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MASTER

A GENERAL THEORY OF INHOMOGENEOUS SYSTEMS

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Abstract. Inhomogeneous systems are modeled using maximum entropy methods so that only explicitly stated properties are taken into account, with no arbitrary assumptions. Sandstones are considered as an example. A phase diagram describes the evolution of one inhomogeneous system into another. Methods from statistical mechanics, including Monte Carlo simulation, series expansions, and the renormalization group should be useful as well for other maximum entropy problems involving many degrees of freedom.

We consider the application of maximum entropy methods¹ to the study of inhomogeneous systems.² Typical examples of inhomogeneous systems include cermets (fine mixtures of insulating ceramic and conducting metal), sandstones, vycor (a porous glass network), granular films, precipitates from solution, biological tissues, etc.³ Both the structural and transport properties of inhomogeneous systems will be considered.

The problem of inhomogeneous systems forms connections between maximum entropy methods and those of recent statistical mechanics that are not apparent in other maximum entropy work. These methods of statistical mechanics, including Monte Carlo simulation, series expansions, the renormalization group, and exact solutions should be useful in many other maximum entropy studies.

The first section of this paper is a brief review of previous work on inhomogeneous systems. The second section describes the present theory (see also Ref. (2)), and the third contains a summary and conclusions.

1. PREVIOUS MODELS FOR INHOMOGENEOUS SYSTEMS

The most widely studied model for inhomogeneous systems is the percolation model.⁴ In its simplest form, the percolation model requires that the sites of an infinite lattice (for example cubic) be independently occupied, each with a probability p . Two occupied sites

belong to the same (connected) cluster if there is a path between them on occupied nearest neighbor sites.

Some of the key results of percolation theory are the following:

- (1) The fraction of sites belonging to the infinite cluster is proportional to $(p - p_c)^\beta$ as $p \rightarrow p_c$. Here, p_c is the percolation threshold (equal to .59 for a square lattice), and β is a critical exponent (equal to 5/36 in two dimensions). For $p < p_c$, no infinite cluster exists.
- (2) The largest diameter of finite clusters, with exponentially rare exceptions, is $\xi \sim |p - p_c|^{-\nu}$ where ν is another critical exponent (equal to 4/3 in two dimensions).⁵ This formula applies as p approaches p_c from either side.
- (3) If occupied nearest neighbor sites are connected by a resistor of resistance R , the conductivity of a large block is proportional to $(p - p_c)^t$ as $p \rightarrow p_c$. The static exponents β and ν , and the transport exponent t are universal, in that they do not depend on the type of lattice (although they do depend on the spatial dimension). The percolation threshold p_c is not universal.

Percolation is perhaps the simplest example of a continuous phase transition. Others include the appearance of magnetism as the temperature is lowered through the Curie point, and the gas-liquid critical point [Discontinuous transitions, such as ice melting, are perhaps more familiar.] Continuous transitions have unusual properties, including fluctuations on all length scales. To understand these fluctuations, consider an ordinary gas at atmospheric density. The density of gas in a box 1Å on an edge at an instant in time would not be representative of the density of the entire system (it would contain either one atom or zero). A box of edge larger than about 100Å would, however, be representative. At a continuous transition, any finite box, no matter how large, is too small to be representative. This is a statement that there are fluctuations on all length scales. The structure of the system is self-similar. If one defines the spatial dimension D of the system in a standard way (the Hausdorff dimension), one finds that D is not an integer. These objects are called fractals.⁶ For example, the Hausdorff dimension of the infinite percolation cluster at $p = p_c$ is 1.896.

Percolation is an adequate model for some inhomogeneous systems, but it fails to describe the properties of others. Percolation fails, for example, as a model of sandstones. Sandstones empirically have a percolation threshold at or near zero; fluid can be forced through the pores of a sandstone even when the pore volume fraction is less than 0.01.⁷ In contrast, percolation models have the property that when $p < p_c$ (p_c is generally near 0.3 in three dimensions), the pore space becomes disconnected.

Historically, the response to this failure has been to invent specialized models that have a percolation threshold at zero. One model, proposed by Sen et al.,⁸ starts with randomly packed spheres, puts smaller spheres in the interstices, yet smaller spheres in the remaining interstices, etc. A second model, proposed by Wong et al.,⁹ begins with a cubic lattice of pipes. A pipe is chosen at random, and

its cross section reduced by a constant factor (e.g. $1/2$). Another pipe is chosen at random (perhaps the same one), and its cross section reduced. As the process is continued, a zero threshold model eventually results. A third model has been proposed by the author and Weinrib.¹⁰ It is a type of continuum percolation model in which a random surface is created and then flooded to a constant depth. A two-dimensional realization is shown in Fig. (1).

Fig. (1) The figure is a realization of a continuum percolation problem that has a percolation threshold at zero (see Ref. 10). (b) The black network connects arbitrarily distant points, in spite of the fact that its volume fraction is small. (a) The volume fraction is essentially zero, corresponding to the width of a line, and yet arbitrarily distant points remain connected

(a)

(b)

A problem with these zero threshold models for sandstones is that they seem ad hoc and arbitrary. It is not clear which, if any of them, forms an adequate model for sandstones. The problem is compounded by the fact that many other zero threshold models could clearly be proposed.

These problems lead to the following question: Is it possible to start from an explicit list of given properties (e.g. $p_c = 0$) and to construct a unique model containing no additional arbitrary assumptions? This question appears to be wildly underdetermined and perhaps even ill-posed, but it does in fact have an answer in the context of maximum entropy theory.

11. MAXIMUM ENTROPY THEORY OF INHOMOGENEOUS SYSTEMS

To implement the maximum entropy method, one assumption is required, which is the prior probability.¹ Perhaps the simplest way to dispose of this problem is to assume that the system has no structure on

a length scale smaller than b . Depending on the system, b may correspond to the size of a grain, the size of an atom, etc. We will in fact make a somewhat stronger assumption and put the system on a lattice (for example cubic) of lattice constant b . The fundamental cubes of the lattice are occupied by either material A or material B. It is hoped that by universality the long distance properties will not be affected by the particular choice of lattice. The lattice contains a finite but large number of sites N .

One may now ask, making no further assumptions (other than a two component lattice system), what is the generic inhomogeneous system? There are 2^N different configurations. Maximum entropy theory assigns an equal probability to each. (To do otherwise would imply that additional arbitrary assumptions are being made.) This model can be recognized as the percolation model with $p = 1/2$. Note that p was unspecified, and that the maximum entropy method chose $p = 1/2$.

The generic model can be compared to the particular system of interest. We will again consider a sandstone to have a specific example. One finds that the model fails. The most conspicuous failure is that the fraction of the volume occupied by the pores of a particular sandstone is perhaps 0.02, whereas the fraction occupied in the model (the A sites) is 0.5.¹¹

One may proceed by adding the constraint that the model must have a volume fraction of A sites equal to $q = 0.02$. Now all of the 2^N configurations that satisfy the constraint $p = q$ are taken with equal probability. This model is recognized as percolation, but now with $p = q$. The new model is again compared with the system of interest. It now fails for a different reason. The pore space of the model at $q = .02$ consists of tiny disconnected pockets, whereas that of a sandstone is a connected network capable of transporting fluid an arbitrary distance. A straightforward way to proceed is to add a second constraint: The A sites must form a single connected cluster. All configurations satisfying both constraints are now taken with equal weight. This model is not equivalent to percolation. It is the generic zero threshold model.¹² It correctly models some properties of sandstones. If it is found not to accurately model other important properties of sandstones, the response would be different from that discussed in Section I. Previously, one would hire more theorists to construct new models, hoping that at least one would work. In the present formulation, one returns to the experimentalist and informs him that there is an important property of the system that has not yet been stated, and that a new model cannot be constructed until the property is specified.

It is sometimes convenient to specify the Lagrange multiplier conjugate to a constraint, rather than imposing the constraint explicitly. These two procedures are essentially equivalent for large systems. (A familiar example is the study in statistical mechanics of either the microcanonical or the canonical ensemble.) Now all of the 2^N configurations are allowed, with a relative weight W given by

$$W = \exp(-\lambda_s n_s - \lambda_c n_c) \quad , \quad (1)$$

where n_s is the number of sites and n_c the number of connected clusters. The Lagrange multipliers λ_s and λ_c are adjusted until $\langle n_s \rangle$ and $\langle n_c \rangle$ have the desired values.

Any set of constraints and conjugate multipliers may be used, but they must all be explicit.¹³ The nature of the inhomogeneous system changes continuously with the vector (λ_s, λ_c) . One would like to understand the properties of an (infinite) inhomogeneous system at a given point (λ_s, λ_c) , and in particular to know whether there are special points at which the structure changes qualitatively. (Special points do exist, as will be discussed below.)

The problem is to determine the macroscopic properties from the microscopic weights of equation (1). Several methods from statistical mechanics are useful, and may indeed help to understand other problems that are analyzed by maximum entropy methods. Only a brief description is given; references are provided for further information.

A system whose properties are not understood is, if possible, often first studied in mean field theory.¹⁴ Mean field theory is simpler to implement than the methods described below, and will often predict correct qualitative features. Mean field theory does not, however, treat fluctuations correctly and does not quantitatively describe the nature of singularities (it gives incorrect critical exponents unless the number of spatial dimensions is large). The methods that follow, in contrast, do treat fluctuations correctly.

One generally useful method is Monte Carlo simulation.¹⁵ From a starting configuration, one generates a proposed new configuration (for example by choosing a fundamental cube at random and changing the substance that occupies it.) The new configuration is accepted with probability W_2/W_1 if its weight W_2 is less than that of the previous configuration W_1 . It is accepted with probability one if $W_2 > W_1$. It has been shown that this algorithm will generate an ensemble in which configurations appear with weight W . Some preliminary Monte Carlo simulations for the inhomogeneous systems weight (Eq. 1) have been performed.¹⁶

The remaining methods have general applicability, but they are particularly useful for studying continuous transitions. One may perform series expansions in one or more of the Lagrange multipliers about $\lambda = 0$ or about $\lambda = \pm\infty$, known respectively as high and low temperature series. These series, which in practice contain on the order of twenty or fewer terms, can be analyzed with Padé or partial differential approximants.¹⁷

The renormalization group is a method in which the system is coarse-grained in steps.¹⁸ For the inhomogeneous system problem, one version of the renormalization group would choose a single large cube to represent the configuration of several fundamental cubes. This process is repeated again and again, until the long distance behavior is apparent.

Methods of finite size scaling extract the properties of an infinite system by solving for the behavior of strips of increasing width.¹⁹ Monte Carlo renormalization group is a hybrid of those two methods discussed above.²⁰

These methods should be useful for broad classes of maximum entropy problems involving many degrees of freedom.

We return to the question of the nature of an infinite inhomogeneous system as a function of (λ_s, λ_c) . One can draw a phase diagram with lines to separate regions of different qualitative behavior (see Fig. (2)).

Fig. (2) The phase diagram for inhomogeneous systems is shown as a function of p and λ . The connected and disconnected phases are labeled, with ordinary percolation on the line $\lambda_c = 0$. A region with antiferromagnetic (checker board)^c order is labeled AF. The shaded area is one of phase separation. This area would contract to a line if λ_s , rather than p , were plotted on the x-axis.

Some aspects of the phase diagram are speculative, and some are well understood. The vertical axis is the Lagrange multiplier λ_c controlling clustering. When $\lambda_c \rightarrow \infty$ the system has one connected cluster, and when $\lambda_c \rightarrow -\infty$, the system has as many clusters as possible. On the horizontal axis the volume fraction p of component A is plotted, which is somewhat more convenient than the conjugate Lagrange multiplier λ_s .

We first discuss the well understood regions of the diagram. In the upper left corner, labeled "a", the configurations are identical to those of a well studied problem known as lattice animals (see Ref. 4). There is a cluster connecting opposite faces of the system even when a vanishing fraction p of the sites are occupied. As discussed previously, the line $\lambda_c = 0$ is identical to ordinary percolation. There is a second order phase transition at $p = p_c$, where large fluctuations occur in the cluster size distribution and in the conductivity. The static critical exponents are known exactly in two dimensions and approximately in three dimensions.^{4,5} An infinite connected cluster is present for $p \geq p_c$.

The line $\lambda_c = -\infty$ is also understood. For $p \leq 1/2$ the system can be shown to be equivalent to the lattice gas with infinite nearest neighbor repulsion. The equivalence follows from the fact that for $p \leq 1/2$ the maximum number of clusters $n_c = n_s$ is formed if nearest neighbor occupation is forbidden. The known properties of the lattice gas²¹ allow the following description: For small p , the A sites form a dilute, nearly ideal gas. As p increases, the hard-core repulsion becomes more important until a continuous phase transition occurs with "checker-board" or "antiferromagnetic" long-range order for $p > p_2$. (If A sites are identified with spin up and B sites with spin down, the system has antiferromagnetic long-range order.) The point $p = p_2$ is labeled e in Fig. 2, with $p_2 = 0.371$ for a square lattice.²¹ At $p = p_1 = 1/2$, labeled f, the entropy per site is zero and only the two equivalent antiferromagnetic ground states are allowed. If p is fixed between p_1 and 1 and the limit $\lambda_c \rightarrow -\infty$ taken, the system is no longer equivalent to a lattice gas with short-range repulsion. In this region, the system becomes macroscopically inhomogeneous and phase separates into an antiferromagnetic phase and a connected phase (one in which all sites are occupied). The phase separation can be seen most clearly by induction on the number of B sites. The region $p_1 < p \leq 1$ is thus one of phase coexistence, characteristic of a first-order phase transition (see Fig. 3).

The remaining aspects of the phase diagram are speculative, although the diagram is constrained by several physical principles and guided by a tentative mapping to the Potts model.² The lines a-c and e-d mark continuous phase transitions with large scale (fractal) fluctuations and critical exponents. To the right of line a-c-f, it is possible to travel an arbitrarily large distance on a single connected cluster of A sites. The region just below and to the right of point "a" in the connected phase is expected to provide the best model of sandstones available in this plane.

A quantity called the order parameter indicates which phase occurs; it is zero on one side of a continuous phase transition and nonzero on the

Fig. (3) The diagram illustrates the phase separation that occurs between points f and g of Fig. (2), at $\lambda_c = -\infty$. The checkerboard phase floats in a connected phase.^c If one moves slightly upward in the phase diagram ($\lambda_c > -\infty$), the checkerboard develops defects and some uncolored sites detach and form a dilute gas in the connected region.

other. The fraction of A sites in the largest connected cluster, denoted P_∞ , is an order parameter that is nonzero to the right of a-c-f, and indicates that the fluid contained in A sites can move an arbitrarily large distance. There is a second order parameter, m_s (the staggered magnetization), that is nonzero in the antiferromagnetic, or checkerboard phase.

III. SUMMARY AND CONCLUSIONS

A general model for the structural and classical transport properties of inhomogeneous systems has been proposed. It requires as input an explicit list of specified properties of the system, and makes no further arbitrary assumptions. The behavior of an inhomogeneous system with two specified properties (the number of sites and the number of connected clusters) has been determined in part, although further Monte Carlo studies will be required to resolve remaining questions.

The ideas and methods of statistical mechanics should apply to many maximum entropy problems with a large number of degrees of freedom. In particular, there should be special points where the properties (including the entropy) are not smooth functions of the Lagrange multipliers and qualitatively new properties arise. These special points, corresponding to continuous and discontinuous phase transitions, can be plotted in a phase diagram. Order parameters can be used to indicate the phase. Methods from statistical mechanics, including mean field theory, Monte Carlo, the renormalization group, and series analysis should be generally useful.

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