

THEORY OF POWDERS

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Starting from the observations that powders have a large number of particles, and reproducible properties, we show how statistical mechanics applies to powders. The volume of the powder plays the role of the energy in conventional statistical mechanics with the hypothesis that all states of a specified volume are equally probable. We introduce a variable X – the compactivity – which is analogous to the temperature in thermodynamics. Some simple models are considered which demonstrate how the problems involved can be tackled using the concept of compactivity.

1. Introduction

There is an increasing interest in applying the methods of statistical mechanics and of transport theory to systems which are neither atomistic, nor in equilibrium, but which still fulfil a remaining tenet of statistical physics which is that systems can be completely defined by a very small number of parameters and can be constructed in a reproducible way. Powders fall into this category. If a powder consists for example of uniform cubes of salt, and is poured into a container, falling at low density uniformly from a great height, one expects a salt powder of a certain density. Repeating the preparation reproduces the same density. A treatment such as shaking the powder by a definite routine produces a new density and the identical routine applied to another sample of the initial powder will result in the same final density. Clearly a Maxwell demon could arrange the little cubes of NaCl to make a material of different properties to that of our experiment, but if such demonics are ignored, and we restrict ourselves to extensive operations such as stirring, shaking, compressing – all actions which do not act on grains individually – then well defined states of the powder result.

In this paper we will set up a framework for describing the state of the powder, basing our development on analogies with statistical mechanics. Some attempts have been made to apply information theory ideas directly to powders

[1–3], but we want to introduce a formulation closer to conventional statistical mechanics in order to use the powerful ideas developed there. Although much information is available on powders and a notable literature exists [4–6], one is struck by the rather advanced situations discussed. It seems to us that the most elementary problems have not been fully addressed, so that this paper will study some powder problems at a very elementary level of statistical mechanical technique. We aim at new physical ideas and offer no new mathematical ideas.

The number density of a powder lies between 10^0 ml^{-1} and 10^{16} ml^{-1} . Although much less than the 10^{22} of atoms, this range takes one into the region where Van der Waals forces and plain electric charges become dominant. Although we do not need to refer to a density, we have in mind the range 10^3 to 10^6 , i.e. friction is important but attractive forces are not dominant. For bulk samples, the numbers are still very large so that statistical arguments are entirely appropriate.

We will argue that powders have an entropy, but it will be the volume which plays the role of the energy in normal statistical mechanics: the energy corresponding to the powder's thermal temperature 300 K is negligible. In statistical mechanics the most fundamental entry is via the microcanonical ensemble. This is a closed system, contained in a volume V , which is assumed to take up all configurations subject to the Hamiltonian function taking the value E with equal probability. Thus the distribution function is

$$e^{-S/k_B} \delta(E - H),$$

where the entropy S is defined in terms of the total number of configurations

$$\Omega = \int \delta(E - H), \quad S = k_B \ln \Omega,$$

k_B being Boltzmann's constant which harmonizes units of measurement.

Although the microcanonical ensemble is the most fundamental, E is not easy to measure and the δ function is difficult to handle, so it is easier to use the canonical ensemble and define the free energy F by the distribution function

$$e^{(F-H)/k_B T},$$

where

$$e^{-F/k_B T} = \int e^{-H/k_B T}$$

and

$$T = \frac{\partial E}{\partial S} .$$

The energy is now given by

$$\begin{aligned} E &= F + TS \\ &= F - T \frac{\partial F}{\partial T} . \end{aligned}$$

The most important variable describing the state of the powder is its density, or equivalently, but more usefully its volume V . The volume here is the actual volume taken up by the powder – i.e. as would be measured by letting a piston rest on the top of the powder. The volume therefore depends on the configuration of the particles – unlike the conventional case where the volume is set externally, and only the energy depends on the configuration of the particles. In principle other variables may be necessary to describe the state of a powder, i.e. if a powder is sheared, then it may develop an anisotropic texture, but we will not consider this possibility here.

We now introduce a function W of the coordinates of the grains which specifies the volume of the system in terms of the positions and orientations of the grains. The form of W will depend on how the configuration of the grains is specified, and on the shape and size of the grains. We also introduce a function Q which picks out valid configurations of the grains – that is stable arrangements, where the particles can remain at rest under the influence of the confining forces, and with no overlap between particles. On the assumption that for a given volume all these configurations are equally probable, a table can be drawn up developing the analogy. (See table I.)

There are model systems with very simple Hamiltonians available, e.g. the perfect gas or the Ising model, but in general H is not simple, for example a true ferromagnet has complicated many ion potentials. For powders, W and Q are never simple, e.g. hard spheres already offer a major problem from this point of view (though they can be written simply as is well known and discussed below).

In table I we have introduced two new variables X and Y . X is the analogue of temperature and measures the “frothiness” or “fluffiness” of the powder. Since $X = 0$ corresponds to the most compact powder and $X = \infty$ to the least, we may name it the compactivity of the powder; it is the inverse of the compaction. A powder prepared with a larger volume than that corresponding to $X = \infty$, and so with $X < 0$, would be unstable: given any vibration the powder would tend to compact, increasing its entropy, and reducing its

Table I

Statistical mechanics	Powders
E	V
H	W
S	S
k_B (which gives S the dimensions of energy)	λ (which gives S the dimension of volume)
$\int \prod dr_i \prod dp_i$	$\int \prod dr_i Q$
$e^{-S/k_B} \delta(E - H)$	$e^{-S/\lambda} \delta(V - W)$
$T = \frac{\partial E}{\partial S}$	$X = \frac{\partial V}{\partial S}$
$e^{-F/k_B T} = \int e^{-H/k_B T}$	$e^{-Y/\lambda X} = \int e^{-W/\lambda X}$
$F = E - TS$	$Y = V - XS$
$E = F - T \frac{\partial F}{\partial T}$	$V = Y - X \frac{\partial Y}{\partial X}$

potential energy. Our assumption that all configurations of a given volume are equally probable implies that the same X should characterize arrangements around particles in the powder with different sizes densities, coefficients of friction, etc. An obvious name for Y would be the free volume, but that phrase is already appropriated in glass and liquid theory, hence we propose the name “effective volume” for Y . Notice that our new functions have fewer dependencies than those of thermodynamics, e.g.

$$E = E(S, V, N)$$

whereas

$$V = V(S, N).$$

Similarly

$$F = F(T, V, N), \quad Y = Y(X, N),$$

as a consequence, there are no analogies of the Maxwell relations of classical thermodynamics.

For a thermodynamic system

$$\frac{\partial S}{\partial V} = \frac{\partial S}{\partial E} \frac{\partial E}{\partial V} = \frac{P}{T},$$

but since $P = 0 = T$ in our powder, there is no value in an identification of X in these terms. The general problem of pressure in the resistance of a powder to

compression is more advanced than anything at the level of this paper. This is because whereas the exertion of pressure will decrease volume irreversibly, there comes a point when the volume can no longer decrease by rearrangement, but requires deformation of the grains. This involves stress finding (multiply connected) “percolating” pathways through the solid, and this requires a different kind of analysis which is downstream from the present problem. Here we can omit a discussion of the pressure because we always assume that frictional thresholds are such that the powder can rest in the specified configuration. For simple frictional forces ($F \leq \mu N$), and hard particles, the absolute gravitational field, or confining pressure does not matter.

In a stable configuration the particles must be touching, so that these states are a subset of measure zero of the total phase space of a hard particle gas. Of itself this is no problem – it is only if states with different numbers of degrees of freedom exist that there is a problem because, since this is a purely classical problem, there is no natural scale analogous to Planck’s constant, h . For frictionless particles stable states are local volume, minima, and so form a discrete set of states – the only remaining possibility is that the minima should have different weights.

Two simple criteria for stability are possible. The simplest local criterion for stability is that no single particle is free to move. A global criterion is obtained if we use the Maxwell condition: the number of constraints greater than or equal to the number of variables. For spheres this implies that the average number of contacts per particle is at least 6. If the particles are not frictionless, then the true condition will lie between the local and global criteria. In particular states with fewer contacts will be stable, and maximising the entropy will select those states which minimise the number of contacts, whilst still being stable.

To illustrate these ideas we study the packing of a simple one species powder. The crude model illustrates overall features, rather than detailed study of particular local environments.

2. The volume of a simple powder studied by the compactivity concept

We start with the highly artificial, but instructive model of a powder in one dimension. Now powders obviously cannot exist in one dimension as gravity will always fully compact them, but we can still learn useful lessons. If the grains are rods of length a , whose midpoints are x_n , with $x_n < x_{n-1}$, then clearly trivially

$$W = x_N - x_0 + a .$$

However we can also write W as a sum of local volumes,

$$W = \sum_1^N (x_n - x_{n-1}) + a .$$

The volume exclusion implies that

$$x_n - x_{n-1} \geq a .$$

If we put as the stability condition that each rod touches its neighbour, so that

$$Q = \prod \delta(x_n - x_{n-1} - a) \Theta(x_n - x_{n-1} - a) ,$$

where

$$\Theta(x) = \begin{cases} 1, & x \geq 0, \\ 0, & x < 0, \end{cases}$$

then the problem is trivial; there is one configuration, and $e^{S/\lambda} = \delta(V - Na)$.

We can produce a model for a real – two- or three-dimensional – powder, if we consider our one-dimensional system as a section of the actual powder. The grains need not be touching in the section, but can have a range of separations up to a maximum b . Q then becomes

$$Q = \Theta(a + b - (x_n - x_{n-1})) \Theta(x_n - x_{n-1} - a) ,$$

and the integral for S is

$$e^{S/\lambda} = \int \delta \left(V - \sum_1^N (x_n - x_{n-1}) - a \right) \prod \Theta(a + b - (x_n - x_{n-1})) \\ \times \Theta(x_n - x_{n-1} - a) \prod dx_n .$$

Using the canonical ensemble we have

$$e^{-Y/\lambda X} = \left(\int_a^{a+b} e^{-v/\lambda X} dv \right)^N ,$$

so that

$$Y = N \left(\frac{a + b}{2} \right) - N \lambda X \ln(\lambda X (e^{b/2\lambda X} - e^{-b/2\lambda X})) ,$$

and

$$V = N \left(\frac{a+b}{2} \right) + N\lambda X - N \frac{b}{2} \coth \frac{b}{2\lambda X}.$$

In two or three dimensions, this form using the particle coordinates is intractable: we have taken the hard particle fluid form, and added some difficult conditions. To do anything we must choose a smaller set of variables, with the same dimensionality as the set of stable states, and so making the stability and compatibility conditions simpler. By doing this we also bring in a Jacobian.

The simplest problem in three dimensions is the compactivity of a simple powder of uniform grains of the same material in approximately spherical form. Each grain will have neighbours touching it with a certain coordination and angular direction. There will also be a certain number of near neighbours which do not touch. If we want to set up an analogy with the statistical mechanics of alloys or magnetism, we want to consider that each grain has a certain property, and this property interacts with its neighbours, e.g. in an AB alloy there are A and B type atoms with interactions v_{aa} , v_{ab} , v_{bb} . Suppose we take the coordination of a grain as such a property, i.e. suppose we assign a volume v_c to any grain with c neighbours. Clearly this is not a comprehensive description of the powder, but we can suppose that

$$W = \sum_c v_c n_c + \sum_{c,c'} v_{cc'} n_{cc'} \dots,$$

where n_c is the number of grains with c neighbours, and $v_{cc'}$ the refinement of the volume function when there are $n_{cc'}$ pairs of neighbouring grains with one with c and one with c' neighbours. A problem arises: there must be some labelling of which grain is which, unlike the situation where a lattice exists and can be referred to. This is not as serious as may at first sight appear, for given the overall density one can consider the site of each grain as the distortion of a lattice which has the correct mean coordination (which is still of course to be discovered). But even cruder one can label the grains according to say a simple cubic lattice with the right lattice spacing, i.e. one can say this particular grain is the l th in the m th row of the n th column. One only needs a label: the quantification of distance and volume comes from the formula for W . At the level of this paper, this labelling issue will not actually arise and we discuss it here only to assure the reader that there is no real problem. There are still compatibility conditions in this formulation: clearly one cannot have a grain with coordination 4 next to a grain with coordination 12. It is difficult to quantify these conditions, and we will not attempt to do so here, but hope to return to it in a later paper.

Suppose then we label our grains i meaning that their true positions can be deformed affinely onto lattice points r_i . Suppose that grain i has a coordination c_i so that

$$W = \sum_i v_{c_i} + \sum_{\substack{i,j \\ \text{neighbours}}} v_{c_i c_j} + \dots$$

The final form of the integral will then be

$$\sum_{c_i=0}^1 \delta(W - V) J(\{c_i\}),$$

where $J(\{c(r_i)\})$ expresses the combined effect of the Jacobian from the change of variables, and the stability and no-overlap conditions. We will not attempt to evaluate J in this paper, but work through the very simplest examples: firstly that of one kind of grain, and with the volume depending only on the coordinations of the individual grains. Since we are illustrating a point rather than being realistic we can be even simpler and say that there are just two types of coordination c_0 and c_1 which leads to an Ising model,

$$\begin{aligned} e^{-Y/\lambda X} &= \sum_{c_i=0}^1 e^{-\sum v_{c_i}/\lambda X} \\ &= (e^{-v_0/\lambda X} + e^{-v_1/\lambda X})^N, \end{aligned}$$

or

$$\begin{aligned} Y &= N \left(\frac{v_0 + v_1}{2} \right) - N \lambda X \ln \cosh \left(\frac{v_0 - v_1}{\lambda X} \right), \\ V &= N \left(\frac{v_0 + v_1}{2} \right) + N (v_0 - v_1) \tanh \left(\frac{v_0 - v_1}{\lambda X} \right). \end{aligned}$$

The two limits of V are Nv_0 corresponding to $X = 0$ and having the maximum density and $N(v_0 + v_1)/2$ which corresponds to $X = \infty$ and is the lowest density. Although this is a very simplified model, it clearly will be related to the real problem of an array of c 's and n 's and compatibilities. There will be a maximum density possible which will correspond to the highest coordination but then the other extreme is that of all the (stable) coordinations being equally likely. This crude analysis does not address the subtleties of sphere packings in three dimensions which arise because almost thirteen spheres can touch a central sphere; so that for small clusters one can achieve higher densities than the 0.7405 of face centred cubic. (Perhaps the demon we have forbidden might

be able to beat f.c.c. in the large but not in extensive operations.) In practice the reproducible maximum density obtained by packing for example ball-bearings is lower [7] (0.6366, “random close packing”). A large literature exists discussing the details of sphere packings (see Gray [8], or Cumberland and Crawford [9] for a review), although there is no satisfactory intrinsic – rather than operational – definition of the random close packed state. The general result will remain that the highest density concentrates on a particular type of coordination whereas the lowest has all coordinations.

3. Mixtures of particles

As another example, at the simplest level, we consider a mixture of powders of type A and type B. Let us focus on the fact that when an A is next to an A there is a contribution to the volume which is different from an A next to a B and a B next to a B. Thus although the nature of coordination number matters as in the example above, we just concern ourselves with the nearest neighbour quality. This one aspect is enough to throw interesting light on the separation and miscibility of powders. Suppose the number of A type at r_i is m_A^i (=0 or 1), and similarly for B, so that

$$W = \sum_{\substack{i,j \\ \text{neighbours}}} m_A^i m_A^j v_{AA} + \dots$$

Then following Bragg and Williams we write

$$v_{AA} + v_{BB} = 2v_{AB} = v$$

and since $m_A^i + m_B^i = 1$, then if we write

$$m_i = 2m_A^i - 1,$$

$$-m_i = 2m_B^i - 1,$$

we have

$$m_i = \pm 1.$$

We now quote Bragg and Williams who give $\phi = \tanh v\phi/\lambda X$ where $\phi = \langle m_i \rangle$ so that for

$$\frac{v}{\lambda X} < 1, \quad \phi = 0,$$

$$\frac{v}{\lambda X} > 1, \quad \phi \text{ small}, \quad \phi = \pm \sqrt{\frac{3\lambda^3 X^3}{v^3} \left(\frac{v}{\lambda X} - 1 \right)},$$

until for

$$\frac{v}{\lambda X} \gg 1, \quad \phi = \pm 1.$$

Thus the A and B grains are miscible for $v/\lambda X < 1$, but, for $v/\lambda X > 1$, the powder forms domains of unequal concentrations, until at $X = 0$ the material separates into domains of pure A and pure B.

If A and B are particles of different sizes, then we expect $v < 0$ and that the powders will be miscible for all X – at least as long as the pure phases are expected to be disordered. The well-known phenomenon where large particles rise to the top in a vibrated powder is a purely dynamical phenomenon [10]. The analysis here is relevant if we invert the powder at intervals, so that there is no extrinsic bias, or if we consider particles of the same size, but different shapes (e.g. cubes and spheres). An interesting computational study of this problem has been given by Barker [11].

4. Discussion

This paper argues that, although detail of local structure is needed for a complete theory of powders, there are large scale behaviours which fit into the structure of statistical mechanics in the sense that analogues exist of Gibbs type integrals and relationships. The compactivity provides a useful way to characterize theoretically states of a powder with different densities, although, unlike the case with energy and temperature, the volume is the easier experimental quantity.

We have illustrated the problems by some rather trivial examples, but have in hand some more detailed and significant examples for future publications.

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