randomness in the initial condition, will grow and finally cause the cylinder to pinch off into a series of droplets whose area is lower than that of the initial cylinder. (These droplets may coalesce to reduce the area still further, but that is another issue.)

Suppose now that the interface between the fluids has neutrally wetting colloids adsorbed on it. If the areal colloid density is low, these colloids might perturb the progression of the instability but cannot halt it. However, if the colloidal particles are nearly close packed on the interface, they can present an energy barrier to the peristaltic deformation mode, possibly restoring stability. That is, an infinitesimal sinusoidal deformation of the interface must either take the particles with it (which becomes increasingly difficult as close-packing is approached), or the interface must move at fixed particle positions. However, as previously discussed, there is an energy barrier to displacing the interface away from the midplane of any given particle which is very large compared to $k_B T$. So, at least for a perfectly close-packed interface (e.g., a hexagonal close-packed layer of particles wrapped around the cylinder), we expect the linear instability arising from the Rayleigh–Plateau mechanism to be removed. This would represent a second instance in which the combination of colloidal and capillary physics leads to global arrest in a metastable minimum of the free energy.

Our lattice Boltzmann simulations are designed to test this idea. Figure 3 shows new results for the time evolution of such a cylinder. The simulation details and parameters are similar to those of figure 8 in [8], where the cylinder finally broke, but with a somewhat higher particle density. A method described there for replicating short cylinders to create a long one that forms

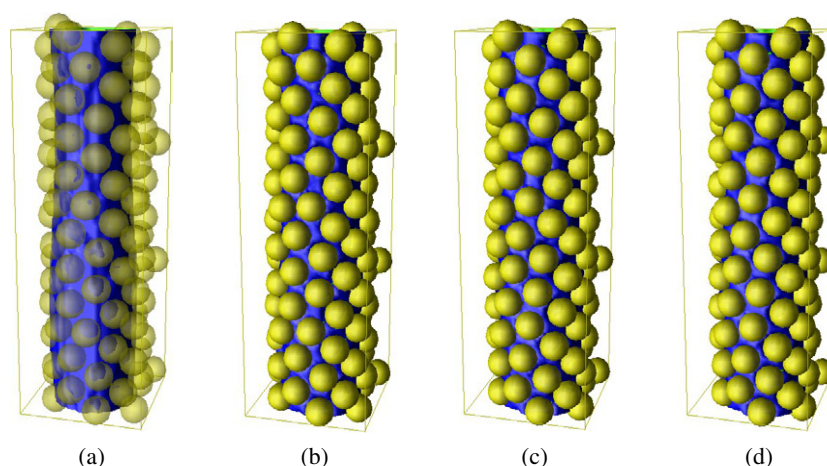


Figure 3. Evolution of a monodisperse particle-coated fluid cylinder. Frames are at 0, 50 000, 150 000 and 300 000 lattice Boltzmann timesteps. Simulation details as in figure 8 of [8], but with higher colloid coverage. In the first frame the particles are rendered translucent to expose the perturbed fluid cylinder.

the initial state was used, with some further adaptation, in this new simulation. (This method prevents the instability from growing before particles have been placed on the interface.) The initial particle packing covers the interface at fairly high density, but is random, not ordered. Close inspection of the time evolution shows that, following a finite initial perturbation in which the fluid interface is displaced sinusoidally, it first relaxes back towards a cylindrical state, even when the perturbation lies within the range of unstable wavelengths of the Rayleigh–Plateau problem. In combination with Brownian motion, the perturbation then triggers rearrangement of the particles into a much more ordered structure, as is evident by the crystalline packing visible in the final frame—all particles have six neighbours. (Of course, this might be in part a finite size effect caused by the use of periodic boundary conditions; the crystalline axes in fact develop a helical twist which is perhaps such an effect.) Despite remnants of the initial finite perturbation and the effects of thermal noise, either of which should help the system find any remaining instability, this structure appears completely stable, unlike the case studied in [8]. Certainly, without the particle coating, pinch-off would have occurred rather early in the same simulation ($\sim 75\,000$ timesteps) whereas there is no sign of it here, even after hundreds of thousands of timesteps.

It is perhaps not surprising that a dense crystalline film of colloids can solidify the interface of a fluid cylinder and suppress the instability: even if not a completely close-packed layer, such a film is a solid in two dimensions, and a solid cylindrical shell clearly does not have a Rayleigh–Plateau instability in general. Less obvious is whether the same effect still arises without crystalline order. In other words, can the instability be suppressed by formation by the colloids of a two-dimensional amorphous packing (a colloidal glass) rather than a crystal?

To investigate this, we performed a similar simulation with bidisperse particles. These particles have hydrodynamic radii $a_1 = 3.7$, $a_2 = 2.8$; there is an equal number of each size. We observe (figure 4) that initially a very similar arrest seemingly occurs, now with an amorphous packing on the interface. This can be checked in the figure by noting that the number of nearest neighbours varies between particles. However, after a rather long time interval (several times the one that would lead to pinch-off without particles) the cylinder develops an instability which grows, over a relatively short time window, leading to pinch-off.

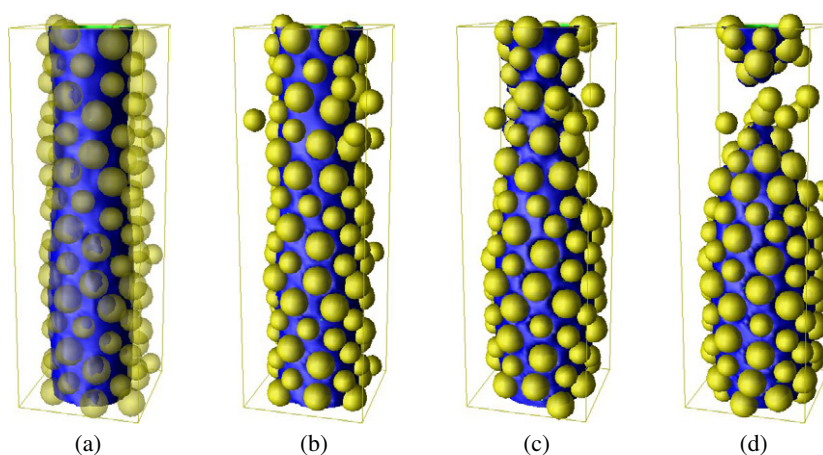


Figure 4. Evolution of a bidisperse particle-coated fluid cylinder. Frames are at 0, 50 000, 400 000 and 500 000 lattice Boltzmann timesteps. Simulation details as in figure 8 of [8], but with higher colloid coverage (and bidisperse particles). In the first frame the particles are rendered translucent to expose the perturbed fluid cylinder.

During the final detachment several particles are expelled from the interface; we are not sure yet whether this last feature is a discretization artefact or not.

These results show that colloidal particles with near-neutral wetting properties can, under monodisperse conditions at least, arrest for long periods of time one familiar interfacial instability that would otherwise be present in the binary fluid system. It is not yet clear why this did not also happen in the bidisperse run. Note however that the initial condition for that run was created from the monodisperse one by reducing the size of half the particles. This creates lower surface coverage, while bidispersity also raises the coverage at which glass-like arrest can be expected to occur. We anticipate that arrest by an amorphous monolayer may still be possible at higher colloid densities, and continue to investigate this. An important issue is whether a similar arrest of such systems in more general geometries can be achieved in the same way; this will be addressed elsewhere [10].

4. Bistability of dense colloidal droplets

Our third problem concerns the role of capillary forces at the solvent–air–colloid contact line. The relevant geometry consists of a macroscopic droplet of a colloidal suspension surrounded by air. The question is whether capillary stresses, acting at the surface of the droplet, can cause the interior to solidify. That this might be possible is suggested by recent theories of jamming, based on the notion of a stress-induced glass transition in colloids [11]. At densities close to, but below, the quiescent glass transition, some colloidal systems undergo extreme shear-thickening behaviour and, arguably at least, a form of jamming in which the existence of a sufficient shear stress causes solidification of a state that is fluid at lower stresses [11–13]. In hard-sphere systems, the natural scaling for the critical stress is the Brownian scale, $\Sigma_B = k_B T/a^3$ [11].

Assuming such a stress threshold does exist, capillary forces are quite capable of exceeding it: the stress scale involved in poking a monolayer of colloidal particles partly out of their solvent and into air (or a second solvent) vastly exceeds Σ_B . (The ratio is in fact $\Delta U/k_B T$ as defined in the introduction; the mechanics of this is discussed further in [14].) This accords with common experience that colloidal particles in suspension do not spontaneously poke out

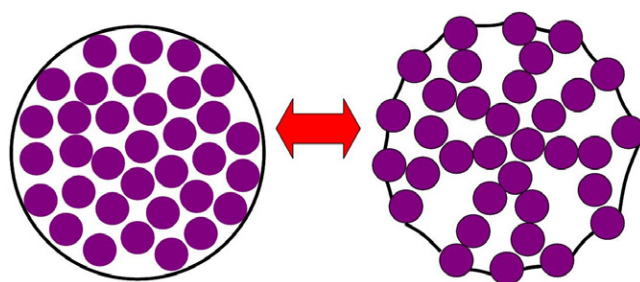


Figure 5. Two states of the same droplet of colloid, one shiny and fluid, one matt and solid. In the granule (right) the internal solid phase is maintained in a jammed state by the capillary forces at the surface. (Because it is a solid, these can set up shear stresses in the interior.) The capillary forces in the fluid droplet (left) create only an isotropic Laplace pressure within the interior; this is carried by the solvent and does not jam the suspension.

of the surface of the sample into air under the action of Brownian motion. If they did, the surface of the sample would look matt or dull in appearance, rather than shiny: the protruding colloids would create roughness on length-scales of order the wavelength of light.

Remarkably, though, exactly such a matt surface is observed if a droplet of sufficiently dense colloid is deformed with a spatula [12, 14]. The same thing can be seen in the kitchen if a dense suspension of cornflour is prodded firmly with a spoon: the surface starts to look dry, and then cracks appear. The effect is related to the apparent drying out of wet sand when one's foot is placed upon it, and stems from the phenomenon of dilatancy, well known in granular materials such as sand. Namely, for a very dense granular material to undergo shearing motion, it must expand [15]. A dry unconfined powder can do so with ease, but a wet one, immersed in solvent, cannot expand its volume since the solvent is incompressible. The result is a partial emergence of the particles, generating very large capillary stresses, at the surface of the sample.

Combined with the concept of stress-induced jamming, this leads us to an intriguing bootstrap scenario [14] whereby a finite strain deformation of a colloidal droplet causes enough dilatancy to produce the dry-looking state at the surface, and this produces enough stress to maintain jamming in the bulk (figure 5). This may be an explanation for the observed transformation of such droplets into matt irregular solid objects called granules [14]. Such granules, once formed, require no external stress to maintain their solid state, but can be returned to a fluid droplet state (with a shiny surface) by applying a high frequency vibration [12]. Currently we know of no other explanation of this remarkable bistability.

According to the speculative theory of [14], granule formation is robust only in a regime where the stress-induced glass state of the dense colloidal suspension, created at stresses of order Σ_B , does not remelt at stresses a few times higher than that. (Otherwise the very large capillary stresses would typically create a re-entrant fluid regime within the droplet rather than a jammed solid.) This places interesting constraints on the development of models for stress-induced jamming, and suggests that the ability to form granules may depend not only on colloidal concentration but also on the details of colloidal interactions: in combination these could control whether the re-entrant melting occurs.

5. Conclusions

In this paper we have brought new comparative insights into three recent studies of capillary-induced colloidal arrest. At first sight the problems are all very different, but the unifying theme is the separation of energy scales between thermal motion of a colloid and the capillary

forces acting upon it, once an interface between two solvents (or one solvent and air) enters the problem. The capillary scale is so large that it can easily overcome Brownian motion of the colloids and cause arrest of their configuration in a metastable state. This arrest, in turn, can pin the interface itself, leading to a variety of interesting new structures. A simple and concrete example, confirmed for the first time in this paper (section 3), is the arrest of the Rayleigh–Plateau instability by spontaneous formation of an ordered crystalline array of monodisperse colloids, adsorbed (initially at random) onto the surface of a fluid cylinder as a result of the neutral wetting condition. Ongoing research attempts to see the same phenomenon for bidisperse particles and addresses similar avenues for arrest in more complex geometries [10].

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References

- [1] Aveyard R, Binks B P and Clint J H 2003 *Adv. Colloid Interface Sci.* **100–102** 503
- [2] Meeker S P, Poon W C K, Crain J and Terentjev E M 2000 *Phys. Rev. E* **61** R60836
Anderson V J, Terentjev E M, Meeker S P, Crain J and Poon W C K 2001 *Eur. Phys. J. E* **4** 11
Nakamura H, Meeker S P, Taira Y, Poon W C K and Crain J 2001 *Mol. Cryst. Liq. Cryst.* **368** 167
Cleaver J, Vollmer D, Crain J and Poon W C K 2004 *Mol. Cryst. Liq. Cryst.* **409** 59
- [3] Cleaver J 2004 *PhD Thesis* University of Edinburgh
- [4] Vollmer D, Hinze G, Poon W C K, Cleaver J and Cates M E 2004 *J. Phys.: Condens. Matter* **16** L227
Vollmer D, Hinze G, Ullrich B, Poon W C K, Cates M E and Schofield A B 2005 submitted
- [5] Cleaver J and Poon W C K 2004 *J. Phys.: Condens. Matter* **16** S1901
- [6] West J L, Glushchenko A, Liao G, Reznikov Y, Andrienko D and Allen M P 2002 *Phys. Rev. E* **66** 012702
- [7] Cates M E, Stratford K, Adhikari R, Stansell P, Desplat J-C, Pagonabarraga I and Wagner A J 2004 *J. Phys.: Condens. Matter* **16** S3903
- [8] Cates M E, Desplat J-C, Stansell P, Wagner A J, Stratford K, Adhikari R and Pagonabarraga I 2005 *Phil. Trans. R. Soc. A* at press
(Cates M E, Desplat J-C, Stansell P, Wagner A J, Stratford K, Adhikari R and Pagonabarraga I 2004 *Preprint cond-mat/0411490*)
- [9] Faber T E 1995 *Fluid Mechanics for Physicists* (Cambridge: Cambridge University Press)
- [10] Stratford K, Pagonabarraga I, Adhikari R, Desplat J-C and Cates M E 2005 in preparation
- [11] Holmes C B, Fuchs M and Cates M E 2003 *Europhys. Lett.* **63** 240
Holmes C B, Fuchs M, Cates M E and Sollich P 2005 *J. Rheol.* **49** 237
- [12] Bertrand E, Bibette J and Schmitt V 2002 *Phys. Rev. E* **66** 60401R
Warren P B 2001 private communication
- [13] Head D A, Ajdari A and Cates M E 2001 *Phys. Rev. E* **64** 061509
Head D A, Ajdari A and Cates M E 2002 *Europhys. Lett.* **57** 120
- [14] Cates M E, Haw M D and Holmes C B 2005 Dilatancy, jamming and the physics of granulation *J. Phys.: Condens. Matter* at press (Special issue on Granular Matter, ed M Nicodemi)
- [15] Reynolds O 1885 *Phil. Mag.* **20** 469
Jenkin C F 1931 *Proc. R. Soc. A* **131** 53
Frank F C 1965 *Rev. Geophys.* **3** 485