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New Directions in Sorption Technology

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PREFACE

Adsorption (sometimes called sorption to include dissolution of sorbates into certain kinds of sorbents) has become increasingly important in both the traditional chemical and petrochemical industries as well as in developing industries such as biotechnology. Sorption processes range in size from those used in analytical chemistry to massive units processing millions of cubic feet of gas or liquid per day. In acknowledgment of the importance of sorption, a full-day Symposium on Improved Adsorbents and Adsorption Processes was held at the American Chemical Society's 193rd National Meeting in 1987 in Denver. At the same meeting, an Award Symposium on Separation Science and Technology was held to honor Professor F.G. Helfferich for his contributions to the areas of chromatography (a type of sorption process) and ion exchange.

This book includes selected papers presented at the two symposia as well as added papers. All papers were subjected to critical peer review, and the revisions are published here. Our objective is to report current developments in sorption technology from which new directions will emerge. The coverage is selective rather than exhaustive. Four areas are examined in this book: new sorbents, chromatography, pressure swing adsorption, and bioseparations involving sorption. Keller provides an overview concentrating on the technical maturity of various sorption processes.

Helfferich reviews the powerful concept of coherence, which he developed in 1963 to describe the behavior of concentration waves of a multicomponent mixture in a chromatographic column. He suggests broader applications of this concept to the dynamics and optimization of industrial chemical processes. His ideas are echoed by Harwell's treatise on the complex system of chromatographic movement of mixed surfactants. Here the predictive power of the coherence concept is demonstrated, including unexpected behaviors at the critical micelle concentration.

The fundamental sorption properties and the characterization of two new sorbents are described by two groups: Suzuki and Sohn on activated carbon fibers manufactured by a Japanese company and Hearn et al. on macroreticular resins manufactured by one British and three U.S. companies. The unique advantages of these new sorbents for certain applications are shown by experimental results.

In the area of continuous steady-state chromatography, Carta and Byers describe their successful operation of the annular rotating bed chromatograph, which is the only remaining hope for the moving-bed chromatograph. Results of the separations of sugars, metal ions, and amino acids are given. An authoritative review of liquid chromatographic systems, both batch and continuous, is given by Barker and Ganetsos. The chapter includes many important bioseparations. Chapters on separation and purification of biomolecules naturally follow those on chromatography, which is the workhorse for bioseparations. A useful account of liquid chromatographic systems is given by Cramer and Subramanian. The emphasis of their chapter is, however, on displacement chromatography, on which they have had extensive experience. Nigam and Wang describe their development of a new type of sorbent for bioseparations: an immobilized affinity sorbent. The sorbent is encapsulated in a membrane that provides an additional kinetic selectivity for separation.

Three chapters related to pressure-swing adsorption (PSA) for gas separations are included. Pan et al. demonstrate the underlying principles for kinetic separation by PSA through their experimental results on nitrogen production from air using 4A zeolite. Amlinger discusses the sizing of vacuum pumps for desorption in PSA and shows how pumping systems can be optimized for minimizing energy consumption. Landfill gas (methane-carbon dioxide) separation is accomplished by kinetic PSA separation using molecular sieve carbon. A new adsorption process for purifying landfill gas before its entrance to the PSA system at a commercial plant in West Germany is described by Schilling and Hinz. Finally, a promising technique for regenerating spent activated carbon in aqueous applications is suggested by Roberts et al. In this technique, called surfactant-enhanced carbon regeneration, a concentrated surfactant solution is passed through the spent bed, and the adsorbate desorbs and is solubilized into micelles, which are highly concentrated in desorbed adsorbate.

We wish to express our appreciation to the authors and reviewers and to Butterworth Publishers for their patience and fine work that made this book a reality.

George E. Keller II
Ralph T. Yang

CONTENTS

Chapter 1

Coherence: Power and Challenge of a New Concept

Friedrich G. Helfferich

An overview of the coherence concept is given, outlining its nature, origin, predictive power, past and potential future applications, and challenges within the broader context of evolution of dynamic theory.

This presentation does not describe new hard-core developments or results, nor is it a comprehensive review. It attempts to provide a broad-brush overview of the concept of coherence, of what I meant when I chose that word twenty-five years ago, of what it has done for us and what I believe it still can do to bring us beyond where we stand today.

What Is Coherence?

For proper perspective, a good start may be to outline what coherence is and is not. It is certainly not one of the great ideas that have changed the picture we draw of our world. To name only some of the most prominent: the law of gravity, the first and second laws of thermodynamics, the quantum, the concept of relativity. Coherence is much more mundane in that it changes not one iota in the mathematical description of our world. Anyone looking for such exalted content tries to find what is not there.

Coherence is also not a method, technique, or device invented to make difficult mathematical problems more tractable. In this class would be, for example, the Laplace transform, matrix algebra, and the method of characteristics.

What coherence does is identify a particular facet, a fact of life, that had all the time been inplicit in our equations, to formulate it explicitly, and to forge it into a concept that helps us to understand phenomena, to recognize cause and effect, to predict without much need for calculation - something that makes us know what will happen. To name examples from this class of ideas: equilibrium, steady state, and entropy. We could work with our differential equations of motion, heat transfer, reaction, etc., and obtain the same results without ever having defined equilibrium or steady state. We could do thermodynamics without ever defining entropy. Yet these concepts facilitate our calculations and greatly help us in understanding what goes on.

The closest cousins to coherence are, indeed, equilibrium and steady state. Both are states to which a system settles down if not further disturbed (with exceptions in both cases). So is coherence. Equilibrium is restricted to a closed system. For the steady state, we allow the system to be open, but restrict it to fixed boundaries and constant boundary conditions. Coherence is not so restricted. In fact, it can be defined so that it includes equilibrium and steady state as special cases, but it also covers deviations from those states - typically, the propagation of perturbations through systems otherwise at equilibrium or steady state.

The idea that non-equilibrium, non-steady state systems shake themselves down to simple "modes" that are independent of the initial conditions is not new at all. In mechanics we have the pendulum, the harmonic oscillator, the musical string, with modes mathematically characterized by eigenvalues. All around us we see many such manifestations, from ocean swell to a flag in high wind: The world we live in is full of eigenvalues. It is just in physical chemistry and chemical engineering that our preoccupation with equilibrium and steady state has never before let us specifically and explicitly identify such dynamic behavior. Coherence does just that.

A Simple Example

To see how coherence may manifest itself in the world of physical chemistry and chemical engineering, consider a very simple physical system (1). Imagine an empty tube into which a water-oil mixture is introduced at the bottom, with no turbulence in the tube and with an oil lighter than water (see Figure 1). As oil in the tube will rise faster than water, a layer of oil will form and grow at the top of the rising column of liquid. The single change of inlet conditions (the start of oil-water flow) is propagated not as a single wave, but as two waves with different velocities - "waves" being defined as traveling variations of composition. In the distance-time plane, with distance from inlet and time as coordinates, the waves trace different trajectories (see Figure 2). If the entering fluid had contained additional immiscible phases, there would have been more than two waves. The generation of a whole spectrum of waves by a single perturbation and the formation of new zones of compositions that could not have been obtained by mixing the initial and injected fluids, such as the oil zone in our tube, are typical of multicomponent coupled dynamic systems. In the language of coherence theory, the original perturbation - the wave between air in the tube and the oil-water mixture just beginning to enter - is "noncoherent" and is resolved into two "coherent" waves: between air and oil, and between oil and oil-water. The original, noncoherent wave cannot travel as such because the oil layer immediately starts to form. In contrast, the two coherent waves travel maintaining their identities and will keep doing so until exiting the tube or being disturbed by some new manipulation.

A picture useful in more complex situations is to view a noncoherent wave as a superposition (not an additive one, though) of coherent waves which will separate from one another as they travel.

This very simple example also yields immediately a necessary and sufficient condition for a wave to be coherent. Any multicomponent wave can be viewed as a composite of single-component waves. For instance, the wave between oil and the oil-water mixture entails composition variations of both oil and water and so can be regarded as a composite of an oil wave and a water wave. For the composite wave to be coherent, that is, to travel without splitting up, the wave velocities of water and oil must obviously be the same. Equating these wave velocities leads to an eigenvalue problem, with eigenvalues characteristic of the velocities of coherent waves, and with eigenvectors characteristic of the composition variations across such waves.

The example can also serve to show one essential point that can be used to define coherence. Since the wave velocities with respect to all components must be equal at any point in a coherent wave, a complete set of values of dependent variables coexisting at such a point in space and time will travel jointly, in the same direction and at the same speed, and so remain in each other's company. A possible definition of coherence is the conservation of such sets. This definition includes equilibrium and steady state, conditions in which no value moves with time, so no existing set is ever broken up.

In this simple example, the coherence condition may appear trivial, yet it provides the key to the mathematical treatment and leads directly to the predictive tools coherence theory employs.

Tools

The coherence condition constrains the composition variations across coherent waves to eigenvectors, to definite directions in the composition space (that is, the space with the dependent variables as the coordinates, usually species concentrations, fractional phase volumes, or the like, also called "hodograph space" in the more rarified language of higher mathematics). In this space, curves meeting the coherence condition can be mapped as a grid. Several examples of such path grids in three- and four-component systems, taken from practical applications of the concept to ion exchange and enhanced oil recovery, are shown in Figures 3 to 7. In each case, the space is completely covered by an infinite number of curves, of which only some at regular intervals are shown. Any composition variation along a curve of the grid is coherent, any other is not. Coherence theory tells us that a system, in response to a perturbation, will shake itself down to a coherent state, as happened in our tube - that is, it will settle down to composition variations that follow the curves of the grid, in a sequence given by some very simple selection rules that are obvious in practice.

The important point here is that the grid is given by the type of basic equations and parameters of the system - the separation factors in adsorption and ion exchange, the relative volatilities in vapor-liquid systems, the relative permeabilities in multiphase flow in porous media, etc. - and is independent of the compositions of the initial and injected fluids. Therefore, for given components, the grid can be established once and for all and then be used to predict responses to any arbitrary initial and injection conditions. One may look at the grid as constituting the "groves" into which a system wants to settle, or as a road map on which a system's response can be mapped like a vacation trip. The combination of the distance-time diagram with the route which a system traces in the composition space provides a complete and compact quantitative description in space and time.

Calculation of an exact grid requires solutions of the eigenvalue problem at closely spaced points in the entire composition space. This is, of course, laborious. The art in applying coherence theory in practice is to realize how key features of the basic equations of equilibrium and motion are reflected in the topology and other properties of the grid. A single example may suffice to illustrate such a generation of an approximate path grid (5). In the grid of the brine-oil-surfactant system in Figure 6, paths exist only in the two-phase region (any composition variation in the single-phase region being automatically coherent). For the type of phase behavior as in the figure and with normal behavior of relative permeabilities, the path topology is always as shown. The straight paths are the tie lines of the two-phase region; the path originating from the plait point is the "equivelocity curve," easily calculated as the locus of equal velocities of the two phases; the points at which a curved path is tangential to a straight one are singularities, easily located as satisfying the condition that the two eigenvalues be equal. With all these features taken from the phase-equilibrium information or accurately calculated with simple algebra, an approximate grid is readily filled in without need to solve the eigenvalue problem at any point.

Once this art of grid generation is mastered, the practitioner can quickly predict at least qualitatively the response of his system to any perturbation, with little or no further recourse to mathematics. In fact, he can outguess a computer by predicting fairly accurately and with just pencil and paper the results of numerical simulations in less time than normally required for turn-around on most machines.

When to Resort to Coherence?

For systems as simple as the example shown in Figure 1 there is neither need nor good reason to invoke coherence. The results can be obtained as easily or more so with a conventional approach.

All that coherence can contribute here is a proof of uniqueness of the solution, as a purist may demand. Not so if subsequent perturbations generate new sets of waves, and waves of different sets begin to interfere with one another. The most complex cases are those involving gradual starting perturbations (as in gradient elution in chromatography) or interference of diffuse coherent waves with one another, producing finite regions of noncoherence in the distance-time plane (see Figure 8). No pre-coherence approach has been capable of handling such cases, except by blind numerical step-by-step integration in space and time of the differential equations or with other essentially equivalent methods. In contrast, coherence theory provides immediate qualitative answers as well as simple quantitative approximations (3). In essence, when two waves of different eigenvalues meet, local noncoherence arises temporarily and is resolved into new coherent waves in the same way as is a noncoherent perturbation at the inlet: A noncoherence does not know or care whether it was generated at start and at the inlet or arose later and within the system from wave interference. Also, except for differences in sharpness of the resulting coherent waves, it does not matter whether the noncoherent wave being resolved is sharp or diffuse. The general picture mentioned earlier, that of a noncoherent wave as a superposition of coherent waves that will separate upon propagation, still is valid. In fact, the mathematical proof for attainment of coherence from arbitrary starting conditions (6) is more easily given for a gradual then a discontinuous starting variation.

A Critical View

This overview would not be complete without addressing the concerns of critics and skeptics. There is the applied mathematician, to whom the development of coherent patterns seems trivial and not worth making a great fuss about - but he seems unaware of the predictive power of the concept in practice. Then there is the practical engineer, who well realizes the implications but has that nagging doubt whether all this can be true - if it were, why has it not long been in our textbooks? More specifically and factually, a chemist or engineer hearing about coherence for the first time is apt to ask: "In the real world, do systems actually become coherent, and if so, how long does that take?"

To those two questions there are direct answers. First, in our ideal oil-water tube, granted all kinds of simplifying premises, behavior is coherent from the start. The same is true for comparable systems involving adsorption, ion exchange, multiphase flow, etc. But resolution into coherent waves is no longer instantaneous if the perturbation at the inlet is gradual. How long a time attainment of coherence then requires depends on several factors, the most important one being the differences in eigenvelocities of the coherent waves. In a grid region where the curves of different families are almost parallel, the velocity differences are small and resolution will take a long time. At a point where the curves become tangential, it will take forever. Worse, once the simplifying premises such as ideal flow behavior or infinite inter-phase mass transfer rates are relaxed, coherence is no longer attained at all, it is only approached asymptotically. So, in our real world, strictly speaking, nothing is ever coherent. Of course, this is disappointing. It might even tempt us to relegate coherence to the role of an academic toy rather than a practical tool.

Allow me to approach the answer indirectly and on a personal note. I well remember when I was five years old and my mother explained equilibrium to me. In the first place, I did not believe what she said was true. And if so, it seemed a fascinating idea, but one without much practical value because the world I saw was push and pull, with hardly anything at "equilibrium." And even if something ever was, nothing happened any more and so the whole thing had become kind of pointless. About eight or ten years later, my first reaction to the concept of steady states was similar. No wonder that coherence at first encounter tends to evoke in almost anyone just such an intuitive response.

Of course, such critique notwithstanding (rather well taken for a five-year old, I still feel), we use equilibrium and steady state extensively. Indeed, physical chemistry and chemical engineering without them would be unthinkable. It does not matter that in the real world, strictly speaking, nothing is ever in equilibrium or steady state as both are only approached asymptotically. In fact, we use equilibrium even where we know fully well that our system is and will remain far from it. Any engineer will appreciate just one example, that of a countercurrent gas absorption column. In principle, there can be no equilibrium between the bulk phases because equilibrium curve and operating curve cannot coincide - and if local equilibrium were forced into the equations, the immediate but hardly useful answer would be that an infinitesimally short column should then suffice to do any specified job.

What equilibrium does for us in all these situations is two things: It provides key parameters in our mathematical equations, and it tells us conceptually the direction in which the system wants to move - toward equilibrium - and so lets us better understand the physical forces at work, identify cause and effect, become proficient at predicting qualitatively what will happen under given circumstances, acquire judgment, conceive better solutions. The practical importance of this cannot be overestimated, because before we can start calculating we must decide <u>what</u> to calculate.

Coherence can do the same for us in its more complex dynamic context. Even if it is no more than an idealization never strictly realized, it gives us a much better understanding of phenomena. To illustrate its predictive power, consider just one example: Let the flow of a multicomponent gas of constant composition through an adsorption column, with competitive adsorption equilibrium, be interrupted by a pulse of an inert gas; coherence theory without <u>any</u> calculation predicts the number and sequence of the resulting pulses (as many as there are sorbable components), the directions of the concentration variations in each, and the skewedness of each, apart from providing a complete picture of how and why this particular pattern arises (3).

Horizons

The concept of coherence was originally developed in 1963 for multicomponent fixed-bed ion exchange and adsorption operations (7), essentially preparative chromatography. Later major extension were to multiphase systems in enhanced oil recovery (5,8,10) and allowance for reactions at equilibrium (4,9,11-15) including precipitation (13-16) and micelle formation (11). A number of contributions to this symposium describe or review such developments.

But what can coherence do for us that it has not already done? What new and useful results can we still reasonably expect?

To answer this question, let us recall the gas absorption column, in which the concept of equilibrium contributed a much better understanding of what was happening and why, although bulk gas and liquid at any point were far from being in equilibrium with one another. It is almost certainly fair to say that in engineering practice the majority of applications of the equilibrium concept, even of thermodynamics more generally, are of this type: not a description of an equilibrium system, in which by definition "nothing happens," but an application to a system in a different state but with its tendency to approach equilibrium blocked or compensated by other forces.

The same can be said for the practical value of the coherence concept. For single, abrupt perturbations somewhere introduced and almost immediately resolved into coherent waves, coherence theory has little to contribute. It comes into its own in providing an understanding of the vastly more complex noncoherent situations - and simpler mathematics for handling them quantitatively. To date, the vast majority of applications of coherence theory has been to simple, completely or largely coherent systems. The power of the concept in the more general noncoherent context has as yet hardly been tapped.

As just one example of what I believe we can expect in the future, an investigation recently initiated in our laboratories comes to mind: a study of propagation of perturbations in countercurrent operations otherwise at steady state (17-19), with the long-range objective of providing a fundamental understanding of dynamic phenomena in multicomponent fractionation columns. We hope to come up eventually with guidelines for design of columns (or modification of existing ones) to make them less sensitive to perturbations and so operable at lesser reflux. With hundreds of thousands or even millions of such columns in operation, the potential savings in energy could be staggering.

The picture that is beginning to emerge is that of the column at steady state containing a number of standing waves, each corresponding to a different eigenvalue. A noncoherent perturbation at the feed tray is resolved into a set of response waves which are propagated up or down, each seeking out the standing wave of same eigenvalue, there to fade out eventually. As the response waves ride over the steady-state profile, their velocities change with the background compositions of the phases. Moreover, how sensitive any one standing wave is to perturbation depends strongly on whether its basic nature is self-sharpening or nonsharpening. An added complication is the possibility of wave reflection by the condenser and reboiler. The system is noncoherent wherever perturbed from to the steady state, the basic phenomenon being interference of the perturbation waves with the standing waves of the steady state. I believe we are beginning to understand the dynamic elements of the situation, but much work still remains to be done.

A perhaps even more challenging extension of coherence theory would be to reactors, for example, sparged towers, catalytic fixed beds, and especially trickle-flow reactors. Here, again, one must expect a perturbation to be resolved into response waves, which then travel over a steady-state composition profile. Added complications are the need to include chemical reactions with finite rates in the basic mass balances and, usually, to account for nonisothermal behavior, introducing temperature as an added dependent variable. However, both reactions (20) and nonisothermal behavior (21,22) have been included previously in the treatment of simpler, coherent systems by various other workers.

Lastly, we must realize that coherence theory is general in that it does not require time and distance to be the two independent variables. Systems with more dimensions in space, or with another independent variable instead of time, can be fitted into the general framework. Three-dimensional modeling of oil recovery operations or of chemical or oil spills and their clean-up - indeed, the entire field of what has recently come to be called chemodynamics - are obvious applications of the former. I would not even want to speculate at this point what doors a replacement of time by another variable might open.

Coherence in Broader Context

As this brief survey has shown, there is no lack of interesting problems to which coherence could be applied. However, it is not really the specifics of applications that matter most for an assessment of what impact coherence may have in the future.

I firmly believe we are at the threshold of a new era in industrial chemical engineering, an era with much greater emphasis on dynamics. When I left industry seven years ago, and I doubt much has changed since, design and optimization in grass-roots process development were done on a steady-state basis, and dynamics - that is, start-up, regular and emergency shut-down, controlability, etc. - was only invoked when the main features of the overall design were frozen. I know of at least two major recent processes that would look rather different, had they been optimized on a dynamic basis.

Today, our computers are large enough, fast enough, cheap enough for dynamic design and optimization. One bottleneck, in no relation to the topic at hand here, is software. The other,