THE INTERACTION BETWEEN FLOATING PARTICLES

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Communicated by R. C. Evans

Received 19 March 1947, *and in revised form* 1 May 1948

1. *Introduction.* The existence of forces between small particles floating on the surface of a liquid is well known, and qualitative accounts appear in a number of text-books. They have been recently used by Bragg (1, 2) to demonstrate, with remarkable success, the properties of some of the more important kinds of imperfection found in crystal and polycrystal lattices. This is done by producing rafts of bubbles floating on a soap solution and constituting a two-dimensional lattice. In these 'crystals' the existence and properties of dislocations, grain boundaries, grain growth and other phenomena giving a valuable insight into the behaviour of metals may be easily demonstrated.

It is found that bubbles of different sizes have somewhat different properties, and in order to choose a size which is roughly representative of actual atoms and also because quantitative studies of the bubble rafts may be useful in other contexts, the following calculation of the interaction between floating particles has been made.

2. *General considerations.* We first consider a single bubble of radius R, at rest on the horizontal surface of a fluid (Fig. 1). There is cylindrical symmetry about the vertical through the centre of the bubble. The forces acting are therefore the vertical component of the surface tension exerted on a ring of radius b, and the buoyancy arising from the immersion of part of the bubble and the consequent hydrostatic pressures exerted upon it. A balance can be set up between these forces, and a position of stable equilibrium results. If we now consider the case where the free surface (that is, the surface in the absence of the bubble) is no longer horizontal but inclined at an angle θ, then the resultant surface tension remains perpendicular to the surface, while the buoyancy B has a component $B\cos\theta$ perpendicular to the surface and in addition a component $B\sin\theta$ along the surface.

It is this latter component that we regard as responsible for the observed motion of particles floating on a surface. One bubble causes an inclination of the fluid surface in its neighbourhood, and a second similar bubble, if sufficiently near to the first, then experiences a force due to buoyancy causing it to rise up the incline, and thus towards the first bubble. This argument also holds if particles not wetted by the fluid are considered. The first particle causes a depression in the fluid surface; the second particle, whose weight is only partly balanced by surface tension, now tends to move down the depression, again resulting in an apparent attraction. Similarly, if the second particle is wetted by the fluid (and is therefore by implication less dense than the fluid) the resultant gravitational force (including buoyancy and weight in this term) is directed

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upwards, and therefore the second particle floats up the slope and is apparently repelled by the first. These results are of course well known, and explanations, based on a consideration of the asymmetric hydrostatic pressure on one bubble under the influence of a second, will be found in the text-books (3). The point of view described above, however, leads to an essential simplification of the problem, since attention need only be directed to the configuration of the fluid surface in the presence of a single bubble.

The arguments used above, based on buoyancy and inclination, show in fact that we need to calculate the height z of the surface in the neighbourhood of one bubble, and the buoyancy B of the second; then the potential energy of the second is $-Bz$, provided that it is sufficiently small to allow us to neglect second-order effects arising from the non-linear variation of z across the dimensions of the bubble. It should be pointed out that we have assumed that the presence of the second bubble does not distort the field of the first. In other words it is assumed that the height of the surface z satisfies a linear equation, so that the fields of the two bubbles are added independently at any point. This assumption holds, as will be shown, if we restrict our application to cases in which angles of inclination are small. In this case it will be noticed that the buoyancy B in equilibrium with the surface tension forces is unaffected by the inclination. If when the free surface is horizontal, equilibrium is achieved by the immersion of the bubble until the ring of contact is of radius b, say (Fig. 1), then an inclination of the plane of the free surface through an angle θ is equivalent to rotating the direction of gravity through the same angle. The configuration will in general have to change, since the component of gravity counterbalancing the surface-tension forces is now $g\cos\theta$. In consequence b will diminish until a new equilibrium configuration has been reached. If $\cos\theta \doteqdot 1$ we can neglect this complication.

A further simplification of detail can be secured if we establish the conditions under which the bubble, or at least the submerged portion of the bubble, can be assumed to remain spherical. (The emergent cap of the bubble cannot have the same radius as the remainder of course, since there are two films on this part and only one on the submerged part.)

To express the condition that the bubble should be spherical, we introduce the parameter a (Laplace's constant) defined by

$$a^2 = T/\bar{\rho}g, \tag{1}$$

where T is the surface tension and $\bar{\rho}$ the density of the surrounding fluid. (The bar is used to distinguish this quantity from ρ, a radial coordinate to be used below.) If the radius of the bubble is R, then the internal pressure is $2T/R$, and the variation in hydrostatic pressure over a depth equal to the radius (which causes the departure from the spherical form) is given by $\bar{\rho}gR$. If this variation is small compared with the internal pressure the required adjustments in curvature will also be small and thus the bubble will be nearly spherical. This condition is therefore that

$$\frac{2T}{R} > \bar{\rho}gR,$$

i.e.

$$R^2 < 2a^2, \tag{2}$$

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or if we introduce α (Greek symbols will be reserved for dimensionless variables) defined by

$$\alpha = R/a \tag{3}$$

we obtain

$$\alpha < \sqrt{2}. \tag{4}$$

The assumption that the bubbles are spherical is therefore a reasonable approximation for small values of α, but errors may be expected for values of α exceeding unity, that is, for radii exceeding about 1·5 mm. in the case of soap solution. In the bubble model, interest is confined to much smaller bubbles than this, usually a few tenths of a millimetre.

3. *Calculation of height of surface in neighbourhood of a single bubble.* We consider a single bubble of radius R, in a fluid of surface tension T, and density $\bar{\rho}$; the quantity $\alpha = R/a$ (equation (3)) is a dimensionless measure of the radius in terms of the Laplace constant (equation (1)). At any point in the neighbourhood of the bubble, let the height of liquid above that at infinity be z, and choose Cartesian axes Ox, Oy parallel to the principal sections of curvature of the surface. Then the principal radii of curvature at the point are given by expressions such as

$$\frac{1}{R_1} = \frac{\partial^2 z}{\partial x^2} \Big/ \left\{1 + \left(\frac{\partial z}{\partial x}\right)^2\right\}^{\frac{3}{2}}, \tag{5}$$

or approximately, if $\dfrac{\partial z}{\partial x} \ll 1$, by

$$\frac{1}{R_1} = \frac{\partial^2 z}{\partial x^2}, \tag{6}$$

and hence the drop in pressure in crossing the surface, namely, $T(1/R_1 + 1/R_2)$, becomes $T\nabla^2 z$. Since $\nabla^2 z$ is invariant under rotation of axes, it is no longer necessary to restrict our axes to principal sections, and any pair of perpendicular axes is sufficient. The pressure at a point just below the surface is given by $-\bar{\rho}gz$, and hence the equation to the surface becomes

$$\nabla^2 z = \frac{\bar{\rho}g}{T} z. \tag{7}$$

With cylindrical symmetry, we may put

$$\nabla^2 z = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial z}{\partial r}\right), \tag{8}$$

where r is the distance from the vertical axis, so that

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial z}{\partial r}\right) = \frac{\bar{\rho}g}{T} z. \tag{9}$$

Now introduce the dimensionless coordinates $\zeta = z/R$ and $\rho = r/R$; then with

$$\alpha^2 = R^2/a^2 = R^2\bar{\rho}g/T$$

as in equation (1), equation (9) may be written

$$\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho\frac{\partial \zeta}{\partial \rho}\right) = \alpha^2 \zeta,$$

i.e.

$$\frac{d^2\zeta}{d\rho^2} + \frac{1}{\rho}\frac{d\zeta}{d\rho} - \alpha^2\zeta = 0.$$

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This is the modified Bessel equation of order zero. The only solution tending to zero as ρ tends to ∞ is of the form

$$\zeta = AK_0(\alpha\rho), \tag{10}$$

where A must be chosen to satisfy the conditions at the inner boundary. These must now be considered.

4. *Boundary conditions.* The boundary condition at infinity has already been satisfied. The boundary condition at small ρ is given by some assumption as to the 'angle of contact' or its equivalent in the case of the bubble. For the spherical particle whose contact angle is ψ we have the condition

$$\tan\theta = \frac{d\zeta}{d\rho} = -\frac{\tan\phi - \tan\psi}{1+\tan\psi\tan\phi}, \tag{11}$$

where ϕ is the semi-angle subtended at the centre of the sphere by the circle of contact of radius b, i.e. if we put $\beta = b/R$,

$$\tan\phi = \beta/\sqrt{(1-\beta^2)}.$$

In particular, for zero angle of contact (11) becomes

$$\frac{d\zeta}{d\rho} = -\beta/\sqrt{(1-\beta^2)} \quad (\rho = \beta). \tag{12}$$

For the bubble, the required condition is that of continuity of slope between the cap of the bubble, which is spherical and of radius $2R$, and the remainder of the fluid surface. This continuity follows from the absence of any localized forces acting on the upper surface; in fact, the only discontinuity in passing out of the film and into the neighbouring liquid is a discontinuity in pressure; this results in a discontinuity in curvature but not in gradient. There is, however, a discontinuity in the gradient of the internal surface of the bubble at $\rho = \beta$; this is a consequence of the assumption introduced in § 2 that the submerged portion of the bubble remains rigidly spherical; the buoyancy forces which are, strictly, distributed over the whole of the submerged part of the bubble are regarded as being localized at the rim of the spherical cap. The departure from the spherical form introduces a negligible error in the buoyancy force.

The condition of continuity in gradient at $\rho = \beta$ gives us

$$\frac{d\zeta}{d\rho} = -\beta/\sqrt{(4-\beta^2)}. \tag{13}$$

Substituting for ζ from (10) we find

$$A\alpha K_0'(\alpha\beta) = -\beta/\sqrt{(4-\beta^2)},$$

and using the identity

$$K_0'(x) = -K_1(x),$$

we obtain

$$A = \frac{1}{\alpha K_1(\alpha\beta)}\frac{\beta}{\sqrt{(4-\beta^2)}}. \tag{14}$$

As we have neglected second-order terms in the inclination when deriving the differential equation, it may seem unnecessary and inconsistent to retain them here. It is, however, at this boundary that the angles of inclination are greatest, so that what may be a reasonable approximation in the remainder of the field is not necessarily justified on the boundary.

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5. *Equilibrium of bubble.* To use equation (14) we must first find β. This is determined by the equilibrium between buoyancy and surface-tension forces. The vertical component of the force due to surface tension acting on a ring of radius b is $2\pi bT \cdot b/(2R)$, i.e. $\pi R\beta^2 T$, so that if the buoyancy be denoted by B, and the weight of the film be neglected, we have

$$B = \pi RT\beta^2. \tag{15}$$

To calculate B we use Archimedes' principle. In Fig. 1 it will be seen that the hydrostatic pressure at the ring of contact PQ is less than atmospheric pressure (i.e. negative if we take atmospheric pressure as our datum) by an amount $\bar{\rho}gz_0$, where z_0 is the height of the fluid at the ring PQ. Let us apply an additional uniform pressure equal to $\bar{\rho}gz_0$ at all points of the liquid. Then the upthrust is given by the weight of liquid displaced, i.e. by $\bar{\rho}gV$, where V is the volume of the portion PQS of the sphere. This is greater

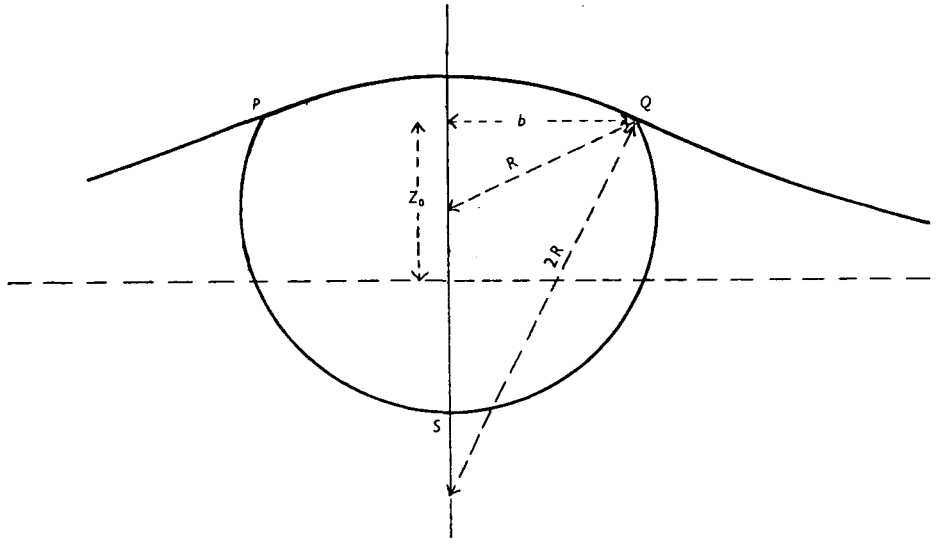


Fig. 1. Single bubble floating on liquid PQ is the ring of contact of radius b. The free surface is indicated by the broken line.

than the true upthrust B required by the amount $\bar{\rho}gz_0 \cdot \pi b^2$ which is the thrust due to the additional pressure. Hence

$$B = \bar{\rho}g(V - \pi b^2 z_0). \tag{16}$$

Evaluating V, we find eventually

$$B = \tfrac{2}{3}\pi R^3 \bar{\rho}g[1 + \sqrt{(1-\beta^2)}\,(1 + \tfrac{1}{2}\beta^2) - \tfrac{3}{2}\beta^2\zeta_0]. \tag{17}$$

Using this in (15) and putting ζ_0 equal to $AK_0(\alpha\beta)$, we find the following implicit equation for β in terms of A,

$$\beta^2 = \tfrac{2}{3}\alpha^2[1 + \sqrt{(1-\beta^2)}\,(1 + \tfrac{1}{2}\beta^2) - \tfrac{3}{2}\beta^2 AK_0(\alpha\beta)]. \tag{18}$$

This may be solved simultaneously with (14) to give A as a function of α. Equation (10) then gives ζ as a function of α and ρ.

6. *Repulsion forces at short range.* The inclination of the liquid surface caused by a bubble at the origin will result in the apparent attraction of a second bubble at distance $r = R\rho$. This attraction persists until contact occurs, when a more or less rapidly

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increasing repulsive force sets in. The origin of this repulsion is taken to be the excess pressure inside one bubble acting on the area of contact with the other (Fig. 2). If we confine our attention to equal bubbles of body radius R, then the excess pressure is $2T/R$ and the area of contact is plane. Neglecting all effects such as the rise in pressure due to distortion of the bubble and the thickness of the film separating the bubbles, we obtain for the repulsive forces the expression

$$\pi R^2\left(1-\frac{\rho^2}{4}\right)\frac{2T}{R}, \tag{19}$$

or, since $\frac{1}{2}\rho$ is very nearly unity, $2\pi RT(2-\rho)$. (20)

This holds for $\rho \leqslant 2$ only. For $\rho > 2$ the bubbles are not in contact.

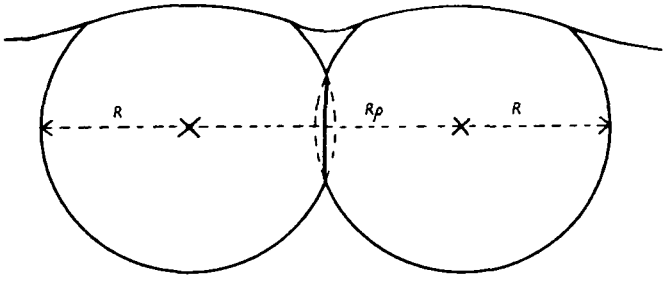


Fig. 2. Two bubbles in contact.

7. *Potential energy of two similar bubbles.* We now consider the potential energy of one bubble in the field of a second similar bubble supposed fixed at the origin. If the buoyancy of the first is B and the height of the fluid surface, due to the presence of the second, is z, then the potential energy of the first in the field of the second is $-Bz$ or $-RB\zeta$.

If their distance apart is such that $\rho < 2$, there is an additional potential energy given by integration of (20) as $\pi R^2T(2-\rho)^2$.

The total potential energy may therefore be written as

$$-RB\zeta+\begin{cases}\pi R^2T(2-\rho)^2 & (\rho\leqslant 2),\\ 0 & (\rho\geqslant 2).\end{cases} \tag{21}$$

From (15) we have $B = \pi R\beta^2T$, and from (1) and (3) $T = a^2\bar{\rho}g = R^2\bar{\rho}g/\alpha^2$. Replacing B and T in the above we now find that the potential energy is given by

$$\pi R^4\bar{\rho}g\,V(\alpha,\rho), \tag{22}$$

where

$$V(\alpha,\rho) = -\frac{\beta^2}{\alpha^2}\zeta+\begin{cases}\dfrac{(2-\rho)^2}{\alpha^2} & (\rho\leqslant 2),\\ 0 & (\rho\geqslant 2).\end{cases} \tag{23}$$

Some calculated values of β and V are given in the tables below, and Fig. 3 gives graphs of V in terms of ρ for $\alpha = 0{\cdot}2$ and $1{\cdot}0$.

Table 1. *β and A as functions of α [equations (14) and (18)]*

α	0	0·2	0·4	0·6	0·8	1·0
β	0	0·2304	0·4527	0·6466	0·7958	0·8972
A	0	0·0268	0·1094	0·2515	0·4513	0·6973

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Table 2. *$V(\alpha, \rho)$ as a function of α and ρ*

$$V(\alpha,\rho) = -\frac{\beta^2}{\alpha^2}\zeta + \begin{cases} \dfrac{(2-\rho)^2}{\alpha^2} & (\rho \leqslant 2), \\ 0 & (\rho \geqslant 2). \end{cases}$$

ρ \ α	0	0·2	0·4	0·6	0·8	1·0
1	—	24·94	6·09	2·55	1·31	0·764
1·6	—	3·95	0·90	0·31	0·12	0·054
1·7	—	2·21	0·47	0·13	0·03	0·007
1·8	—	0·96	0·16	−0·001	−0·041	−0·042
1·9	—	0·21	−0·022	−0·073	−0·077	−0·062
1·95	—	0·022	−0·062	−0·089	−0·088	−0·065
2	—	−0·040	−0·079	−0·093	−0·084	−0·064
2·5	—	−0·033	−0·059	−0·063	−0·051	−0·035
3	—	−0·028	−0·045	−0·042	−0·031	−0·019
5	—	−0·015	−0·016	−0·010	−0·005	−0·002

(The results for $\alpha = 0{\cdot}2$ and $\alpha = 1{\cdot}0$ are plotted in Fig. 3.)

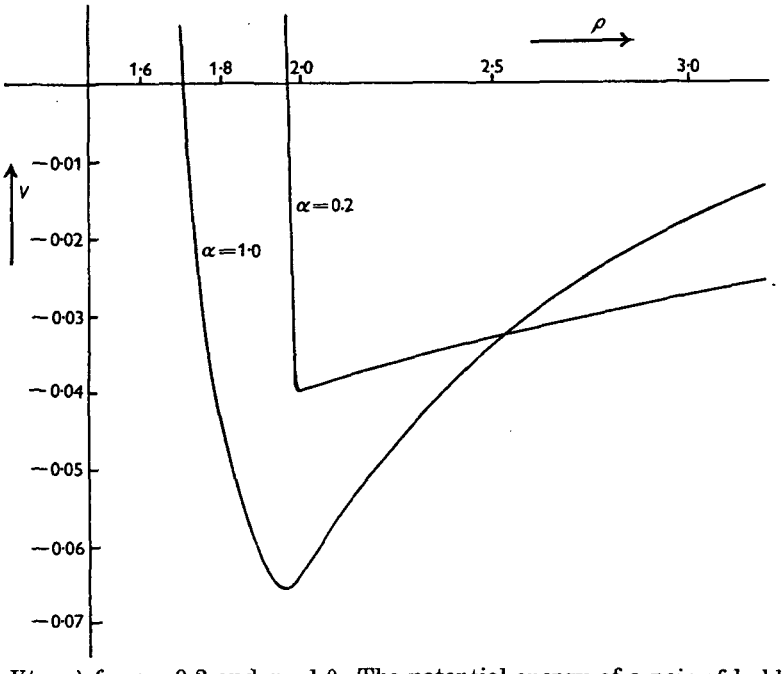


Fig. 3. $V(\alpha, \rho)$ for $\alpha = 0{\cdot}2$ and $\alpha = 1{\cdot}0$. The potential energy of a pair of bubbles is given by $\pi R^4 \bar{\rho} g\, V(\alpha, \rho)$. Contact occurs at $\rho = 2$.

8. *Summary and conclusions.* A quantitative study of the law of force between bubbles floating on a fluid has been made and the results exhibited in the form of a potential energy-distance curve. The main approximations made are that the inclination of the surface of the fluid is small (so that the equations for the surface become linear), and that the submerged portion of the bubble remains spherical. The latter

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assumption restricts the validity of the results to small bubbles of about 3·0 mm. diameter and less.

One object of the work was to determine the size of bubble which simulated most nearly a typical atomic interaction curve. This application arises in connexion with Prof. Bragg's 'bubble' model of crystal lattices. Exact simulation cannot be expected, for the bubble model is two-dimensional, and also does not exert forces analogous either to Coulomb repulsion or to the metallic bond. It can be shown, however, that the law of force between bubbles of a particular size is a remarkably close fit to the law of force between inert gas atoms, that is, to an interaction consisting of a van der Waals attraction and a short-range or 'overlap' repulsion. Fig. 4 illustrates this point. The two full curves are the energy-distance curves for krypton and argon atoms (plotted from Fowler, *Statistical Mechanics*, 2nd ed., Chapter x, Table 29). The circles mark the corresponding curve for bubbles with $\alpha = 1{\cdot}0$ (i.e. of diameter 3 mm. in soap solution). The units of energy and distance are chosen so as to bring the minimum of each curve to the point (1, −50). It will be seen that the curves are remarkably similar over the range shown.

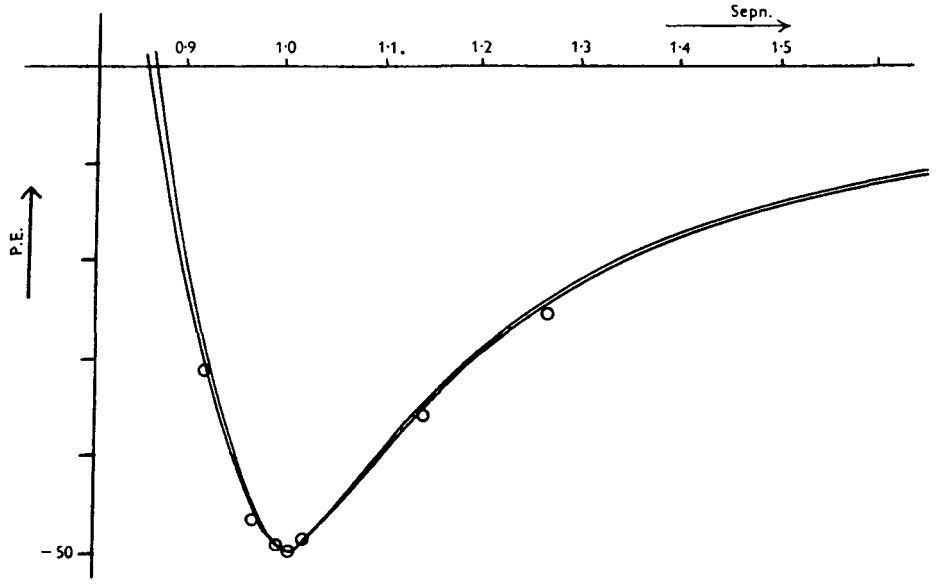


Fig. 4. The curves refer to the interaction between krypton and argon atoms. The encircled points refer to the interaction between bubbles of radius 1·5 mm. ($\alpha = 1{\cdot}0$).

The units are chosen so as to make the minima coincide at (1, −50) in arbitrary units.

I wish to thank Prof. Bragg for suggesting this problem, and to acknowledge my indebtedness to Mr J. F. Nye, M.A., King's College, for a number of very valuable discussions.

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