

# REAL TIME CONTROL OF SOFT ADAPTIVE INTERFACIAL MATTER

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**Abstract:** The process control of fragile materials in low dimensional environments offers a number considerable materials and processing challenges. It will be appreciated, for example, that these materials may not be at the thermodynamic limit so that they are technically small systems for which the usual bulk theory either does not apply or is in need of more or less drastic revision. From the standpoint of constructing the kind of coupled chemical kinetic and transport models that are essential within the context of intelligent materials processing these aspects of soft fragile matter may have important consequences. In this paper we review and illustrate a general theory as applied to soft interfacial matter and illustrate the phenomena with some new and counterintuitive experimental results.

**Keywords:** Intelligent, control, system, process, models, interfaces.

## 1. INTRODUCTION

At the most simplistic level one may view materials and process development as an activity that focuses on the control of the transformation of matter from "reactant" to "products". From elementary textbooks we remember that matter can only do two things: it can mix physically and/or react chemically. All materials and process behavior can ultimately be expressed as an attempt to describe this reacting and mixing of both starting materials and products. However, it will also be appreciated that, except in very special and unique circumstances, it is hardly ever the case that an isolated molecule of reactant "A" interacts and reacts with a single molecule of reactant "B". It is usually a "blob" of "A" that is mixed and is stirred or shaken or otherwise made intimate with a blob of "B". All kinds of interactions take place in the reaction mixture over a range of distance and time scales. Clearly, it will be necessary to define in suitable capture these phenomena and process models. Such models capture existing knowledge of the system and are essential in process control especially if the process involves an irreversible step, and no "rework" is possible.

The development of an adequate understanding of materials and process phenomena is, and will continue to be, a long-term goal in materials development and

processing. It is appropriate, therefore that adequate attention be paid to developing process models that are sufficiently accurate and precise to warrant inclusion in major materials and process operations. It might be added that in a very real sense it is the process model that really captures our in total knowledge of the system.

Intelligent materials processing requires that machine-based intelligence be adapted to the materials and process operations. In order that a machine be able to process chemical knowledge it is essential that the machine obtain information on the physico-chemical state of the system. This information is supplied by some suitable number of sensors. Just as the human senses supply information on the world around that enables us to make decisions so too suitably chosen physical and chemical sensors may be engineered to make specialized materials and process computers that have senses that are particularly well suited to the materials and processing task. The particular sort of sensors, their number and type is clearly a matter that will be determined by the specifics of the particular process operation. Also, the degree of sophistication that is used to interpret this knowledge will to a significant degree depend on the type of materials and process transformation that is taking place. In general some type of process model will be required. The model tracks the time evolution of the physico-chemical state of the system and has the ability to

project this state into the future based on the recent history of the system. This ability to measure what is happening within the material, to predict what should be happening and to reason as to how to adjust process parameters to take the system through an acceptable trajectory in phase space is the key to implementing artificial intelligence in advanced materials processing.

In order to discuss the formation of novel structures within the contemporary paradigm of thermodynamics of interfaces, it is useful to review briefly some modern ideas in two emerging, overlapping, and active areas of theory. These are the fields of non-equilibrium thermodynamics (including non-linear systems) and the thermodynamics of statistically small systems. It will be argued that it is in the overlap between these two fields that the effects of small perturbations such as microgravity and surface perturbations have their most profound impact on the structure and properties of macroscopic matter. Let us point out at the outset that despite the fundamental nature of the theoretical ideas, such work is of decidedly practical significance and no proper discussion of such technologically important areas as thin film growth, polymer interfaces, nucleation, and crystal growth phenomena, phase transitions, or critical phenomena is possible without explicit recognition that these are all examples of non-linear systems and are therefore amenable to a common description. Moreover, both interfacial and critical point phenomena are examples of thermodynamically small systems so they may be described using similar theoretical approaches. It is in this interplay between "smallness" and nonlinearity that even very weak symmetry breaking fields may have enormous influence on the structure, thermodynamic, and transport properties of solids and interfaces.

## 2. THEORETICAL BACKGROUND

There has been considerable progress in the understanding of both equilibrium (Rowlinson and Swinton, 1961) and non-equilibrium (deGroot and Mazur, 1984) thermodynamics. Attention has now focused on the extension of classical notions in thermodynamics to systems of such complexity that until recently, they would have been thought generally to be of such complexity as to defy any attempt at rigorous analysis. To be sure, the real enabling advance has been in the mathematical analysis of non-linear systems and these methodologies have opened the door for far more detailed "universal" analysis of complex systems. Of course, the notion of universality has been well established in the classical theory for a very long time and arises from the fact that the equilibrium properties of the system are governed by the extremum of one of the thermodynamic potentials. Universality fails if the system is removed from equilibrium (e.g., crystal growth) for now some kinetic description must be attempted to take into account the return to equilibrium

$$\frac{\partial \mathbf{x}}{\partial t} = -F(\mathbf{x}, \lambda) \quad (1)$$

In this vector equation,  $\mathbf{x}$  represents the set of state variables  $\mathbf{x} = (x_1, x_2, x_3, \dots)$ ,  $F$  is a suitable evolution operator, and  $\lambda$  is a control parameter which acts on the system from the surroundings. In the realm of linear irreversibility the notion of microscopic reversibility to link the flux of conserved variables to the generalized force is used, in which  $\Gamma$  is a definite positive matrix and  $\Phi$  is the thermodynamic potential. For example, if  $x_i$  were the number density in a small but statistically macroscopic volume element in a dense fluid, then if the volume element undergoes a density fluctuation, the rate at which equilibrium is restored is proportional to the generalized force. If the system is forced to be out of equilibrium by virtue of the boundary conditions or other externally imposed constraints, then so long as the non-equilibrium state is not too far removed from the equilibrium state, then Prigogine's minimum entropy production theorem can be used with the proviso that

$$\frac{\partial x_i}{\partial t} = -\Gamma \frac{\partial \Phi}{\partial x_i} \quad (2)$$

Onsager's reciprocal relations remain valid and in that the generalized transport coefficients are independent of both the state variables and generalized forces.

This was the state-of-the-art up until the mid-seventies. At this time, the mathematical theory of non-linear systems advanced significantly (Cvitanovic, 1989) and the role of bifurcation, complexity, and deterministic chaos began to be appreciated more widely within the thermodynamic context. For example, any system which is brought close to a "pitchfork" bifurcation may be described by a single order parameter,  $z$

$$\frac{dz}{dt} = (\lambda - \lambda_c) z - uz^3 \quad (3)$$

where  $\lambda$  is the control parameter and the value of the parameter  $u$  depends on the system under study. The set of state variables follow  $z$  via equations of state. In analogy with Equation (2)

$$\frac{dz}{dt} = -\frac{\partial u}{\partial z} \quad (4)$$

where  $u$  is the so-called kinetic potential. While the potential  $u$  has nothing to do with a normal thermodynamic potential and is related to the kinetic evolution of the system, integration over  $z$  yields,

$$u = -\frac{1}{2}(\lambda - \lambda_c)z^2 + \frac{1}{4}az^4 - C \quad (5)$$

where  $C$  is a constant of integration. Equation (5) is remarkably similar to the well-known Landau theory of phase transitions. In fact, even for very complex systems such as polymerization reactions, the observation of a pitchfork bifurcation (Maguire *et al.*, 1994) allows an essentially thermodynamic discussion of instability and pattern formation. For our purposes here it is sufficient to recognize that the theory of non-equilibrium systems has undergone sufficient advance as to allow a more fundamental treatment of pattern formation and "structure."

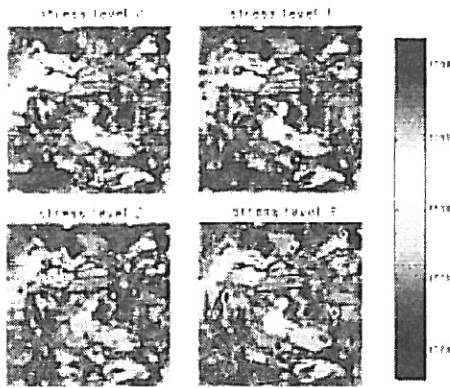


Fig. 1. Stress distribution in a granular structure.

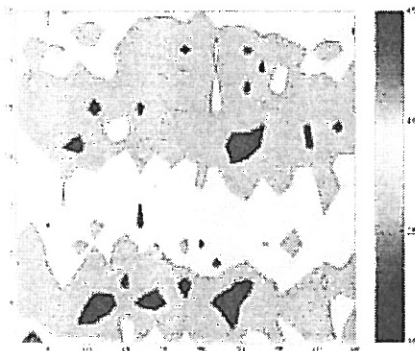


Fig. 2. Grain Orientation

Such matter is almost always characterized by some granularity or structure on a range of distance scales.

For example, Figure 1 shows a Raman image of the stress distribution with a granular material. Figure 2 shows the formation of "stripped" regions of a superconductor, again obtained from Raman scattering.

The ability to probe the nature of fluctuation at the irreversible step in the process, as captured by a poses

the central challenge in developing models that predict microstructure.

### 2.1 The Thermodynamics of Small Systems

In the usual elementary treatment of thermodynamics and statistical mechanics, the basic idea is that one is calculating averages for systems that are very large and which are not subject to an applied field. In reality, of course, no system is infinitely large and even very large systems are confined by vessels in which the interfacial region with the wall of the container must be considered small. If we take the solid-liquid transition as an example, then, for chemical potential  $\mu$ , if  $\mu > \mu_T$ , the system will be completely solid and if  $\mu < \mu_T$ , it will be completely fluid. However, as pointed out by Rowlinson and Swinton (1961), if  $\mu = \mu_T$ , exactly, the system can be completely solid, completely liquid, or any arbitrary mixture of both. We have then the apparent paradox that a large system is homogeneous even if it contains more than one phase. Such considerations present challenges for computer simulation and process modeling. The reasons for this are well-known results of fluctuation theory. In a large system in the macrocononical ensemble, the fluctuation in the number of particles,  $N$ , is proportional to  $\sqrt{N}$  in each of the pure phases so as  $N$  gets large, the relative fluctuation becomes minuscule,  $\sim 1/\sqrt{N}$ . However, when  $\mu = \mu_T$ , the fluctuations in  $N$  become of order  $N$  and are thus never small. In such situations the fluctuations in the local thermodynamic properties can completely dominate the behavior of the system. At the solid-fluid transition, for example, the system could be all solid, all fluid, or any mixture in between. At this point, measurement of the size and range of the density fluctuations at and near a surface will provide very detailed information on the kinetics of the growth of the interface.

In order to produce the non-uniform system of our everyday experience or pattern of "microstructure" one must apply an external field of which the very weak gravitational and surface fields are the most ubiquitous, i.e.,

$$\mu = \mu(\mathbf{r}) + w(\mathbf{r}) + v(\mathbf{r}) \quad (6)$$

and

$$w(\mathbf{r}) = mg(h - h_0) \quad (7)$$

where  $m$  is the mass of a single molecule,  $g$  is the acceleration due to gravity, and  $h$  is the height above some reference height,  $h_0$ , and  $v(\mathbf{r})$  is the surface potential. The surface potential provides a perturbation which is longer range ( $r^{-3}$ ) than the intermolecular

interaction ( $r^6$ ). At the point of transition it is the gradient in this surface term plus that of the gravitational term which is responsible for the development of mass fluxes within the interfacial region. It is this gradient which is responsible for the structure and morphology of the interface.

The surface term provides a sizable perturbation to the fluid, and the gravitational term,  $w(r)$ , is also important. Note that if  $w(r)$  or  $v(r)$  have spatial **gradients**, even minute gradients, then the nonlinear system will have two or more phases. We may, for example, have a bulk phase, a surface phase, and a fluid phase in equilibrium. There has been a good deal of recent interest (Maguire and Leung, 1991) and more than a little controversy (Strandberg, 1988) regarding the detailed nature of the melting transition in two dimensions. As pointed out by Maguire and Leung (1991), if such a system is subjected to a shear force above a critical value it will flow like a cold plastic solid in which ordered hexatic vortices may form. The presence of orientational *per se* will not be sufficient to establish the existence of a thermodynamic transition. It is this ability of the gradient of even minute applied fields to induce huge density difference that lies at the heart of the physics of small systems. Moreover, we might, even on the basis of these simple arguments, infer that the magnitude and form of this applied gradient may have an effect, possibly a substantial effect, on the morphology and structure of the materials which are formed during a mechanical deformation during processing operations. Notice that in the above case the system is, strictly speaking, a small system in that the length scale is determined by  $dw(r)/dr$ . For a liquid at the triple point, the "gravitational" length  $kT/mg$  is about 10  $\mu\text{m}$ . For a liquid system, the pair radial distribution function  $g(r)$  decays to unity on a length scale of order 2.0 nm. Under these circumstances, it is essentially exact to assume that the chemical potential is a functional of the local density and write

$$\mu(r) = \mu[\rho(r), T] \quad (8)$$

Equation (8) states that the chemical potential and therefore all of the physical properties of the system are equal to those in the field-free state in a fluid of the appropriate density and temperature. It can be used, therefore, to calculate the chemical potential in bulk phases.

The important point for our purposes is to recognize that there are two common situations in which Equation (8) is **not** valid. The first is near a critical gas-liquid point or consolute point in a fluid. Here, the correlation length is no longer determined by the range of the intermolecular potential, but diverges to an infinite length. The other is *within* an interface. In this

case, the external field is a combination of both gravity and the surface potential. In such circumstances, the external field varies on the same distance scale as the oscillation in the "surface radial distribution function" so that here too, especially at the point of transition, minor variation in the field may have a huge effect on structure. It is for this reason that microgravity plays such an important role in crystal growth at the molecular level. In order to explain interfacial phenomena and growth, it is necessary then to extend the argument to take into account these gradient effects. There are two levels of approximation at which this may be attempted.

The chemical potential,  $\mu(r)$ , and the free energy density,  $\alpha(r)$ , have formally exact definitions that are not useful except for the purpose of conducting an evaluation using molecular dynamics or Monte Carlo calculations (Frenkel and Maguire, 1981 and Frenkel and Maguire, 1983). The crudest approximation is the point approximation of Equation (8), which will hold only when the inhomogeneity is weak on the scale of the correlation length.

Following earlier attempts by Laplace and Rayleigh, van der Waals (see Henderson, 1992) recognized that it is a free energy that is required to describe an interface, and developed the well known "square gradient" approximation for the free energy density.

$$\phi(r) = \phi[\rho(r), T] + \frac{1}{2} m |\nabla \rho(r)|^2 + \dots \quad (9)$$

where  $m$  is given by

$$m = -\frac{1}{6} \int r_{12}^2 U_{\text{att}}(r_{12}) dr_{12} \quad (10)$$

and  $U_{\text{att}}$  is the attractive part of the intermolecular potential.

For many years, the significance of this result was not appreciated until it was independently derived in slightly different form by Cahn and Hilliard (1958). The Cahn-Hilliard equation has been widely used to describe small systems such as wetting phenomena (Rowlinson and Widom, 1982). The need to extend the treatment beyond the point approximation for crystal growth has been well illustrated in, for example, the recent theoretical investigations of Kupferman *et al.* (1995) on the coexistence of symmetric and parity-broken dendrites in a channel. These authors have solved the diffusion equation for crystal growth using the assumption that  $\mu$  can be approximated by the Gibbs-Thomson equilibrium relation. Interestingly enough, they find that for a large range of parameters stable symmetric and stable parity broken solutions co-exist. The branches of parity-broken solutions have

their origin in symmetric solutions and arise from standard bifurcations.

The free energy density can be regarded as a functional expansion of the formally exact expression of the free energy density,

$$\phi(\mathbf{r}_1) = \phi[\rho(\mathbf{r}_1)] - \frac{1}{2} \int \rho(\mathbf{r}_1, \mathbf{r}_2) [c(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)] d\mathbf{r}_2 \quad (11)$$

where  $c(\mathbf{r}_1, \mathbf{r}_2)$  is the direct correlation function between points 1 and 2, which is related to the total correlation function

$$h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1 \quad (12)$$

where  $g(\mathbf{r}_1, \mathbf{r}_2)$  is the two body distribution function, and  $h(\mathbf{r}_1, \mathbf{r}_2)$  is given by the Ornstein-Zernike equation

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \int c(\mathbf{r}_1, \mathbf{r}_3) \rho(\mathbf{r}_3) h(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3 \quad (13)$$

The non-local approximation contains correlation functions such as  $c(\mathbf{r}_1, \mathbf{r}_2)$ , which we do not know much about. Note that in Equation (13) the density, which now depends on position, is inside the integral (sometimes called the OZ2 equation) and that this identity requires the use of closure relations, such as the hypernetted chain approximation (HNCA), the mean spherical approximation (MSA), or the Percus-Yevick approximation (Kupferman *et al.*, 1995).

This discussion has provided an outline of the essential physics of small interfacial systems and has emphasized the necessity of taking into account both surface and gravitational effects with a suitable local or non-local approximation for the free energy density or chemical potential. It is the gradients in this local free energy density which drive diffusion, phase separation, crystal growth, and the growth of thin films in such systems. We may, therefore, write a generalized Smoluchowski-Langevin equation,

$$\frac{\partial}{\partial t} c(\mathbf{r}, t) = D \nabla^2 \mu + \delta \quad (14)$$

where  $\delta$  represents a fluctuation term. In this equation,  $\mu$  is given by Equation (6), which includes both a gravitational term and either the point, local, or non-local approximation for  $\mu(r)$ ,

Notice that Equation (14) does not include a convective term. If such an effect were present, it will, of course, be quite difficult to sort out the relative importance of the above contributions.

### 3. CONCLUSION

It can be seen that the nature of surface and interfacial interactions, especially in the presence of small applied fields such as gravity, may have a very important influence on the structure and properties of matter. When it is recognized that all materials and process operations are conducted in systems which are not at equilibrium and that the thermodynamic criteria of "smallness" are met at the interfaces, it is perhaps less surprising that what may appear to be rather minor perturbations in process conditions may have what might be considered a disproportionately large influence on the structure and thereby the properties of a material.

It is clearly essential that intelligent control systems be aware that decisions and directives that may take the system into a region of phase space where there is likely great sensitivity to initial conditions should probably be avoided. On the other hand, it may be possible to use this very condition to apply a small external field of the appropriate magnitude and symmetry to prepare a structure of matter that had not previously been possible. In any case, it is clear that the application of these approaches will prove exceedingly interesting in the exploration and processing of new forms of matter both on earth and in space.

In conclusion, it will be appreciated that the ability to predict image formation and evolution *a priori* is critical for two reasons. First, it provides the essential basis for intelligent reasoning. In this sense the model endows the machine with the analytic reasoning tools of the scientist but it does this in such a fashion as to be far faster in application. Also, scientific reasoning can be brought to bear on the process in the factory on a time scale that matches the needs of the materials and process operation.

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