The flow of powders and of liquids of high viscosity

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Abstract. It is argued that powders have so many particles per unit volume that they can be treated in a manner similar to conventional liquids. They have an entropy $S(V, N)$, but as energy is not important the place of temperature $\partial E/\partial S$ is taken by $\partial V/\partial S$. Equations capable of giving plug flow are derived. It is argued that highly viscous liquids approaching the glass transition can have a structural order that differs from that of equilibrium at the ambient temperature, defined by the other majority degrees of freedom. The ideas from powder theory enable one to derive the dependence of the glass temperature on the cooling rate.

1. Introduction

Powders are normally assemblies of a very large number of grains—numbers that imply that there should be well defined laws for their equations of flow and of state. Many powders do indeed flow like liquids and show well defined rules for mixing and demixing of different species.

Thermal properties are usually of little importance, i.e. temperature is a minor feature. The dominant physical feature is the absence of a definite density, since frictional effects are usually dominant and the density can be raised or lowered within well established limits by shaking or compressing.

This dilatancy of powder should be describable by some analogue of temperature in thermal systems, i.e., just as a thermal system has any energy (within limits) and is therefore labelled by a temperature, we argue that a powder is characterized by a compactness which will be shown to be $X = \partial V/\partial S$ in analogy to $T = \partial E/\partial S$. Notice that the entropy $S(N, V)$ is a well defined quantity, the logarithm of the number of ways the grains can be assembled to fill the volume V, so X is well defined.

The argument for the central position of X is given in section 2 where it is argued that whereas a flowing liquid is described by ρ, v, T, a flowing powder is described by ρ, v, X, and some tentative equations of motion are offered there.

The relationship with high viscosity liquids comes about in the following way. When a liquid is cooled towards the glass temperature its configurational structure departs from equilibrium according to the cooling rate. It is fruitful in theoretical physics to look at extreme cases, and an extreme version of disequilibrium is a powder. In such a case a variety of configurational orders are possible, characterized by $\partial V/\partial S$. We argue that the behaviour of the liquid rapidly cooled towards the glass can be described by the deviation of $\partial V/\partial S$ from its equilibrium value. Although this idea is very close to the well known idea of having two temperatures in a system, it will be shown to have some

advantages. Finally, it will be shown how the increasing necessity for cooperation to move from one configuration to another leads to the Vogel–Fulcher form for the final behaviour of the viscosity at the onset of the glass.

2. Compactivity

As a prologue to studying powders, consider two cases of hard spheres of different specification with no forces other than the infinitely hard repulsions in thermal contact. The free energy of each gas is purely entropic, ST, and the pressures on their boundaries equilibrate to $P_1 = P_2$; i.e.

$$T(\partial S/\partial V)_1 = T(\partial S/\partial V)_2 \qquad \Rightarrow \qquad (\partial V/\partial S)_1 = (\partial V/\partial S)_2.$$

It is now argued that this result is much more general than that for the case involving temperature, and for a powder, where T is negligible, there is still an entropy

$$S/\lambda = \int \delta(V - W)\, \mathrm{d(all)}$$

(where W is the function of all the coordinates and orientation of the grains) which, given the volume, is the direct analogue of

$$S/k = \int \delta(E - H)\, \mathrm{d(all)}$$

since, just as k conveniently converts the pure number entropy into an energy, λ converts the pure number entropy of the powder into a volume. As usual it is possible to go to the canonical ensemble and to introduce an effective volume Y such that

$$-Y/\lambda X = \log \int \mathrm{e}^{-(W/\lambda X)}\, \mathrm{d(all)}$$

$V = Y - X\partial Y/\partial X$ being the analogue of $E = F - T\partial F/\partial T$. The analogue of temperature $T = \partial E/\partial S$ is $X = \partial V/\partial S$, an intensive quantity that has to be shared by powders in juxtaposition if their boundary is not disturbed by common extensive motion, e.g. by shaking the juxtaposed powders. Simple examples of this concept have been given (Edwards 1988, Edwards and Oakeshott 1989, Mehta and Edwards 1989, 1990). Using simple models of W in terms of coordination numbers the mixing of powders can similarly be described by Bragg–Williams-type theories. We call X the compactivity.

The great interest in powder lies, however, in dynamic rather than static properties. The general equations must take the form

$$\partial\rho/\partial t + \mathrm{div}(\rho\, \boldsymbol{v}) = 0 \tag{2.1}$$

$$\partial v_i/\partial t = (\boldsymbol{v} \cdot \boldsymbol{\nabla})v_i + (I/\rho)(\partial P_{ij}/\partial x_j) = F_i \tag{2.2}$$

$$\partial X/\partial t + (\boldsymbol{v} \cdot \boldsymbol{\nabla})X + \varphi(X) + K(\dot{e}, X) = 0$$
$$[\dot{e}_{ij} = \tfrac{1}{2}(\partial v_i/\partial x_j + \partial v_j/\partial x_i)] \tag{2.3}$$

where p_{ij} is the stress, F the applied force, $\varphi(x)$ represents the response of the compactivity in the absence of a strain rate and K the effect of the strain rate. In the next section we make some estimates of p, F, φ and K.

3. The equations of motion

The first requirement is to establish the constitutive equation for the powder which we can as usual consider as the reaction of the system to the external forces and to the motion. There are two forms of the viscosity and the coefficients of viscosity will be functions of X, i.e.

$$\partial p_{ij}/\partial x_j = (\partial \mu_1(X)/\partial x_j)\, \partial v_i/\partial x_j + (\partial \mu_2(X)/\partial x_j)\, \partial v_i/\partial x_j. \tag{3.1}$$

Now $X = 0$ corresponds to the closest packing of the powder and $X = \infty$ to the lowest-density packing. Regarding the powder as having a surrounding fluid, which could be air (but it is mathematically simpler if it is a normal liquid), one can postulate that

$$\mu_1(X) = \mu_1/f_1(X) + \mu_{10} \tag{3.2}$$

$$\mu_2(X) = \mu_2/f_2(X) + \mu_{20} \tag{3.3}$$

where $f_1, f_2 \to 0$ as $X \to 0$ since the closest packing has to have infinite viscosity. The usual fitting of such functions suggests a power law, but we adopt the simplest form, which is that f_1 and $f_2 = X$. The normal liquid value of μ_{20} is zero as the liquid is incompressible. The physical implication of these forms is that shearing a powder will tend to increase X and reduce the viscosity until a point is reached where it is no longer valid to describe the system as a powder with liquid or gas between the grains, since it has become a suspension.

   The rest of the stress tensor which is not dependent on the motion is the response to the external force. A powder as such cannot exert a pressure in the normal way as there is no thermal motion, but it can resist an external applied force. Thus if a force F_{ext} is applied, there is part of p_{ij} that is a response to F_{ext} and which we can designate $F_{\text{int}}(X, F_{\text{ext}})$. The simplest form would be to write it as

$$F_{i\,\text{int}} = -R_{ij}(X)F_{j\,\text{ext}} \tag{3.4}$$

where one can expect R to be 1 when the powder perfectly resists compression (but then R will rise until it vanishes as $x \to \infty$). The crudest form for R would be a function like

$$R = 1/(1 + \alpha X). \tag{3.5}$$

The equation for x will reflect both the way in which the powder responds to an initial condition that is not stable and to the effect of stress. For temperature one has the standard form for a normal liquid:

$$\partial T/\partial t + v \cdot \nabla T - \kappa \nabla^2 T = \mu_{10}(\dot{e}_{ij}\dot{e}_{ji} - \dot{e}_{ii}\dot{e}_{jj}) \tag{3.6}$$

where κ is the thermal conductivity and the right-hand side is the viscosity heating.

   There is no analogue of diffusion, but a powder disturbed by shear flow can be expected to tend to a state of smaller X when the shear is removed. The precise way in which this happens needs a molecular model, but the crudest argument would be to designate some X_1 such that if the strain rate goes to zero the powder compresses to X_1.

In general X_1 must be history dependent but this is quite hard to describe confidently so we accept the crudest version:

$$\partial X/\partial t + (\boldsymbol{v} \cdot \boldsymbol{\nabla} X) + \gamma(X - X_1) = [\dot{e}] \tag{3.7}$$

The obvious right-hand side would be

$$a\dot{e}_{ij}\dot{e}_{ji} + b\dot{e}_{jj}\dot{e}_{ii} \tag{3.8}$$

but I cannot see why a linear term $\dot{e}_{ii}$ cannot be present, for the arguments in fluid dynamics do not apply here. Of course the viscous term in hydrodynamics is derivable from the conservation of energy, so a resolution of the presence or absence of the linear term awaits a microscopic derivation. Thus our phenomenological suggestions are:

$$\partial\rho/\partial t + \boldsymbol{\nabla} \cdot (\rho\boldsymbol{v}) = 0 \qquad \partial v_i/\partial t + (\boldsymbol{v} \cdot \boldsymbol{\nabla})_i - (\partial/\partial x_i)(\mu_{01} + \mu_1/X)\, \partial v_i/\partial x_j \tag{3.9}$$

$$-(\partial/\partial x_j)(\mu_{02} + \mu_2/X)\, \partial v_i/\partial x_j = F_{\text{ext}}(\alpha X/(1 + \alpha X)) \tag{3.10}$$

$$\partial X/\partial t + \boldsymbol{v} \cdot \boldsymbol{\nabla} X + \gamma(X - X_1) = c\dot{e}_{ii} + a\dot{e}_{ij}\dot{e}_{ji} + b\dot{e}_{ii}\dot{e}_{jj} \qquad \dot{e}_{ij} = \tfrac{1}{2}(\partial v_i/\partial x_j + \partial v_j/\partial x_i). \tag{3.11}$$

Crude as these equations are, they show interesting features: the stress is not monotonic in the strain rate, so they show plug flow, i.e. the coexistence of two strain rates in say a pipe flow. However, I will use the rest of my paper to consider some speculations (i) about the form of the equations and (ii) about the application of the ideas in the study of very viscous liquids as the glass transition is approached.

4. Refinement of the equations

These naturally arise when models are considered. The basic equations themselves can be derived from the underlying Boltzmann equations, but these are unconventional. For example, suppose one considered the first approximation to a basic description to be a coordination number, i.e. each grain to have c neighbours. Suppose there are n_c such grains and consider the rearrangements as a kind of chemical reaction, $\{c_i\} \rightarrow \{c_i^1\}$, with the analogue of the Boltzmann equation $v + v_1 \rightarrow v' + v_1'$ implying $f(v) f(v_1) - f(v') f(v_1')$ to be

$$\Pi n(c_i) - \Pi n(c_1').$$

This is all very complicated, but the optimist can make progress, for example, by noting that c is always rather large and that a Fokker-Planck approach is possible. We have made some progress in this direction. It is an interesting problem because the same difficulty arises with foams and with the flow of packed soft objects.

Aspects of the equations appear in the current literature. For example, one can use the literature of the hard-sphere gas to find how $\partial V/\partial S$ behaves as the density approaches the maximum random close-packed packing. There is also much literature on the behaviour of F (Schofield and Wroth 1968). A characteristic of the terminal behaviour of variables approaching the $X \rightarrow 0$ limit is of the Vogel–Fulcher type. For example we can expect $F(1 - R)$ as a function of X to start at zero and rise from a cusp at A/F to a terminal value of X. The X at which the reaction is total depends on F, perhaps like

$$R = [1 - \exp(-B/(FX - A))]\, \Theta(X > A/F). \tag{4.1}$$

A similar VF cusp appears in the viscosity when in the terminal region, except more and

more elaborate cooperations are required for any movement to take place; see, e.g., Edwards and Vilgis (1986). A final improvement arises in the compactivity equation when attempts are made to give a microscopic derivation because the crude $\gamma(X - X_1)$ must really involve at least two effects; the relaxation time of the system as a function of X and the 'Boltzmann' increase and decrease of X due to rearrangements in the system. This is the topic of the next section.

5. An application to highly viscous liquids

When a liquid is cooled quickly the glass temperature depends on the cooling rate. Experimental study shows that there is little that is simple about this process but it is always worth building an *extreme* model, to get oriented for a better theory. So, suppose the orientational freedoms of the liquid contribute little to the thermal energy so that the temperature can still be defined and measured, this coming from vibrational and electronic degrees of freedom. It then follows that the orientational entropy can be defined as for a powder, and a value of $\partial V/\partial S$ will exist for this order which is *not* the same as the overall T/P.

Let us define $Z = (\partial V/\partial S) - (\partial V/\partial S)_{eq}$. For a rapidly cooled liquid Z is non-zero, but an equilibrium liquid will have $Z = 0$. We now argue that Z is rather like the X of our powder in that there will be some equation which relates Z to the cooling rate $\dot{\tau}$, $\dot{\tau} = 0 \rightarrow Z = 0$. Thus if one argues that there is some Z-dependent relaxation time, one can expect

$$\mathrm{d}Z/\mathrm{d}(t/t_0) = \text{effects generating } Z - \text{effects reducing } Z. \tag{5.1}$$

t_0 will have a natural equilibrium value decreased by Z, e.g.

$$t_0 = (\alpha - \beta Z). \tag{5.2}$$

Effects generating Z must depend on, and be even in, Z, say βZ^2, whereas effects reducing Z are plausibly proportional to Z itself. Thus we can guess a form

$$\mathrm{d}Z/\mathrm{d}t = (\alpha - \beta Z)(\dot{\tau}^2 - \varepsilon Z). \tag{5.3}$$

The cessation of motion $Z = 0$ corresponds to the glass transition and this equation (Edwards 1989) does indeed give $T_g(\tau)$. The experimental dependence is logarithmic and this suggests that the above equation is too simple and must again be of the VF type, plausibly enough. Finally the viscosity of the liquid can be constructed as in section 3, with Z playing the part of X, and in this way a viscosity which depends on the cooling rate results.

Acknowledgments

References

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