Tellus (1987), 39B, 100–113

On the application of lattice statistics to bubble trapping in ice

By I. G. ENTING, *CSIRO, Division of Atmospheric Research, Private Bag 1, Mordialloc, Vic 3195, Australia*

(Manuscript received August 26, 1985; in final form March 3, 1986)

ABSTRACT

The use of the percolation model from lattice statistics to represent the distribution of trapping times for air bubbles in polar ice is discussed. A number of relevant techniques and results from the statistical mechanics of phase transitions are reviewed in order to propose suitable approaches for performing a more refined lattice statistics analysis of bubble trapping.

1. Introduction

Over the past few years, there have been a number of attempts to determine the atmospheric concentrations of various trace gases in the past by measurements on air from bubbles trapped in polar ice. These studies have included measurements of CO_2 in ice from the period back to 40,000 BP (Neftel et al., 1982). For the purposes of reducing current uncertainties in the behaviour of the carbon cycle on the time scales of interest in connection with possible anthropogenic climatic effects, the period of most interest is the last 200 years.

Several studies have estimated a "pre-industrial" concentration applying before about 200 years ago (Barnola et al., 1983). More recently, a study by Neftel et al. (1985) has given a sequence of estimated CO_2 concentrations for 12 time intervals covering the last 200 years. In order to clarify the extent to which the CO_2 increase has been due to net biospheric sources, a detailed description of the timing of the changes is essential. In particular it would be very useful to be able to distinguish between the pattern of biospheric release proposed by Houghton et al., (1983) on the basis of ecosystem modelling and the release strength reconstructed by Freyer and Belacy (1983) on the basis of $\delta^{13}C$ in tree-rings.

The use of measurements on air from polar ice for obtaining a reconstruction of relatively recent CO_2 changes is complicated by the fact that the bubbles are trapped some time after the original snow is deposited. The main difficulty arises from the existence of a distribution of times between snow deposition and bubble trapping. In order to reconstruct past concentrations it is necessary to determine the distribution of trapping times and then perform a deconvolution of the measured concentrations. In the notation defined by Enting (1985a) concentration $q(z)$ of a tracer in air in an ice layer z years old is related to $c(z')$ the atmospheric concentration z' years ago by

$$q(z) = \int_0^z R(z - z')\, c(z')\, \mathrm{d}z', \tag{1.1}$$

where the trapping distribution function, $R(x)$, for any layer, is the proportion of gas that was trapped x years after the layer was deposited as snow and assuming that the air has atmospheric composition at the time of trapping.

There have been several attempts to model the distribution of trapping times using what are known as the "percolation models" in lattice statistics. Percolation models describe the connectivity or alternatively the isolation of clusters of elements in random networks which are most commonly randomly generated subgraphs of regular lattices. Stauffer et al. (1985) introduced the percolation model of bubble trapping and emphasised that it implies a sharp cutoff in that the total gas trapping occurs within a finite time. Enting (1985a) extended this approach and emphasised that the behaviour near the cutoff should be described by a "critical exponent" giving a power-law divergence in the trapping-time distribution function.

In the transition from firn to ice, a number of structural changes are occurring simultaneously (Stauffer, 1981). Among these are compaction of the firn which reduces the volumes of air in both interstitial sites and their connecting channels. Ultimately, this leads to closure of the channels and possibly the disappearance of some sites. After close-off, the trapped clusters undergo further changes including compression of the gas, closure of internal channels and restructuring of trapped clusters to form spherical bubbles. Most of these processes represent gradual changes of local properties and so it should be relatively easy to fit them to observed properties of ice cores. The exception is the closure process which is a non-local cooperative effect giving changes in the long-range connectivity of the firn. The present paper concentrates on presenting a mathematical description of the percolation model which describes this dominant physical process.

Although the percolation model has been proposed as a model of various phenomena such as spread of disease in plantations, dilute magnets, quark confinement, and many others (Zallen, 1983, Table 1), the most extensive studies of the percolation model have been undertaken by theoretical physicists interested in the statistical mechanics of cooperative phase transitions (Essam, 1972). Such studies have treated percolation models as just one class from a wide range of stochastic lattice models. The aim of the present paper is to use the connection between the percolation model and statistical mechanics in order to draw on a large body of theoretical results from statistical mechanics. The limitations of the simple percolation models used by Stauffer et al. (1985) and Enting (1985a) are reviewed and the problems involved in analysing more refined models are discussed.

2. Lattice statistical mechanics

For many years there has been an extensive study of various lattice systems as models of cooperative phase transitions (Domb, 1960; Fisher, 1967; Stanley, 1971). The simplest (and most widely studied) of these systems is the Ising model (Ising, 1925). The Ising model is generally studied on regular lattices and has a binary variable $\sigma_1 = \pm 1$ at each site i of a lattice of N sites. Associated with each of the 2^N configurations of the σ_i variables is an energy term

$$U(\boldsymbol{\sigma}) = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - \sum_i H\sigma_i. \tag{2.1}$$

The first term sums over all pairs of nearest neighbours, i and j (which are coupled by an interaction of strength J) once. The second sum is over all N sites at which a field H applies. Each spin configuration $\boldsymbol{\sigma}$ is assigned a probability

$$\text{Prob}\,(\boldsymbol{\sigma}) = Z^{-1} \exp\,(-U(\boldsymbol{\sigma})/kT). \tag{2.2}$$

The normalising factor Z is called the partition function, and it acts as a moment generating function for spin expectations. T is the absolute temperature and k is Boltzmann's constant. The probability distribution (2.2) has proved very difficult to analyse. Analytic solutions are possible on a one-dimensional lattice for general J, H and on various regular two-dimensional lattices for the special case $H = 0$. The main reason that such systems have been studied is that they exhibit phase transitions. In two or more dimensions the Ising model defined above has a spontaneous magnetisation M. This can be defined in various ways such as

$$M = \lim_{H \to 0^+} \lim_{N \to \infty} E[\sigma_i], \tag{2.3a}$$

or

$$M^2 = \lim_{r(i,j) \to \infty} \lim_{N \to \infty} E[\sigma_i \sigma_j], \tag{2.3b}$$

where $E[\ ]$ denotes statistical expectations.

Each of these expressions defines a tendency for all the σ_i to be aligned (i.e., to have the same sign). This occurs in the thermodynamic limit which is denoted $N \to \infty$. The increase in size in the lattice must be performed in such a way that all dimensions increase in a similar manner and the sites i and j become arbitrarily far from any boundary. The order in which the limits are taken is essential to this definition. The magnetisation goes to zero at a critical temperature T_c and so the system models the sudden disappearance of ferromagnetism at the Curie temperature.

While lattice statistics problems of this type have proved relatively difficult, a number of standard approaches have been devised. These can be described as "exact solutions", "closed form approximation", "series expansions", "Monte Carlo" and "renormalisation group techniques". Exact solutions are the ideal but only a very special class of lattice statistic problems can be solved exactly and most of the interesting solutions are confined to two-dimensional systems. Exact solutions have been reviewed by Baxter (1982).

The closed form approximation consist of taking various closure approximations to the probability distribution (Burley, 1972). They can be quite accurate away from the critical point but do not give an accurate description of the critical behaviour.

Series expansions express the partition function Z or its logarithm in powers of suitable variables. The difficulty with using series expansions to analyse transition behaviour is that the singular behaviour is determined by the asymptotic behaviour of the series coefficients but only a relatively small number of coefficients can be determined. The effort required to derive the coefficients tends to grow exponentially with the number of terms. Significant improvements have been made by replacing the combinatorial complexity in the series derivation with algebraic complexity (e.g., Sykes et al., 1965; Wortis, 1974; Enting, 1978a, b; Baxter and Enting, 1979).

The most recent approach to the study of phase transitions uses the various renormalisation group techniques (Wilson, 1971, 1983, Domb and Green, 1976). The transition behaviour in models such as the Ising model is dominated by large fluctuations. (This is why closed form approximations break down). The renormalisation group analysis makes use of the fact that these critical fluctuations occur on all length scales and show the statistically self-similar behaviour of the type which was described by Mandelbrot (1977) as defining various 'fractals': objects with non-integer dimensionality. The renormalisation group describes the way in which probability distributions such as that defined by eq. (2.2) behave under a change of length scale. The critical points at which the probability distributions are statistically self-similar correspond to the fixed points of the renormalisation group transformations. Fig. 1 shows configurations sampled from the Ising model probability distribution on the square lattice at its critical point, emphasising the irregular and long range nature of fluctuations. Fig. 1a is a sample showing each site while in Fig. 1b only sites where both co-ordinates are even are shown. The qualitative similarity is a characteristic of the critical point.

3 Percolation

As indicated in the introduction, Stauffer et al., (1985) and Enting (1985a) have used the lattice statistics of the percolation model in order to describe the trapping of air bubbles in ice. The analysis by Stauffer et al. considered a "bond percolation" model while Enting pointed out that for the purposes of discussing the general characteristics (and in particular the critical exponent) of the bubble trapping, the distinction between the "bond" and "site" models (Essam, 1972) is unimportant.

Like the Ising model described in Section 2, percolation models describe lattice systems for which the underlying stochastic character is simple but for which the physically interesting questions concern rather intractable aspects of the joint probability distribution. Percolation models have lattice elements (sites or bonds) that are independently open or closed with a specified probability. The interesting and very difficult questions are those concerning the statistics of connected clusters of open elements. Of particular interest is the question of whether there is an infinite connected cluster of open sites and, if so, what proportion of the lattice is part of such a cluster.

For the purposes of constructing a more detailed model of bubble trapping a special percolation model is considered here. The system is defined on a lattice with sites connected to various nearby sites by bonds. Each bond can be open (i.e., connected) or closed (i.e., broken). The probability of being open is denoted by p. The lattice statistics problem is to analyse the statistics of clusters of sites connected by open

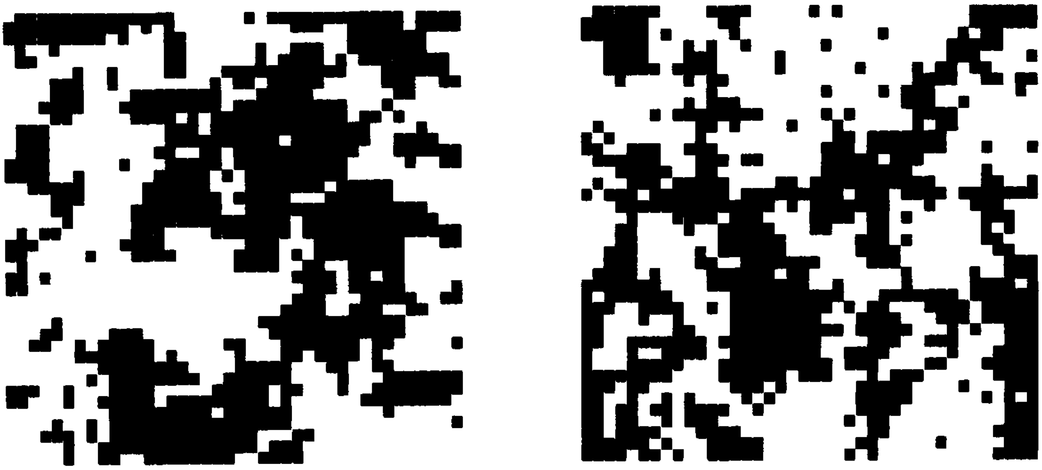

Fig. 1. Sample configurations from a Monte Carlo simulation of the square lattice Ising model at its critical point. (a) Every site plotted, (b) only sites with even co-ordinates are plotted. A comparison of (a) and (b) illustrates the statistical self-similarity.

bonds. Of particular interest is the percolation probability $P(p)$ which gives the probability that a given site will be part of an infinite cluster of sites connected by open bonds. This problem will be referred to as the Potts/percolation problem in the absence of a suitable common terminology. The 'bond' percolation problem has the same system of randomly open or closed bonds but the statistics involved concern connected clusters of bonds rather than sites. The 'site' problem considers connected clusters of 'open' sites in a system in which it is the sites that are randomly open or closed with probability p. Most studies of percolation models have been of either the "site" or the 'bond' problems. The Potts/percolation problem has been considered relatively infrequently. (Note that in his review, Wu, 1982, uses the term "bond percolation" in connection with the Potts/percolation model. This is at variance with the more common usage defined above). The Potts/percolation model is the most natural percolation model to apply to bubble trapping near the transition from firn to ice. The sites correspond to the relatively large interstitial cavities in which air is trapped and the bonds correspond to the narrower connecting pathways that are closed as the firn compacts. Thus, when considering the amount of air trapped, we need to consider the statistics of clusters of sites connected by randomly closed bonds as in the Potts/percolation model. In the earlier stages of the close-off process it is not a good approximation to locate all the porosity at the sites. In the upper levels of the firn, the bonds will contribute a significant proportion of the porosity. To cover a wide range of depths would require a percolation model that considers the statistics of clusters in terms of the numbers of both sites and bonds.

For the purposes of modelling bubble trapping by identifying $P(p)$ with the proportion of bubbles trapped, the important properties are that:

$$P(1) = 1 \tag{3.1a}$$

and that there is a critical probability p_c such that

$$P(p) \sim (p - p_c)^{\beta} \quad \text{as} \quad p \to p_c^+, \tag{3.1b}$$

$$P(p) = 0 \quad \text{for} \quad p < p_c. \tag{3.1c}$$

Fig. 2 shows simulations of a square lattice percolation system near its critical point. The randomly occupied elements are the bonds as in bond percolation and Potts/percolation. The accentuated cluster is a cluster of connected sites as considered in the Potts/percolation model and

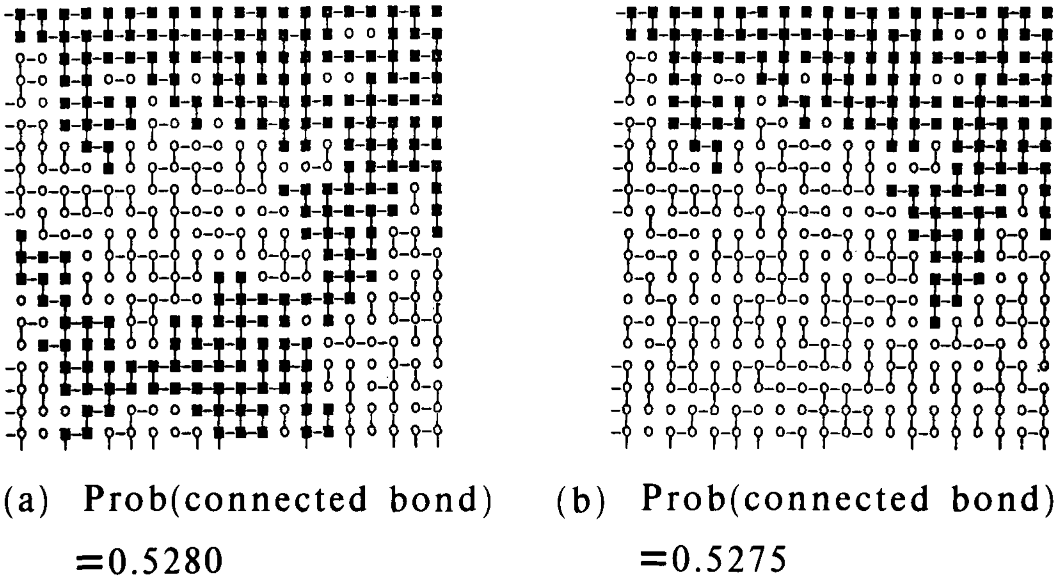

Fig. 2. Sample configuration for bond percolation on the square lattice at its critical point. The cluster is of sites connected to the surface is emphasised. The difference between (a) $p = 0.5280$ and (b) $p = 0.5275$ shows how, near p_c, small changes in p lead to large changes in cluster size.

furthermore it is the cluster connected to the upper boundary, thus giving a schematic representation of the way in which percolation models would apply to the bubble trapping problem. Comparison of Fig. 2a and 2b shows how small changes in the probability p results in large changes in clustering when $p \approx p_c$. For square lattice bond (and Potts) percolation, it is known that $p_c = \frac{1}{2}$ (Potts, 1952; Wu, 1982). For general lattices it is known that the critical probability for percolation is the same for bond and Potts percolation.

The term Potts/percolation model is introduced because this system can be defined as a special limit of the Potts model (Potts, 1952) in statistical mechanics. The Potts model generalises the Ising model described in Section 2 to a system with q-state variables $\rho_i = 0, 1 \dots q-1$. The probability distribution is given by

$$\text{Prob}\,(\rho) = Z(q, u, m)^{-1} \exp\,(-E(\rho)/kT), \tag{3.2}$$

with

$$E(\rho) = -J \sum_{\langle i,j \rangle} \delta(\rho_i - \rho_j) - H \sum \delta(\rho_i), \tag{3.3}$$

$$u = \exp\,(-J/kT), \tag{3.4a}$$

$$\mu = \exp\,(-H/kT); \tag{3.4b}$$

$$\delta(n) = 1 \quad \text{if} \quad n = 0 \tag{3.5}$$
$$\quad = 0 \quad \text{otherwise.}$$

The statistical mechanics of the Potts model has been reviewed by Wu (1982). For the present purposes, the most important result is that the statistics of what we have denoted the Potts/percolation model can be obtained from the $q \to 1$ limit of the Potts model (hence our terminology). This requires generalising the Potts model by defining a function that is equivalent to $Z(q, u, \mu)$ for any finite lattice and for any positive integer q. This is called the 'random-cluster model' (Fortuin and Kasteleyn, 1972) and can be used to define the percolation limit of the Potts model. For $\mu = 1$, it is defined as

$$Z_{rc}(q, u, 1) = \sum_{\text{graphs}\,g} u^{b(g)} (1-u)^{B - b(g)} q^{\gamma(g)}, \tag{3.6}$$

where if B is the number of bonds in the lattice, the sum is over all 2^B graphs generated by having bonds present or absent in all possible ways, $b(g)$ is the number of bonds present in graph g and $\gamma(g)$ is the number of connected components in g. Expression (3.6) is related to various well known problems in algebraic graph theory (Biggs, 1974; Enting, 1978b).

The generalisation to $\mu \neq 1$ is constructed by adding an additional V bonds connecting each site of the lattice to an auxiliary vertex.

The percolation probability is given by

$$P(p) = \lim_{q \to 1} M(q, u = 1 - p) \tag{3.7}$$

where

$$M(q, u) = 1 - \frac{q}{q-1} \frac{\partial}{\partial \mu} \ln Z_{\mathrm{rc}}(q, u, \mu)_{\mu=1}, \tag{3.8}$$

and is the generalisation of the Ising model magnetisation (2.3). This connection between Potts models and the Potts/percolation model was exploited by Enting (1986) in deriving the series presented below. Wu (1982) also shows how the statistics of numbers of bonds in a cluster can be obtained in the Potts model formulation. In addition, he considers a Potts model formulation of a more general percolation model in which both sites and bonds can be randomly closed. The possible relevance of this more general model is discussed in Section 4 below.

Closed form approximations for Potts models have been described by Kihara et al. (1954). Their approximation is exact in the $q \to \infty$ limit. Series expansions applicable for general values of q have been given by Kihara et al. (1954) and Straley and Fisher (1973). There have been numerous series studies of particular cases (see Wu, 1982 for references). The basic technique of series derivation is to define a subgraph expansion such as (3.6) so that the series coefficients are obtained from the number of ways particular classes of graph can occur as subgraphs of the lattice. The numbers of subgraph embeddings are almost invariably enumerated by digital computer.

Early attempts to apply renormalisation group techniques to the study of the Potts model were generally unsuccessful in that they could not reproduce the result due to Baxter (1973) of a first-order transition on the square lattice for $q > 4$ and a continuous transition for $q \leqslant 4$. A successful analysis of the Potts model using renormalisation group techniques was ultimately achieved by Nienhuis et al. (1979) using a parameter space that included diluted systems.

Fig. 3 shows estimates, based on series expansions, of the bond percolation probability $P(p)$ for various three dimensional lattices, plotted in terms of u/u_c. The dashed curves are estimates of the conventionally defined percolation probability for bond percolation models and are based on series given by Gaunt and Sykes (1983). The solid curves represent percolation probabilities defined in terms of the Potts/percolation model using eq. (3.8). The series for the simple cubic lattice are from Gaunt et al. (1981) and the series for the ultramarine lattice (discussed below) are from Enting (1986). Each of the curves is an estimate of the form

$$P(u) \approx (R(u)/T(u))^{\beta},$$

where the exponent β is 0.454 as estimated by Gaunt and Sykes (1983) and R and T are polynomials in u whose coefficients are chosen to fit the available terms in the series for $P(u)$. In other words $R(u)/T(u)$ is a Padé approximate to $P(u)^{1/\beta}$.

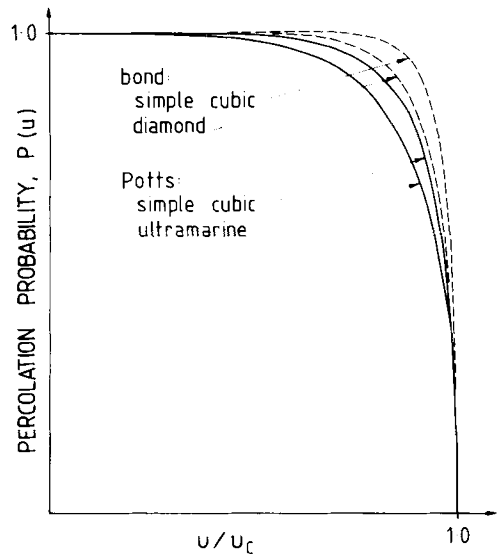

Fig. 3. The percolation probability for various 3-D lattices showing differences due to lattice structure and definition of $P(u)$. Approximations are derived from Padé approximants to $P^{1/0.454}$. Dashed curves are for bond percolation based on series from Gaunt and Sykes (1983). The solid curves show estimates for $P(u)$ for the Potts/percolation model on the simple cubic and ultramarine lattices.

4. Statistical mechanics and bubble trapping

The initial use of percolation models for describing the bubble trapping distribution

(Stauffer et al., 1985; Enting, 1985a) relied on a simple assumed correspondence between the firn system and a three-dimensional percolation model. There are however many aspects of this correspondence that should be examined in the light of existing knowledge of lattice statistics models.

As mentioned in the introduction, the cooperative effect of random bond closures determines the dominant physical process of the transition from firn to ice. The other simultaneous structural changes in the firn can be regarded as simply modifying the parameters that describe the transition and give the details of its local effects. Universality theory states that the underlying physics of the cooperative phase transition will be invariant under changes in the local details of the system. However such local details are important both for constructing quantitative models of the trapping and for calibrating the cooperative behaviour in terms of small scale measurements of bubble statistics.

4.1. *Diffusion*

The lattice statistics models only describe the static aspects of bubble trapping and do not consider the times required for the gas in open channels to equilibrate with the free atmosphere. Observations of ^{39}Ar by Loosli (1983) indicate that the bulk of the gas in the open firn is freely mixed with the atmosphere. Since the half-life of ^{39}Ar is over 200 years, this mixing assumption may not be valid on shorter time scales and it may be necessary to model the movement of gas explicitly. Diffusion on percolating clusters has been reviewed by Mitescu and Roussenq (1983).

4.2. *Changing structure*

The simple lattice statistics models assume that all the structural changes in the ice can be modelled as simple channel closures and ignores any other structural changes associated with the densification. A more detailed description of the sintering of snow grains in the firn is given by Stauffer (1981). As mentioned in the introduction, the additional changes include reductions in the volumes of both sites and bonds prior to close-off and modifications of the sizes and shapes of trapped clusters. The changes occurring after close-off do not influence the amount of gas trapped and so need not be included in the model. However these effects must be considered when observations of trapped clusters are being used to calibrate any model.

For the purpose of determining the amount of gas that is trapped, the important quantity is the size of clusters at close-off. If the mean volume per site at age z is denoted $v(z)$ then the basic percolation model

$$R(z) = -\frac{\partial P(z)}{\partial z} \tag{4.1a}$$

must be modified to

$$R(z) = -kv(z)\frac{\partial P(z)}{\partial z}, \tag{4.1b}$$

with k chosen so as to normalise $R(z)$. Mathematically, the factor $v(z)$ is similar to the factor $\partial u/\partial z$ that will appear when (4.1a) is modified to relate ages z to bond closure probabilities u. Eq. (4.1b) must be further modified if the bonds make a significant contribution to the volumes of clusters at cutoff. The extent of such contributions will depend on the variance of the distribution of channel volumes. If this is small so that all bonds have similar volumes then near the close-off point all channels will have small volumes. The fact that the bonds contribute much of the porosity higher in the firn does not affect the trapping model since little trapping occurs in the upper layers. If however the distribution of channel volumes has a large variance then trapped clusters may contain significant volume contributions from the internal bonds. In this case expression (4.1b) must include an additional term proportional to the derivative of the percolation probability conventionally studied in bond percolation problems. Preliminary analysis of sections of an ice-core from Law Dome suggests that bonds appear to make a significant contribution to the volumes of trapped clusters. However this effect may arise in part from structural changes occurring after trapping and a more detailed analysis is required.

4.3. *Use of regular lattice*

The use of systems on regular lattices to model transitions in irregular systems can be justified using the universality properties that are predicted by renormalisation group arguments. Universality predicts that the critical exponents such as β will be the same for all systems of a given symmetry and dimensionality. In particular the exponent $\beta \approx 0.454$ should be the same for all percolation models (site, bond or Potts) on all three-dimensional lattices whether regular or irregular. Furthermore the exponent will be unchanged by smooth structural changes such as those described above. In contrast, closed form approximations give $\beta = 1$. This discrepancy is the basis of the claim in the introduction that the percolation model embodies the dominant physics of the firn to ice transition and must form the basis of any detailed model.

4.4. *Identification of the percolation probability with open firn*

The discussion by Stauffer et al. (1985) and Enting (1985a) has used the percolation probability, i.e., the probability that a site is connected to an infinite cluster, as corresponding to the probability that a pore in the ice is connected to the atmosphere, as implied by eq.(4.1a).

By using an unbounded system as a model, the discussion has ignored the role of the free surface. Systems with free surfaces have been often considered in statistical mechanics (Bínder, 1983). Series techniques have been applied mainly for either the Ising model or for self-avoiding walks. One point to note in connection with any more detailed analysis of bubble trapping is the difficulty of using renormalisation group techniques to analyse problems with a free surface.

4.5. *The density gradient*

While systems with a free surface have been considered in statistical mechanics there is, to the author's knowledge, no previous work on systems with a regular change of properties with position. A geometrically realistic model of bubble trapping would have the closure probability p varying with depth and would analyse such a system as a whole rather than representing each separate depth as part of an unbounded three-dimensional system with the local closure probability applying globally. In continuous transitions, the transition occurs when fluctuations occur on all possible length scales. In the firn system with a gradient in p, unbounded critical fluctuations will only occur in the horizontal direction. Fluctuations in the vertical will be cut off because the lattice will be locally non-critical. It was for this reason that Enting (1985) indicated that an ideal model would strictly have a two-dimensional critical behaviour.

However this two-dimensional behaviour will only be apparent very close to criticality. At moderate distances from the critical point the fluctuations will be shorter ranged and will be essentially equivalent in all directions. Thus away from the critical point the system should "cross over" to a typical three-dimensional behaviour. Such cross-over in statistical mechanics has mainly been considered in connection with anisotropic Ising models with a very weak interaction in one direction (Abe, 1970; Paul and Stanley, 1972; Hankey and Stanley, 1972; Oitmaa and Enting, 1972; Stanley, 1974; Enting and Oitmaa, 1977 and Domb, 1974). This case is the reverse of the firn system in that the ideal three-dimensional behaviour only applies very near the critical point and two-dimensional behaviour applies further away.

4.6. *Fluctuations*

Enting (1985a) pointed out that the large seasonal fluctuations in trapped bubble volume that were observed in the transition region by Schwander and Stauffer (1984) were typical of the critical fluctuations associated with continuous phase transitions. The fact that such transitions are associated with fluctuations on all length scales means that such systems can show very large responses to perturbing influences. These responses are characterised by various susceptibilities that typically exhibit power-law divergences at continuous transitions. One potential problem associated with the existence of these fluctuations is that it would be difficult to obtain a representative sample from the transition region. There has been relatively little work on the sample statistics of cooperative lattice systems but Pickard (1976) has considered the sample problem for the zero-field Ising model.

The sampling problems associated with large fluctuations will be important when using observations of bubble statistics to calibrate models. However the main importance of the fluctuations is that the associated large susceptibilities to perturbing influences can cause significant departures from the idealised model of uniform trapping that is embodied in eq. (1.1). Enting

(1985b) suggests that non-uniformities in the trapping process will be the most serious source of error in the deconvolution of ice-core data. Detailed studies on ice-cores are necessary in order to determine the range of possible fluctuations in trapping and the extent to which the ice, after close-off, retains a record of any non-uniformity that can be used to correct deconvolutions based on assuming uniform trapping. Of particular importance is the role of the impermeable layers discussed by Neftel et al. (1985). Further studies are needed in order to estimate the frequency with which they occur and whether they represent abnormal events or whether they should be regarded as part of the range of natural fluctuations associated with the close-off process.

4.7. Corrections to scaling

For many years, much of the effort in statistical mechanics of phase transitions was concentrated on the study of the dominant critical exponents. More recently there have been a number of studies of the correction terms that modify the dominant behaviour. Adler et al. (1983) have reviewed work on corrections to scaling in percolation models and suggest that the percolation probability should be written

$$P(p) = C_p(p - p_c)^\beta \times (1 + a(p - p_c)^{\Delta_1} + b(p - p_c) + \ldots). \tag{4.2}$$

The exponent Δ_1 should, like β, be applicable for all three-dimensional percolation models. Adler et al. estimate

$$\Delta_1 = 0.98 \pm 0.14. \tag{4.3}$$

This result means that the corrections to scaling can be adequately represented by analytic functions since $\Delta_1 \approx 1$. This simplifies both the series analysis presented below and any use of finite size scaling in analysing the trapping process.

5. Percolation on the ultramarine lattice

Stauffer (1981) suggested that the geometry of the firn could be represented by placing the grains on a bcc lattice. The pores and channels are thus the sites and bonds of a lattice whose structure corresponds to the locations of the silicon atoms in ultramarine ($Na_{4+x}(Si_{24}Al_xO_{48})(X_2)_2$ with $x = 10$ to 12 and $X_2 = SO_4^-$ etc.) (cf. Krebs, 1968). Technically, this lattice is formed by taking the vertices of the Wigner-Seitz cell of the bcc lattice as the lattice points. Stauffer et al. (1985) considered a bond percolation model on this lattice and performed a Monte Carlo simulation. They estimated $p_c = 0.42$. Enting (1986) has generated series expansions for the Potts/percolation model on this lattice. The series were derived by using a generalisation of the "code method" or "method of partial generating functions" described by Sykes et al. (1965). The generalisation to Potts models of general q was described by Enting (1975) as an extension of the techniques used for $q = 3$, 4, 5 and 6 by Enting (1974a, b). The advantage of the 'code method' is that it is one of the class of methods described by Wortis (1974) as 'substituting algebraic complexity for combinatorial complexity' (see also Enting (1978a, b)). Using the "code method" it was possible to obtain series for the percolation probability on the ultramarine lattice to order $(1-p)^{15}$. The series was $P(p = 1 - u) = 1 - u^4 - 4u^6 + 4u^7 - 20u^8 + 36u^9 - 106u^{10} + 244u^{11} - 646u^{12} + 1572u^{13} - 3978u^{14} + 9708u^{15} + \ldots$. As part of the series derivation technique it was also possible to obtain a series expansion for $S(p)$ the mean number of sites per finite cluster. The series for small u was $S(u) = u^4(1 + 8u^2 - 8u^3 + 62u^4 - 108u^5 + 426u^6 - 996u^7 + 3170u^8 - 8092u^9 + 23222u^{10} - 60208u^{11} \ldots)$.

A low density expansion for small p could also be obtained and to order p^7 is $S(p) = 1 + 4p + 12p^2 + 36p^3 + 98p^4 + 280p^5 + 764p^6 + 2112p^7 + \ldots$.. The series were analysed using Padé approximants as described by Gaunt and Guttmann (1974). This analysis did not allow for any corrections to scaling with non-integer powers. Since the work of Adler et al. (1983) suggests that $\Delta_1 \approx 1$ this should not be a limitation on the validity of the analysis. Padé approximants to the series for $P(u)^{1/\beta}$ were constructed, thus representing $P(u)^{1/\beta}$ by the ratio of two polynomials in u such that the ratio correctly represented the series to order u^{15}. The zeroes in the numerators gave estimates of u_c. Padé approximants are particularly useful in analysing series such as $P(u)$ because they provide a way of continuing a series beyond its radius of convergence. For the series $P(u)$ the radius of convergence is determined by the singularity at $u \approx -0.393$ (estimated from Padé approximants) while the singularity that is of physical interest is at $u_c \approx 0.61$. The value of β used in this analysis was taken as $\beta = 0.454$ on the basis of the study by Gaunt and Sykes (1983). The high-density series $S(u)$ was found to be more difficult to analyse. A similar situation was encountered by Gaunt and Sykes for other lattices.

The low-density series $S(p)$ was easier to analyse because the physical singularity determines the radius of convergence. A ratio method analysis gives $p_c \approx 0.4$. A realistic estimate based on $S(p)$ and $P(u)$ is $p_c = 0.39 \pm 0.02$. As in all such series analysis, the uncertainties are somewhat subjective but the range does just exclude the value 0.42 estimated by Stauffer et al. (1985). The approximation to $P(p)$ based on the [8, 7] approximant is shown as the leftmost curve in Fig. 3.

6. Techniques for analysing a refined model

The main reason for attempting to construct a refined model of the bubble trapping process is to reduce the amount of empirical content involved in determining the distribution of trapping times. There are three ways of determining this distribution.

i By measurements of trapped bubble volume through the transition zone as done by Schwander and Stauffer (1984);

ii By calibrating the age distribution function using concentration measurements for some tracer whose atmospheric concentration history is known. One of the chlorofluorocarbons would be an obvious choice but the determination of R would be poorly-conditioned;

iii By constructing a percolation model that expressed the trapping distribution in terms of easily measurable properties of the ice such as density, depth, accumulation rate etc.

Even in the first two empirically calibrated approaches the results of percolation modelling can be useful in giving a guide to the type of functions to be fitted to the data.

The construction of a model of firn closure that can be directly related to properties of the ice must take into account the various complicating factors discussed in Section 4. This will require information concerning the actual structure of the firn in terms of statistics of channels linking pores at various densities. Once this information is available an appropriate percolation model can be readily constructed. The difficulty comes in the analysis of the system. Monte Carlo techniques should be possible although the irregular structure will make such techniques complex and relatively inefficient. A major difficulty would be in handling systems with enough sites to span the appropriate density changes. A grain size of millimetres and a depth range of 10's to 100's of metres indicates that of order 10^4 lattice spacings are required in the vertical direction. While very useful estimates of uniform regular systems can be obtained with simulations using $100 \times 100 \times 100$ sites, for the firn problem even a simulation with $30 \times 30 \times 10^4$ sites would be an order of magnitude larger.

There seems to be little hope of using series expansions to analyse realistic firn closure models. Series expansions on systems with irregular structure have proved very difficult to derive. More significantly, once a spatial variation in properties occurs, there no longer seems to be any natural expansion variable for series. The role of series studies must be confined to providing a cross-check on other methods by performing tests for special cases.

The best hope for analysing a realistic firn closure model lies with the various renormalisation group techniques. Real-space renormalisation techniques rather than spectral forms would seem to be required for several reasons. Firstly they deal (conceptually) with the actual statistical distributions rather than with dominant components and so the results can be more readily related to actual physical properties of the ice. Secondly the firn system has a variation of properties in real-space that makes a spectral representation unsuitable for this problem. The irregular local structure in the firn is a complication that may be computationally cumbersome but which should not pose fundamental difficulties. The renormalisation group transformation corresponds to a summation over the less relevant degrees of freedom on everincreasing length scales. As the transformation is iterated, the local disorder becomes less and less important. For practical computations, it should be sufficient to regard the first two or three iterations of the transformations as a form of restructuring transformations (Berker, 1975) that maps the irregular lattice into a (sparser) regular lattice.

Apart from the more conventional approaches that construct explicit transformations on the probability distribution Prob(ρ), it may be possible to use the so-called 'phenomenological renormalisation group' (Nightingale, 1976) approach which relies on finite size scaling assumptions. The Monte Carlo renormalisation group approach proposed by Ma (1976) may also be useful (see also Swendsen, 1979).

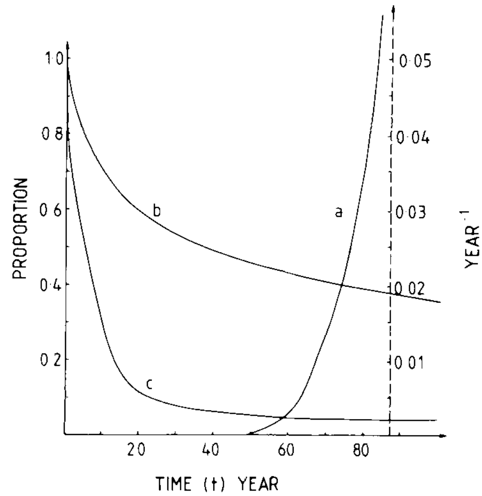

Fig. 4. Comparison of the kernels of three integral equations of interest in carbon cycle studies. (a) The bubble trapping function, $R(z)$, relating bubble concentrations to atmospheric concentrations. (b) The CO_2 response function, $R_c(t)$, relating CO_2 source strengths to atmospheric concentrations. (c) The isotopic response function, $R_\delta(t)$, relating CO_2 source strengths to atmospheric $\delta^{13}C$.

7. Numerical requirements

The modelling of firn closure using the percolation model leads to a number of interesting questions in statistical mechanics as described in the preceding sections. However for carbon cycle studies, the obvious question is how accurate a description is really needed for the interpretation of measurements on trapped bubbles.

The inversion of the bubble concentrations corresponds to the inversion of a Volterra integral equation of the first kind:

$$fx) = \int_a^x R(x-y)\, g(y)\, dy. \tag{7.1}$$

The solution of such integral equations can be ill-conditioned in that the solution $g(y)$ tends to be very sensitive to errors in $f(x)$ and $R(x)$. In general, the smoother the kernel, R, the worse-conditioned the inversion, i.e., the greater the extent of error-amplification. In this regard the inversion of ice-bubble data is relatively well-posed compared to other inversion problems occurring in carbon cycle studies. Fig. 4 compares the age distribution for bubble trapping to two other response functions. The first function $R_\delta(t)$ gives the isotopic response of atmospheric CO_2 (as defined by $\delta^{13}C$) to an injection of CO_2 with a δ^{13} of $-25‰$. The second function $R_c(t)$ gives the response of the atmospheric CO_2 concentrations to an injection of CO_2. It will be seen that the age distribution function changes a more rapidly than either of the other two response functions; in fact, $R(z)$ diverges. Thus the deconvolution of bubble concentrations is a better-conditioned problem than deducing past CO_2 sources from $\delta^{13}C$ changes and very much better-condition than deducing sources from CO_2 changes. Similarly, for a given signal-to-noise ratio, the deduction of CO_2 sources from $\delta^{13}C$ changes is a better-conditioned problem than the deduction of CO_2 sources from CO_2 concentration changes. The reason that high precision is required in the deconvolution of ice-core data is that the atmospheric CO_2 history must be subjected to a second deconvolution to deduce the CO_2 source strengths and that this deconvolution is the most poorly-conditioned of the three examples discussed here. Since this final deconvolution tends to severely amplify any errors in the estimated CO_2 concentration it is highly desirable to minimise such errors by using the best possible representation of the function $R(z)$. The functions R_δ and R_c shown in Fig. 4 were obtained from the box-diffusion model of Oeschger et al. (1975), modified essentially as described by Stuiver et al. (1984).

It is the property of integral equations with smooth kernels being poorly conditioned that makes the determination of the trapping distribution from halocarbon observations poorly-conditioned. Such an approach would involve solving eq. (7.1) for R where the kernel g, being one of the atmospheric halocarbon concentrations, will be a very smooth function of time. Nevertheless, if the concentration of a tracer increases linearly then the mean trapping time

$$\int_0^{z_c} z' \, R(z') \, \mathrm{d}z$$

gives a delay time z_d such that $q(z) = c(z - z_d)$. The delay z_d can be estimated using any tracer with a known atmospheric history that has little curvature and the resulting z_d can be applied to any other tracer showing similar behaviour (Enting and Mansbridge, 1985). This type of situation in which it is possible to deduce a particular mathematical quantity reliably, even though it is defined in terms of the solution of an ill-conditioned problem, has been described in greater generality by Anderssen (1980).

The analysis up to this point has been based on eq. (1.1) and so assumes a uniform trapping process. However the trapping process shows variations on both seasonal and interannual time scales. For example even the total volume of air that is trapped has been found to vary (e.g. Berner et al., 1978; Raynaud and Whillans, 1982). Such variation limits the validity of eq. (1.1) since the trapping distribution is a function of both the time of deposition and the time of the partial close off rather than being simply a function of the difference between these times. The degree of variability in the trapping and thus the size of the error involved in assuming a uniform trapping process will vary between sites; the more uniform the deposition, the smaller the error. As mentioned above, the variability in trapping seems to arise from the fact that cooperative transitions are characterised by large susceptibilities to perturbing influences.

One general point to be noted is that the degree of ill-conditioning in an inverse problem such as the deconvolution of (1.1.) tends to reflect the sensitivity of the solution, $c(z)$, to both errors in the data, $q(z)$, and errors in the problem formulation, i.e., the use of $R(z)$, (see for example Enting, 1985b). Since, as described above, the sharpness of $R(z)$ makes the inversion of (1.1) relatively well-conditioned the errors involved in assuming uniform trapping will lead to relatively small errors in $c(z)$. However these small errors will tend to be more severely amplified if $c(z)$ is used to estimate the biospheric release rate.

8. Summary

The statistics of bubble trapping in polar ice provide an interesting application of the percolation model from lattice statistics. Even the crudest models that consider uniform regular three-dimensional lattices can provide a useful guide to appropriate functional forms to be fitted when using empirical techniques to determine the distribution of trapping times. The construction of more refined models involves more specialised systems. Most of the special aspects involved in constructing a refined model have been studied previously in statistical mechanics, but generally only in isolation and often only for the Ising model. The most promising ways of analysing more refined models of bubble trapping would seem to be the use of some of the various renormalisation group techniques. It will be necessary to find a renormalisation group technique that performs adequately for all the special aspects individually in order to have any confidence in the results obtained when all the special aspects are combined to model the firn closure. This will necessitate testing renormalisation group techniques on a number of special systems by comparing the results to results of series analysis. A number of such comparisons are currently being undertaken.

9. Acknowledgements

The Padé approximant calculations were performed by Dr. J. V. Mansbridge using computer routines supplied by Prof. A. J. Guttmann.

REFERENCES

Abe, R. 1970. Some remarks on perturbation theory and phase transition with application to the anisotropic Ising model. *Prog. Theor. Phys. 44*, 339–347.

Adler, J., Moshe, M. and Privman, V. 1983. Corrections to scaling for percolation. *Percolation structures and processes*, pp. 397–423 (eds. G. Deutscher, R. Zallen and J. Adler). Adam Hilger, Bristol.

Anderssen, R. S. 1980. On the use of linear functionals for Abel-type integral equations in applications. *The application and numerical solution of integral equations*, pp. 195–221 (eds. R. S. Anderssen, F. R. de Hoog and M. A. Lukas). Sijthoff and Noordhoff, Alphen aan den Rijn.

Barnola, J. M., Raynaud, D., Neftel, A. and Oeschger, H. 1983. Comparison of CO_2 measurements by two laboratories on air bubbles in polar ice. *Nature 302*, 410–413.

Baxter, R. J. 1973. Potts model at the critical temperature. *J. Phys. C6* L445–448.

Baxter, R. J., 1982. *Exactly solved models in statistical mechanics*. Academic, London.

Baxter, R. J. and Enting, I. G. 1979. Series expansions from corner transfer matrices: The square lattice Ising model. *J. Statis. Phys. 21*, 103–123.

Berker, A. N. 1975. Critical interactions for the triangular spin-s Ising model by a spin-restructuring transformation. *Phys. Rev. B12*, 2752–2758.

Berner, W., Stauffer, B. and Oeschger, H. 1978. Past atmospheric composition and climate, gas parameters measured on ice cores. *Nature 276*, 33–35.

Biggs, N. L. 1974. *Algebraic graph theory*. Cambridge U.P.

Binder, K. 1983. Critical behaviour at surfaces. *Phase transitions and critical phenomena*. Vol. 8, chap. 1 (eds. C. Domb and J. L. Lebowitz). Academic, New York.

Burley, J. 1972. Closed form approximations for lattice systems. *Phase transitions and critical phenomena*. Vol. 2, chap. 9 (eds. C. Domb and M. S. Green). Academic, New York.

Domb, C. 1960. On the theory of cooperative phenomena in crystals. *Advance Phys. 9*, 149–361.

Domb, C. 1974. In *Phase transitions and critical phenomena*. Vol. 3, p. 464 (eds. C. Domb and M. S. Green). Academic, New York.

Domb, C. and Green, M. S. Eds. 1976. *Phase transitions and critical phenomena*. Vol. 6. Academic, New York.

Enting, I. G. 1974a. Series expansions for the Potts model: high field expansions. *J. Phys. A7*, 1617–1626.

Enting, I. G. 1974b. Series expansions for the Potts model II: partial generating functions in two dimensions. *J. Phys. A7*, 2181–2197.

Enting, I. G. 1975. High-field expansions for multi-state lattice models. *J. Phys. A8*, 727–741.

Enting, I. G. 1978a. Some algebraic techniques for obtaining low-temperature series expansions. *Aust. J. Phys. 31*, 515–522.

Enting, I. G. 1978b. The combinatorics of algebraic graph theory in theoretical physics. *Combinatorial mathematics*, pp. 148–156 (eds. D. A. Holton and J. Seberry). Lecture Notes in Mathematics *686* (Springer-Verlag, Berlin).

Enting, I. G. 1985a. A lattice statistics model for the age distribution of air bubbles in polar ice. *Nature 315*, 654–655.

Enting, I. G. 1985b. A classification of some inverse problems in geochemical modelling. *Tellus 37B*, 216–229.

Enting, I. G. 1986. Lattice models of aspects of firn closures I: Percolation on the interstices of the BBC lattice. *J. Phys. A19*, 2841–2854.

Enting, I. G. and Mansbridge, J. V. 1986. The effective age of bubbles in polar ice. *PAGEOPH 123*, 770–790.

Enting, I. G. and Oitmaa, J. 1977. High field expansions for the anisotropic Ising model. *J. Phys. A10*, 1151–1166.

Essam, J. W. 1972. Percolation and cluster size. *Phase transitions and critical phenomena*, Vol. 2, ch. 6 (eds. C. Domb and M. S. Green). Academic, New York.

Fisher, M. E. 1967. The theory of equilibrium critical phenomena. *Rep. Prog. Phys. 30*, 615–730.

Fortuin, C. M. and Kasteleyn, P. W. 1972. On the random-cluster model. I. Introduction and relation to other models. *Physica 57*, 536–564.

Freyer, H. D. and Belacy, N. 1983. $^{13}C/^{12}C$ records in northern hemisphere trees during the past 500 years, Anthropogenic impact and climatic superstitions. *J. Geophys. Res 88*, 6844–6852.

Gaunt, D. S. and Guttmann, A. J. 1974. Asymptotic analysis of coefficients. *Phase transitions and critical phenomena*. Vol. 3, ch. 4 (eds. C. Domb and M. S. Green). Academic, London.

Gaunt, D. S. and Sykes, M. F. 1983. Series study of random percolation in three dimensions. *J. Phys. A16*, 783–799.

Gaunt, D. S., Whittington, S. G. and Sykes, M. F. 1981. Series estimates of the exponent β for bond percolation on a simple cubic lattice. *J. Phys. A14*, L247–250.

Hankey, A. and Stanley, H. E. 1972. Systematic application of generalised homogeneous functions to static scaling, dynamic scaling and univerality. *Phys. Rev. B6*, 3515–3542.

Houghton, R. A., Hobbie, J. E., Mellillo, J. M., Moore, B., Peterson, G., Shaver, G. R. and Woodwell, G. M. 1983. Changes in the carbon content of the terrestrial biota and soils between 1860 and 1980: A net release of CO_2 to the atmosphere. *Ecol. Monogr. 53*, 235–262.

Ising, E. 1925. Beitrag zur Theories des Ferromagnetismus. *Z. Phys. 31*, 253–258.

Kihara, T., Mudzuno, Y. and Shizume, J. 1954. Statistics of two-dimensional lattices with many components. *J. Phys. Soc. Japan 9*, 681–687.

Krebs, H. 1968. *Fundamentals of Inorganic Crystal Chemistry* (trans. P. H. L. Walter). McGraw Hill, New York.

Loosli, H. H. 1983. A dating method with ^{39}Ar. *Earth planet. Sci. Lett. 63*, 51–62.

Ma, S. K. 1976. Renormalization group by Monte Carlo methods. *Phys. Rev. Lett. 37*, 461–464.

Mandelbrot, B. B. 1977. *Fractals: form chance and dimension*. W. H. Freeman, San Francisco.

Mitescu, C. D. and Roussenq, J. 1983. Diffusion on percolation clusters. *Percolation structures and processes*, pp. 81–100. (eds. G. Deutscher, R. Zallen and J. Adler). Adam Higler, Bristol.

Neftel, A., Oeschger, H., Schwander, J., Stauffer, B. and Zumbrunn, R. 1982. Ice core sample measurements give atmospheric CO_2 content during past 40.000 years. *Nature 295*, 220–223.

Neftel, A., Moor, E. Oeschger, H. and Stauffer, B. 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. *Nature 315*, 45–47.

Nienhuis, B., Berker, A. N., Riedel, E. K. and Schick, M. 1979. First- and second-order transitions in Potts models: renormalization group solution. *Phys. Rev. Lett. 43*, 737–40.

Nightingale, M. R. 1976. Scaling theory and finite systems. *Physica 83A*, 561–572.

Oeschger, H., Siegenthaler, U., Schotterer, U. and Gugelmann, A. 1975. A box diffusion model to study the carbon dioxide exchange in nature. *Tellus 27*, 168–192.

Oitmaa, J. and Enting, I. G. 1972. Critical behaviour of the anisotropic Ising model. *J. Phys. C5*, 231–244.

Paul, G. and Stanley, H. E. 1972. Partial test of universality hypothesis: The case of different coupling strengths in different lattice directions. *Phys. Rev. B5*, 2578–2599.

Pickard, D. K., 1976. Asymptotic inference for an Ising lattice. *J. Appl. Prob. 13*, 486–497.

Potts, R. B. 1952. Some generalised order-disorder transformations. *Proc. Camb. Phil. Soc. 48*, 106–109.

Raynaud, D. and Whillans, I. M. 1982. Air content of the Byrd core and past changes in the West Antartic ice sheet. *Ann. Glaciol. 3*, 269–273.

Schwander, J. and Stauffer, B. 1984. Age difference between polar ice and air trapped in its bubbles. *Nature 311*, 45–47.

Stanley, H. E. 1971. *Introduction to phase transitions and critical phenomena*. Clarendon Press, Oxford.

Stanley, H. E. 1974. *Phase transitions and critical phenomena*. Vol. 3, ch. 7 (eds. C. Domb and M. S. Green). Academic, New York.

Stauffer, B. 1981. Mechanismen des lufteinschlusses in natürlichem eis. *Z. Gletscherkd. Glazialgeol. 17*, 17–56.

Stauffer, B., Schwander, J. and Oeschger, H. 1985. Enclosure of air during the metamorphosis from dry firn into ice. *Ann Glaciol. 6*, 108–112.

Straley, J. P. and Fisher, M. E. 1973. Three-state Potts model and anomalous tricritical points. *J. Phys. A6*, 1310–1326.

Stuiver, M., Burk, R. L. and Quay, P. D. 1984. $^{13}C/^{12}C$ ratios in tree rings and the transfer of biospheric carbon to the atmosphere. *J. Geophys. Res. 89D*, 11731–11748.

Swendsen, R. H. 1979. Monte Carlo renormalisation group. *Phys. Rev. Lett. 42*, 859–861.

Sykes, M. F., Essam, J. W. and Gaunt, D. S. 1965. Derivation of low-temperature expansions for the Ising model of a ferromagnet and an antiferromagnet. *J. Math Phys. 6*, 283–298.

Wilson, K. G. 1971. Renormalization group and critical phenomena I. Renormalization group and Kadanoff scaling picture. *Phys. Rev. B4*, 3174–3183.

Wilson, K. G. 1983. The renormalisation group and critical phenomena. *Rev. Mod. Phys. 55*, 583–600.

Wortis, M. 1974. *Phase transitions and critical phenomena*. Vol. 3, ch. 3 (eds. C. Domb and M. S. Green). Academic, New York.

Wu, F. Y. 1982. The Potts model. *Rev. Mod. Phys. 54*, 235–268.

Zallen, R. 1983. Percolation: A model for all seasons. *Percolation structures and processes*, pp. 3–16 (eds. G. Deutscher, R. Zallen and J. Adler). Adam Higler, Bristol.