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Introduction and summary

Some problems have always been with us. No one knows when man first asked 'What is the origin of our world?' or 'What is life?', and progress towards satisfactory answers has been slow and exceedingly difficult. One aim of this study is to take such a perennial theme, although one narrower than either of these two problems, and see how it has been tackled in the Western world in the last three hundred years. The topic is that of cohesion – why does matter stick together? Why do gases condense to liquids, liquids freeze to solids or, as it has been put more vividly, why, when we lift one end of a stick, does the other end come up too? Such questions make sense at all times and the attempts to answer them have an intrinsic interest, for the subject of cohesion has at many times in the last three centuries been an important component of the physical science of the day. It has attracted the attention of some of the leading scientists of each era, as well as a wide range of the less well known. It is a part of our history that is worth setting out in some detail, a task that I think has not yet been attempted.

This study has, however, a wider aim also. Historians have rightly given much attention to the great turning-points of science – Newton's mechanics, Lavoisier's chemistry, Dalton's atomic theory, Maxwell's electrodynamics, Planck's quantum theory, and Einstein's theories of relativity, to name but half a dozen in the physical sciences. These are the points that Thomas Kuhn described as revolutions [1]. The study of cohesion shows no such dramatic moments, the closest being, perhaps, the discovery of the quantal origin of the universal force of attraction between molecules in 1927–1930. This is, therefore, an account of a branch of 'normal' science that exemplifies how such work is done.

Science is not a logical and magisterial progress in which experimental discoveries lead directly to new theories and in which these theories then guide new experimental work. The practitioners know this on a small scale. Research workers can see how their progress is helped or hindered by chance discoveries, misleading experiments, half-remembered lectures, chance finds in the 'literature', unexpected discussions at a conference, and all the other perturbations of laboratory life. Moreover science can be fun. Investigations can be made just out of curiosity even when it is clear that the answer, when found, will solve no particular experimental or theoretical problem. We shall see that similar disorderliness marks progress on a larger scale. Matters move forward rapidly for a decade or so, and then stagnate for many decades. Here three broad periods of advance have been identified and named after Newton, Laplace and van der Waals. They were, of course, not the only generators of the advances but their contributions were decisive and, perhaps, stretch the concept of normality to its limits. Their names may, however, conveniently be used to identify their periods.

It is of interest to seek for the causes of this punctuated advance. Some of the periods of stagnation are related to weaknesses in the contemporary infra-structure, either experimental or, more usually, theoretical. Thus we shall see that many of the natural philosophers of the 18th century were hampered by their inadequate knowledge of mechanics and of the calculus. What Newton and Leibniz had created needed to be completed by the Bernoullis, Euler and others before it passed into general scientific circulation. This passage occurred notably in the institutions established in 'revolutionary' France at the end of the century, and it is not surprising that a second period of advance in understanding came with Laplace. There were also other less direct reasons for the relative stagnation of the 18th century. Some were cultural. One cannot imagine a present-day undergraduate or research student being told by his or her teacher that there was a worrying metaphysical problem with forces between molecules acting at a distance, or with a model system of hard spheres undergoing elastic collisions, but these were very real concerns in the 18th century. By the 19th they were not so much banished as ignored. An indifference to metaphysical problems seems to be one of the features of normal science. We shall see that scientists have a well-developed defensive mechanism when faced with theoretical obstacles. They ignore them, hope that what they are doing will turn out to be justified, and leave it to their deeper brethren or to their successors to resolve the difficulty. In the 18th century and beyond, this proved to be the right way forward both for gravity and for interparticle forces; they functioned for all practical purposes as if they acted at a distance. It was not until the 1940s that the problem of how this intermolecular action was transmitted had to be faced. This defensive mechanism can go wrong; we shall see that in the early years of the 20th century there were repeated attempts to seek a classical electrostatic origin for the intermolecular forces, in spite of what is to us, and perhaps should have been to them, clear evidence that these were bound to fail.

Another problem in the 18th century that we can broadly call cultural was what we now see as an inadequate way of assessing new theories. The same metaphysical bias that objected to action at a distance without a discernible mechanism to effect it, led to theories that laid too much emphasis on plausible mechanisms, and not enough on means of testing the theories or of seeing if they had any predictive power. By the end of the century (again judging by our notions) matters had improved, and this change, coupled with the 'revolutionary' mathematics of the French, meant that by the early 19th century theoretical physics had taken a form in which we can recognise many of the ways of working that we still use.

But beyond these internal weaknesses and metaphysical doubts there remains an unexplained cause of the flow and stagnation of progress that we can only call fashion. It was obvious to Réaumur as early as 1749 that science was as prone to fashion as any other human activity [2], and these swings may be strongest when there are few in the field. The spectacular experiments that could be made in the 18th century in electricity, and the solid advances in the study of chemistry and of heat, attracted the best men, and left only a few, mainly of the second-rank, to study capillarity and other manifestations of cohesion. To call this fashion is perhaps to go too far in imputing irrationality. Research programmes do degenerate and are justifiably overtaken by rising fields in which progress is easier. Science is like a rising tide; if certain areas are perceived to be open to flooding then the practitioners rush in, leaving other research programmes as unconquered and ignored islands of resistance. But once this is said there remains an element, if not of irrationality, than of adventitiousness about scientific advance.

There are also in the background those changes in the sociological, political, religious and economic aspects of each era whose influence on the science of the day is now the main concern of many historians. If I have not pursued these with the rigour that current practice seems to demand it is not because I doubt their importance but because it becomes hard to discern their effects in a specialised and 'philosophic' subject such as cohesion. In the 18th and 19th centuries religious convictions certainly influenced philosophical thought but I have not seen a direct or strong enough link to the problem of cohesion to follow the subject beyond an occasional remark. No doubt others would tackle the subject differently.

The 19th century is more complex than the 18th but analysis is helped by the greater attention paid to it by historians. Laplace and his colleagues had much success in the first twenty years of the century, in which his solving of the problems of capillarity is the one that is the most central to our story. Then came about what has been called 'the fall of Laplacian physics' [3]. His belief in a corpuscular theory of light, in matter as a static array of interacting particles, and of heat as a caloric fluid that was responsible for the repulsive component of the force between the particles, all told against him and his followers when physics advanced beyond these ideas. But it was again the competition of the rising fields of electricity, magnetism, optics, and later, thermodynamics that attracted the attention; the one field where Laplace's ideas were still important was that of the elasticity of solids, a subject in which the imperfections of his physics were of little consequence.

The big struggle of the 19th century was that between the picture of interacting particles of matter, each surrounded by a vacuum, that had been held by Newton and Laplace, and the continuum picture of matter and space that came to be embodied in field theories. This was not a competition between different scientists, for many adopted both views at different times, or even apparently at the same time, but it was a competition between methods of interpretation. For example the classical thermodynamics of the 1850s and 1860s, a subject apparently independent of any view of the structure of matter, grew up alongside the developing kinetic theory of gases which required a corpuscular theory. The continuum mechanics that proved most successful in describing the elastic properties of solids lived in uneasy conjunction with the Laplacian attempts to interpret these properties in terms of interparticle forces. Cauchy could switch from one view to the other within a few months.

The struggle between field theories and particulate theories is only one example of the great debates that are relevant to the subject of cohesion but whose full discussion would take us too far from the main line. Here we can only follow what was found at the time to be successful in practice. Not until 1954 did a field theory of cohesion appear, and even now it is only of specialist interest. This account is therefore weighted towards those who believed in interparticle forces and so drove the subject forward. Other cognate topics that might have been explored but are not, are 18th century chemistry, which overlaps with what we now call physics, the theory of the optical aether which inspired much of the 19th century work on elasticity, and the final resolution of the atomic debates in the early years of the 20th century.

By the early 19th century chemistry and physics were regarded as distinct subjects. The physical aspects of chemistry had a brief Laplacian flourish at the hands of Berthollet, Gay-Lussac and Dumas but then fell out of fashion under the competition from the electrochemistry of Davy and Berzelius, and the successes of organic chemistry and the problems of atomic weight and molecular structure. Physical chemistry revived towards the end of the century, first as the chemistry of solutions, ions and electrolytes, and then more widely under the impact of quantum theory in the first half of the 20th century. Most of those working on intermolecular forces in the second half of the century would describe themselves as physical or theoretical chemists, not as physicists.

The 20th century brought new dangers. The number of scientists grew rapidly and with this growth came the problems of specialisation. When a field fell out of fashion, as did that of cohesion in the early part of the century, then important work could be forgotten when the next generation returned to the field. The achievements of van der Waals and his school were ignored from about 1910 onwards; work on cohesion and the properties of liquids could not compete with the great developments of the day in quantum theory on the one hand and the experimental work on radioactivity and fundamental particles on the other. The work of many of the leading physicists of the passing generation, published in hundreds of papers in the leading journals of the day, became almost overnight a forgotten backwater of physics. This was not the field where great discoveries were to be made, reputations to be gained, and honours to be won. The same thing still happens, if not so dramatically. The topic of intermolecular forces, a matter of great debate in the 1950s, 1960s, and early 1970s, has now dropped from the front rank. This exit followed one important success, the accurate determination of the force between a pair of argon atoms, but that achievement left plenty of work still to be done. Nevertheless the subject was thought to have gone off the boil, and in the 1980s and 1990s few of those earning the star salaries in American universities were to be found in this field.

With increased specialisation came also a certain arrogance. One can sense in the writing of some of those active in the 1930s and later, a reluctance to believe that anything of importance could have happened before the great days of quantum theory in the 1920s. Spectroscopy is a field that generated many interesting numerical results in the 19th century but which owes its quantitative theory to quantum mechanics. Its practitioners made some late but valuable contributions to the determination of simple intermolecular forces, but they did not bother with the older field of statistical mechanics, and their interpretation of their results was often flawed. These had to be analysed by others before their value could be appreciated. At the very end of the century, however, the spectroscopists made one spectacular advance with the determination of the forces between two water molecules, a system so complicated that it had defied the efforts of those who had been trying to find these forces from the macroscopic properties of water. Little is said here, however, about experimental advances or problems since throughout its history cohesion has been a subject where the experiments have usually been simple but their interpretation difficult. There are exceptions, of which the most obvious is, perhaps, the absence of direct evidence of the particulate structure of crystals which hampered 19th century attempts at a theory of elasticity. But, as so often, this difficulty was resolved by a totally unrelated discovery – that of x-rays and the realisation that they were electromagnetic waves.

Making generalisations about how science is done from the example of one rather narrow field is hazardous. Many may dispute those drawn here, even on the evidence provided, but they are put forward as an attempt to show how this field has advanced over three hundred years. I would not wish to be dogmatic; others should try to draw their own conclusions from this field, and other fields may lead to different conclusions. One can read Popper, Kuhn, Lakatos and other philosophers of science and recognise there many truths that call to mind instances of how it is done, but it is difficult to fit even one physical science into their moulds. Science does in practice seem to move in less logical ways than philosophers would wish. Feyerabend would surely find here examples with which to justify his claim that "Science is an essentially anarchic enterprise" [4].

It is, of course, the common-sense view of practising scientists that the movement of science is an advance, and that, although the advance itself may be irregular, the result is a coherent structure. This narrative would not make sense without that belief. That the advance is not always logical, rarely neat, and occasionally repetitious, is not a theme that can be summarised in the trite phrase 'history repeats itself'. That does happen; a curious example is the repetition in the second half of the 20th century of arguments about the representation of the pressure tensor that duplicate, in ignorance, and almost word for word, some of those of a hundred years earlier. But such repetitions are, I think, curiosities of little consequence. I end, however, with some quotations that show that a certain simile came to mind repeatedly for 150 years, and then apparently disappeared for the next 130. Why, I cannot say, unless it be that astronomy has lost something of its former prestige, so these quotations are offered for their interest only.

We behold indeed, in the motions of the celestial bodies, some effects of it [the attraction] that may be call'd more august or pompous. But methinks these little *hyperbola's*, form'd by a fluid between two glass planes, are not a-whit less fine and curious, than the spacious ellipses describ'd by the planets, in the bright expanse of Heaven.

(Humphry Ditton, mathematics master at Christ's Hospital, 1714) [5]

Peut-être un jour la précision des données sera-t-elle amenée au point que le Géomètre pourra calculer, dans son cabinet, les phénomènes d'une combinaison chimique quelconque, pour ainsi dire de la même manière qu'il calcule le mouvement des corps célestes. Les vues que M. de la Place a sur cet objet, & les expériences que nous avons projétées, d'après ses idées, pour exprimer par des nombres la force des affinités des différens corps, permettent déjà de ne pas regarder cette espérance absolument comme une chimère.

(A.L. Lavoisier, 1785) [6]

Quelques expériences déjà faites par ce moyen, donnent lieu d'espérer qu'un jour, ces lois seront parfaitement connues; alors, en y appliquant le calcul, on pourra élever la physique des corps terrestres, au degré de perfection, que la découverte de la pesanteur universelle a donné à la physique céleste.

(P.-S. Laplace, 1796) [7]

We are not wholly without hope that the real weight of each such atom may some day be known . . . ; that the form and motion of the parts of each atom, and the distance by which they are separated, may be calculated; that the motions by which they produce heat, electricity, and light may be illustrated by exact geometrical diagrams. . . . Then the motion of the planets and music of the spheres will be neglected for a while in admiration of the maze in which the tiny atoms turn.

(H.C. Fleeming Jenkin, Professor of Engineering at Edinburgh in a review of a book on Lucretius, 1868, repeated by William Thomson in his Presidential Address to the British Association, 1871, and quoted from there, in Dutch, by J.D. van der Waals as the closing words of his doctoral thesis at Leiden in 1873) [8]

Notes and references

1 T.S. Kuhn, *The structure of scientific revolutions*, Chicago, 1962.

2 See Section 2.5. For modern instances of the same view, see F. Hoyle, *Home is where the wind blows*, Oxford, 1994, pp. 279–80, on recent fashions in astronomy; F. Franks, *Polywater*, Cambridge, MA, 1981, for the frantic pursuit of a non-existent anomaly in the 1960s; and P. Laszlo, *La découverte scientifique*, Paris, 1999, chap. 8, for a vivid account of a 1969 fad in research on nuclear magnetic resonance. The rapid dissemination of some papers on the Internet and the ease with which the number of times that they have been 'read' can be recorded, has made worse the irrational pursuit of current fashions, according to the report on a discussion at a recent Seven Pines Symposium, by J. Glanz in the *International Herald Tribune* of 20 June, 2001.

3 R. Fox, 'The rise and fall of Laplacian physics', *Hist. Stud. Phys. Sci*. **4** (1975) 89–136.

4 P. Feyerabend, *Against method*, 3rd edn, London, 1993, p. 9. The first edition was published in 1975. J.D. Watson made the same point for the biological sciences in the opening words of the Preface to *The double helix*, New York, 1968.

5 H. Ditton, *The new law of fluids or*, *a discourse concerning the ascent of liquors*, *in exact geometrical figures*, *between two nearly contiguous surfaces*; . . . , London, 1714, p. 41.

6 A.L. Lavoisier, 'Sur l'affinité du principe oxygène avec les différentes substances auxquelles il est susceptible d'unir', *Mém. Acad. Roy. Sci.* (1782) 530–40, published 1785, see pp. 534–5.

7 P.-S. Laplace, *Exposition du système du monde*, Paris, 1796, v. 2, p. 198.

8 [Anon.], 'Lucretius and the atomic theory', *North British Review* **6** (1868) 227–42, see pp. 241–2, and in *Papers*, *literary*, *scientific*, *etc. by the late Fleeming Jenkin*, ed. S. Colvin and J.A. Ewing, London, 1887, v. 1, pp. 177–214, see pp. 213–14; W. Thomson, Presidential address, *Rep. Brit. Assoc.* **41** (1871) lxxxiv–cv, see p. xciv; J.D. van der Waals, *Over de continuiteit van den gas- en vloeistoftoestand*, Thesis, Leiden, 1873, p. 128. Thomson wrote the last word as 'run', not 'turn': either a slip or a reference to the prevailing view of the 1870s that molecular motions were primarily translational, not rotational, as had sometimes been supposed in the early 19th century.

2

Newton

2.1 Newton's legacy

The natural philosophers of the eighteenth century knew Newton's work [1] through his two books, the *Principia mathematica* of 1687 [2] and the *Opticks* of 1704 [3]. His belief in a corpuscular philosophy is clear in both, and is particularly prominent in the later editions of the *Opticks*, but the cohesive forces between the particles of matter are not the prime subject of either book. Together, however, they contain enough for his views on cohesion to be made clear. We, who are now privy to many of his unpublished writings, know how much more he might have said, or said earlier in his life, had he not been so fearful of committing himself in public on so controversial a topic. He was not the first to speculate in this field but his views were better articulated than those of his predecessors [4] and, what is perhaps more important, they carried in the 18th century the force of his ever-increasing authority. It was his vision that was transmitted to the physicists of the early 19th century, and we examine first the legacy that he left to his philosophical heirs. The account is restricted to the subject in hand; that is, how does matter stick together, and wider aspects of Newton's thought remain untouched.

In the Preface to the *Principia* he describes the success of his treatment of mechanics and gravitation, and then continues:

> I wish we could derive the rest of the phaenomena of Nature by the same kind of reasoning from mechanical principles. For I am induced by many reasons to suspect that they may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled towards each other and cohere in regular figures, or are repelled and recede from each other; which forces being unknown, philosophers have hitherto attempted the search of Nature in vain. But I hope the principles here laid down will afford some light either to that, or some truer, method of philosophy. [5]

Here he alludes not only to the short-ranged forces of attraction that he held to be responsible for the cohesion of liquids and solids but also to those other forces that he was to propose later in the book as a possible explanation of the pressure of a gas as a repulsion between stationary particles [6]. Readers of the *Principia* were to learn little more about the cohesive forces although he had at one time intended to take the subject further. In a draft version of the Preface, he had described the cohesion between its parts as being responsible for mercury being able to stand in a Torricellian vacuum at a height greatly in excess of the atmospheric pressure of thirty inches, and he had intended to enquire further into these forces. Then, in a phrase he was to use more than once, he wrote:

> For if Nature be simple and pretty conformable to herself, causes will operate in the same kind of way in all phenomena, so that the motions of smaller bodies depend upon certain smaller forces just as the motions of larger bodies are ruled by the greater force of gravity. [7]

His comment on the relative sizes of the forces betrays a looseness of thought that he was to correct before he published anything in this field.

He made a second attempt to say more about cohesive forces and the forces that lead to solution, to chemical action, to fermentation and similar processes, in a draft Conclusion that was also intended for the first edition of the *Principia*. In this he expressed the same thoughts but now couched more as hopes than intentions. "If any one shall have the good fortune to discover all these [causes of local motion], I might almost say that he will have laid bare the whole nature of bodies so far as the mechanical causes of things are concerned." [8] He discussed the rise of liquids in small tubes, a phenomenon that was later to play an important role in the study of cohesion since it was such an obvious departure from the known laws of hydrostatics. He (like Robert Hooke [9]) thought then that the rise was caused by a repulsion of air by glass, a consequent rarefaction of the air in the tube, and the rise of liquid to replace it.

Newton was holding back twenty-five years later when Roger Cotes [10] was preparing the second edition of the *Principia*. He wrote to Cotes on 2 March 1712/13: "I intended to have said much more about the attraction of small particles of bodies, but upon second thoughts I have chose rather to add but one short paragraph about that part of philosophy. This Scholium finishes the book." [11, 12] Again there are draft versions of this Scholium that go beyond what was printed [13].

In spite of these hesitations and withdrawals the *Principia* of 1687 contains much that hints at the tenor of his thoughts. This material is often in the form of mathematical theorems that could have been used to discuss cohesion, but the application is never made. Thus Section 13 of Book 1 contains in Proposition 86 the statement that for forces that "decrease, in the recess of the attracted body, in a triplicate or more than triplicate ratio of the distance from the particles; the attraction will be vastly stronger in the point of contact than when the attracting and attracted bodies are separated from each other though by never so small an interval." [14] In Proposition 91 the discussion is extended to "forces decreasing in any ratio of the distances whatsoever", and in Proposition 93 he shows that if the particles attract as r^{-m}, where r is the separation, then a particle is attracted by a slab composed of such particles by a force proportional to R^{-m+3}, where R is the distance of the particle from the planar surface of the body. Similarly his discussion of the repulsive forces between contiguous particles in a gas [6] is generalised to forces proportional to r^{-m} which, he shows, lead to a pressure proportional to the density to a power of $(m+2)/3$, so that what we now call Boyle's law requires that m is 1. Propositions 94–96 of Section 14 of Book 1 are "Of the motion of very small bodies when agitated by centripetal [i.e. attractive] forces tending to the several parts of any very great body", but it is soon clear that the application he has in mind is to optics; the "very small bodies" are his particles of light.

John Harris [15], in the first volume of his *Lexicon technicum* of 1704, commented accurately that the word 'attraction' is "retained by good naturalists and, in particular, by the excellent Mr. Isaac Newton in his *Principia*; but without there determining any thing of the *quale* of it, for he doth not consider things so much physically as mathematically." [16] This was true in 1704 but six years later, in his second volume, when he had read the Latin edition of the *Opticks*, he changed his mind and accepted the physical reality of these forces. He was briefly a Secretary at the Royal Society and had seen the experiments performed there, often under Newton's direction as President.

When, in the *Principia*, Newton does discuss the physical consequences of forces steeper than inverse square then his thoughts turn more naturally to magnetism than to cohesion. In Book 3, Proposition 6, Theorem 6, Cor. 4 of the 1687 edition he says of magnetism that "it surely decreases in a ratio of distance greater than the duplicate." [17] By the time of time of the second edition of 1713 he is more precise, and in what is re-numbered Cor. 5, he writes that the force "decreases not in the duplicate, but almost in the triplicate proportion of the distance, as nearly as I could judge from some rude observations." [18] His early remarks may have been based on some observations of Hooke [19] but his later ones stemmed from the experiments made at the Royal Society by Brook Taylor [20] and Francis Hauksbee [21] that started in June 1712 [22]. Taylor deduced that "at the distance of nine feet, the power alters faster, than as the cubes of the distances, whereas at the distances of one and two feet, the power alters nearly as their squares". The interpretation of these results is not simple. Newton speaks of "magnetic attraction", which might imply the force of attraction between two magnets, but Taylor and Hauksbee measured the field of the magnet (in modern terms) by observing the deflection of a small test or compass magnet at different distances from the lodestone. The distances were measured both from the centre of the lodestone or, more usually, from its "extremity", and it is not clear what function of the angle of deflection is taken as a measure of the "power", presumably the angle itself. Such far from simple results did not hold out much