A Mechanical Analogue of Monotropism: Ordering of an Ensemble of Hemispheres†

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An ensemble of randomly oriented, noninteracting, homogeneous, solid, inelastic, identical hemispheres in the gravitational field, having dropped on a rigid horizontal plane will order orientationally, most of them sitting on the vertex of the spherical part rather than on the plane. This state of the ensemble will not have the lowest possible potential energy, as required for stable equilibrium. This shows several analogies to the behavior of polymorphic substances on crystallization from a gaseous or liquid phase, which usually first result in the highest energy solid. The discussion is extended to spherical segments (limited by a single plane) other than hemispheres. If mutual attraction is present, multiple metastable and stable states of the ensemble become possible, featuring positional besides orientational order.

Introduction

Polymorphism describes the possibility of a crystalline solid to take more than one crystalline form.[1] Due to the different arrangements, and hence interactions, of the constituent units, such forms have different specific energy (or chemical potential) values and consequently different physicochemical properties. When a substance proves to be polymorphic, the crystalline form of each batch produced has to be checked. In fact, the different solubilities, vapor pressures, and reactivities can give different physiologic effects and hence permit new patents to be made, if it is a pharmaceutical or agrochemical,[2] can give different color nuances if it is a dye,[3] and different sensitivity if it is an explosive.[4]

Polymorphism is conveniently distinguished into two classes: enantiotropic and monotropic.[5] The former refers to the case in which each phase has a defined range of stable existence, such as the orthorhombic and monoclinic phases of sulfur. Under atmospheric pressure,[6] the orthorhombic phase is stable from the lowest attainable temperatures up to 94.5 °C, where it converts (slowly but reversibly) into the monoclinic phase, which is stable from this temperature up to its melting point at 115 °C.[7]

Monotropic polymorphism (or allotropism) occurs when one or more phases are always less stable (more energetic) than others in the given temperature range. A common example is diamond, which is always less stable than graphite under temperature and pressure ranges in which humans can exist, but inalterable there due to the height of the energetic barrier necessary to reorder the constituent atoms. Monotropism and enantiotropism are not mutually exclusive; for instance sulfur has *also* several *metastable* monotropes ("allotropes").[8] Despite the lower thermodynamic stability, the monotropic phases form due to a more favorable kinetics in the conditions of crystallization, and often persist (like diamond) in the metastable state due to the slowness, or inhibition, of the transformation. The "conditions of crystallization" may be very complex and poorly defined, including the "spooky" presence of unnoticed crystal seeds,[9] heats of mixing, peculiar or "orienting" solvents,[10] narrowly delimited values of temperature, pressure, concentrations, and of their gradients.

There is a generally applicable rule, "the Ostwald's rule of stages" which asserts that in the case of monotropism the first crystal formed is the least stable.[11] While the macroscopic aspects of the Ostwald step rule are aptly discussed by thermodynamic methods,[12] a simple, purely mechanical model shows a behavior presenting a striking analogy to the crystallization of a monotropic substance. The approximations required to assimilate a molecular liquid and crystal to ensembles of purely mechanical objects may make the model to appear unsuitable to analyze the behavior of an ensemble of molecules undergoing crystallization. But this very abstraction allows clear distinctions to be made, whereas real systems present complicated properties and behavior. It is then advantageous to turn to more convenient models. A well-known, successful example of such a procedure, is the mechanical modeling of viscoelastic systems.[13]

Below I discuss the bidimensional ordering of an ensemble of hemispheres, first under the influence of gravity alone and then in the presence of gravity and slight attractive forces. Their effects mimic the characteristic behavior of a polymorphic substance on crystallization.

The Mechanical Model: Independent Hemispheres. A large but finite number of independent, solid, homogeneous, inelastic, identical hemispheres, in random initial orientation and position, is allowed to drop gradually in the field of gravity on a lower, rigid, unlimited, horizontal plane α. In this athermal system, the single direction gravitational forces schematize the tendency of the liquid or gas phase molecules to "fall" on the crystal surface when the temperature is lowered below the equilibrium value, and the gravitational energy is analogous to an appropriate thermodynamic potential of a real macroscopic system. Only a minority of the hemispheres will take the most stable position, the one where the center of mass (com) is in the lowest possible position, which requires the plane face to contact α. Most will sit on the point of the hemisphere farthest from the plane surface, which is the vertex, point B of Figure 1. The process has orientationally ordered the ensemble, but to a metastable state, not the most stable one.

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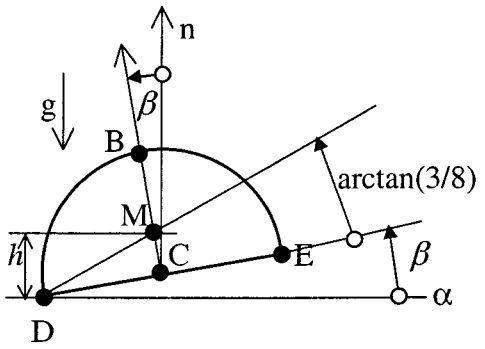

Figure 1. Section of a hemisphere by a plane passing through the unique radius CB, and definition of the angle β.

A possible objection to the analogy is that the process has not oriented the entire system, giving the analogue of a crystal, but only a part of it, giving the analogue of a disordered crystal. But it is well known[14] that any cluster of real molecules, inclusive of those organized as an incipient new phase, tends to disappear below a critical size, and only when larger tends to grow. If a certain organization is more probable than others, the critical cluster size, or crystal seed, will be reached first by that arrangement, which will enlarge, while the other will disappear.

Let us now see why a single, perfectly inelastic, solid hemisphere will tend to end on its vertex when dropped on an horizontal plane α. First we seek the com M of a hemisphere, because its gravitational energy depends on the distance of the com from α. Figure 1 shows a section of the hemisphere of diameter 2*R* through the unique radius CB perpendicular to its planar part. Because the line through C and B is a symmetry axis, which we call *x*, M must stay between C and B. To find its position, cut the hemisphere into slices, of thickness d*x* and perpendicular to *x*. Each circular slice contributes an infinitesimal mass

$$dm = \rho\, dV = \rho\, A\, dx = \rho\, \pi\, r^2\, dx = \rho\, \pi\, (R^2 - x^2)\, dx \quad (1)$$

(where ρ is the density, *V* the volume, and *A* the area of the slice), which can be thought to be concentrated in a single point at its center, which is on CB. The distance of M from C, where $x = 0$ is

$$x_M = \int_0^R x\,(R^2 - x^2)\, dx / \int_0^R (R^2 - x^2)\, dx = (3/8)R \quad (2)$$

Thus, if the initial orientation of the hemispheres is random, the probability *P* that each one may land on the plane face is given by

$$P = \frac{\left(\begin{array}{c}\text{solid angle cut by the cone with vertex in M}\\ \text{and half vertex angle } \theta = \arctan(8/3) = 69.444^\circ\end{array}\right)}{(\text{total solid angle})} = \frac{-2\pi\,[\cos x]_0^{\theta}}{4\pi} = 0.3244 \quad (3)$$

or less than 1/3. If a hemisphere were somewhat (imperfectly) elastic, its final orientation would depend on the elastic coefficient and the initial height with respect to the plane. However, if the rebounds did not modify the randomness of orientation but were sufficient to allow reorientation of the hemisphere, all those which can collide more than one time with α would have each time a probability of less than 1/3 to reach the most stable state.

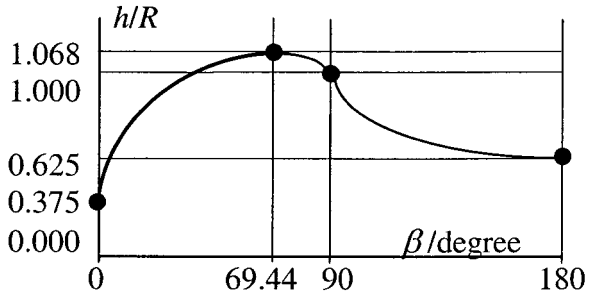

Figure 2. Diagram of the potential energy of a hemisphere in mg units as a function of the angle β.

Defining as β the angle between the oriented segment C→B and *n*, an oriented normal out of α, see Figure 1, the diagram of the gravitational potential energy (proportional to the height *h* of M from α) of a single hemisphere as a function of β is shown in Figure 2. Initially let $\beta = 0°$, so that *h* is at its absolute minimum value of (3/8) $R = 0.375R$. As soon as β starts increasing, the hemisphere rotates anticlockwise, pivoting on a point of its edge, like D of Figure 1, and *h* increases as

$$h(\beta) = \mathrm{DM}\,\sin[\arctan(3/8) + \beta] = R\,[1^2 + (3/8)^2]^{1/2}\,\sin[\arctan(3/8) + \beta] = R\,1.068\,\sin(20.556 + \beta) \quad (4)$$

reaching a maximum (top of the energy barrier, unstable equilibrium) of $1.068R$ for $\beta = 69.444°$. From $\beta = 69.444°$ to 90°, *h* decreases, reaching the value of *R* for $\beta = 90°$.

For $90° \le \beta \le 180°$, the contact point with α, through which the instantaneous axis of rotation (which lies on α) passes, moves on a maximum circle on the spherical surface. The type of point of contact with α has changed, and so does the expression of *h*, which is now given by

$$h(\beta) = R - \mathrm{CM}\,\sin(\beta - 90) = R - 0.375R\,\sin(\beta - 90) \quad (5)$$

Its value decreases further, until it reaches a relative minimum of $5/8R = 0.625R$ for $\beta = 180°$, when the hemisphere sits on B. Due to the symmetry of the hemisphere, the curve representing the gravitational potential energy $V_G(\beta) = mg\,h(\beta)$ is symmetrical about $\beta = 180°$. The minimum here is a well-behaved one, with zero value of the first derivative, whereas the two absolute minima at $\beta = 0°$ and 360° are end point extremes,[15] with one-sided finite first derivatives of opposite sign.

A hemisphere in the metastable status on its vertex B may reach the lowest, stable minimum of potential energy if some external source—vibration of the plane, collision with other hemispheres, or anything emulating the effect of the thermal bath on the molecules—will temporarily supply at least the difference mgR (1.068 − 0.625) necessary to surmount the potential barrier.

The first setting of the hemispheres on the plane depends on probability; the stable one on potential energy, if sufficient energy to overcome the barrier to reorientation is temporarily available.

The above model can be generalized by considering a small set of selected spherical segments, with one of the two planes (0 in Figure 3) tangent to the spherical surface and the other (1−5) cutting it at various distances from the former. Their features are listed in Table 1.

In order to compare the values of the potential energy at the absolute minimum (for $h_{com} = a$), at the top of barrier (for

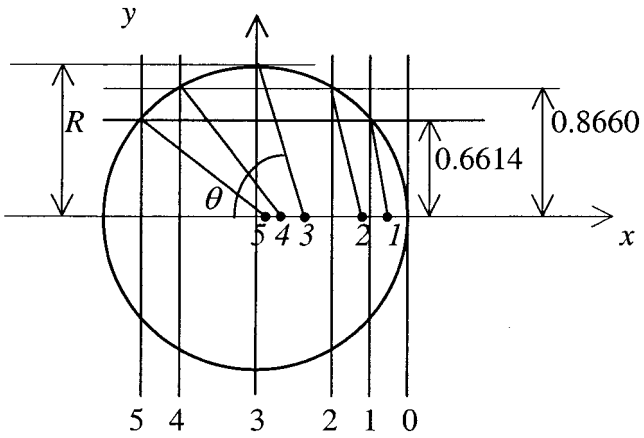

Figure 3. Projection of selected spherical sections on a plane through the axis. Roman numbers indicate the tangent (0) and cutting (1−5) planes; italic ones the centers of mass, shown by dots.

TABLE 1: Features of Selected Spherical Segments

spherical segment	0−1	0−2	0−3	0−4	0−5
v = volume/R^3	0.1799	0.6545	2.0944	3.5343	4.0088
x_{com}/R	0.8352	0.6750	0.3750	0.1250	0.0375
radius of end circle/R	0.6614	0.8660	1.0000	0.8660	0.6614
θ/degree	82.66	78.57	69.44	54.18	40.02
$P = \Omega/4\pi$	0.4361	0.4009	0.3244	0.2074	0.1171
$a = (h_{com\ at\ abs.min.}/R)$	0.0852	0.1750	0.3750	0.6250	0.7875
$b = (h_{com\ at\ max.}/R)$	0.6668	0.8835	1.0680	1.0679	1.0280
$c = (h_{com\ at\ rel.min.}/R)$	0.1648	0.3250	0.6250	0.8750	0.9695
$b' = (b - a)/a$	6.8263	4.0485	1.8480	0.7086	0.3059
$c' = (c - a)/a$	0.9342	0.8571	0.6666	0.4000	0.2222

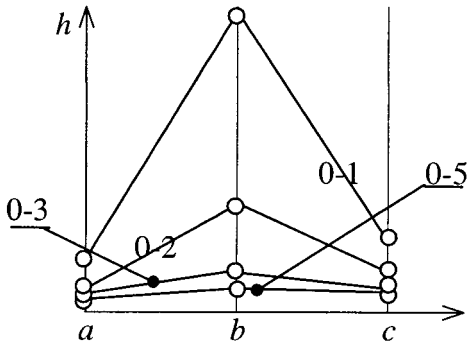

Figure 4. Relative gravitational energies of different spherical segments in the stable (*a* in Table 1), top-of-the-barrier (*b*), and metastable (*c*) orientation.

$h_{com} = b$), and at the relative minimum (for $h_{com} = c$) of the five spherical segments, it is advantageous to divide the gravitational energy of each solid in excess of its minimum value by this minimum value. Since the gravitational energy is $V_G(h) = mgh = g\rho v R^3 h$, where v is the volume of the spherical section divided by R^3, these ratios become $b' = (b - a)/a$ and $c' = (c - a)/a$, and are listed in Table 1 and shown in Figure 5. Along with the change of form of the solid, from disk-like (spherical segment 0−1) to sphere-like (spherical segment 0−5), the relative energy differences decrease, as does the probability to land in the stable position, as shown in Figure 4.

Other solids are being examined to see whether their symmetry may entail features that are closer to those of real molecules.

The Hemispheres Attract Each Other. In normal liquid-to-solid (or vapor-to-solid) transitions under constant pressure, crystallization implies a simultaneous ordering of both orientation (specified for example by the three Euler angles) and position (fixed for instance by the three Cartesian coordinates

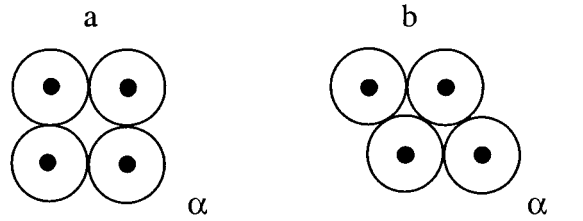

Figure 5. Top view of a, square; b, equilateral triangle arrangement of the hemispheres.

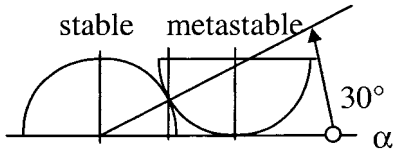

Figure 6. Vertical section of the arrangement of two hemispheres in alternate stable and metastable orientation.

of the com) nature of the elementary entities (polyatomic molecules, ions, radicals). This is not always the case;[16] however, in view of the qualitative nature of the present note we will consider only this case.

Up to this point the discussion has focused on orientational ordering of the hemispheres, assuming no interaction among them, and then avoiding possible positional ordering, because α was unlimited. Now, suppose that there are arbitrarily small attractive forces F_A (with a corresponding potential energy V_A) between the hemispheres, or some condition implying equivalent constraint forces (for instance limitations of accessible surface on α, presence of a small electric dipole moment along CB). Then the distances among the coms will tend to reduce until the rigid units come into contact. The total energy of the ensemble is necessarily dominated by V_G, so possible *stable* states will feature hemispheres with the plane still in contact with α but arranged to minimize the reciprocal distances.

Two ordered patterns will be elicited, one where the coms have a rectangular, and the other a triangular arrangement, see Figure 5a and b, respectively. The area required by each unit will be $(2R)(2R) = 4\ R^2$ in the former, and $(2R)(2R \sin 60) = 3.464\ R^2$ in the latter case.

As to metastable states of the ensemble, we previously observed that if clusters are present, the first orientation of *all* the hemispheres should be the metastable one, because a cluster of this type forms first. If there is some attractive force between pairs of units, two ordered metastable states of the ensemble may form, of the same type and same area as the stable states just discussed. But we know that if half of the hemispheres contact α with its planar part, and half with the vertex B, their effective radius for surface requirement will decrease to $R\cos(30) = 0.866\ R$, as shown in Figure 6, and so both for square and (equilateral) triangle arrangement of the coms. Thus, if 50% (or 17.56% = 67.56% − 50%, if clusters are not present, and the orientation depends on probability only) of the units will change from the gravitationally metastable to the stable position, two new metastable ordered states of the ensemble become possible.

Finally, if V_A for the ensemble becomes comparable to V_G, the requirement to minimize the distances among the coms may force the hemispheres to take the gravitationally unstable orientation with the plane vertical, $\beta = \pm 90°$ and a point such as D or E of Figure 2 in contact with α. Many new patterns would become possible, but they will not be considered here, because a feature of the model proposed is the presence of gravity as the only relevant force acting on the hemispheres.

Conclusion

An ensemble of homogeneous, noninteracting, identical hemispheres dropped in the field of gravity on a lower rigid plane shows the separate effects of probability and potential energy in the determination of the orientation of the solids. Probability controls the initial, metastable setting, while potential energy determines the stable, final one, if energy sufficient to overcome the energy barrier between the two can be borrowed.

If some condition, with a corresponding arbitrarily small potential energy, directs the hemispheres to reduce their distances, four metastable and two stable arrangements of the ensemble become possible.

Even for such a simple unit as a hemisphere, we see that the presence of forces gives rise naturally to multiple metastable and stable states of the ensemble.

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