MOLECULAR THEORY OF METASTABILITY*: AN UPDATE

by

O. Penrose
The Open University, Milton Keynes, England

and

J. L. Lebowitz
Rutgers University, New Brunswick, New Jersey, USA

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This appendix outlines some subsequent developments in the fields discussed in the article, concentrating on rigorous, or at least quantitatively testable, aspects. For an excellent survey with less emphasis on rigour, see Gunton et al (1983, 1984).

In section 2 of the article mention is made of the possibility of extrapolating the free energy function from stable to metastable states, even though the two kinds of states are likely to be separated by a singularity of that function, and of using the extrapolated function to describe the metastable state.

For some models, particularly those for which transfer matrix methods can be used, this extrapolation can be done by analytic continuation, going around the singularity in the complex plane of a parameter such as the activity or magnetic field; the work of Newman and Schulman (1977) and McCraw and Schulman (1978), already mentioned in the article, has been continued by Newman and Schulman (1980), Privman and Schulman (1982a,b) and Roepstorff and Schulman (1984). The analytically continued free energy is complex: its real part is taken to represent the free energy of the metastable state and its imaginary part to be related to the lifetime of the metastable state.

The "evidence" for this interpretation is based on some very simple examples involving systems with one or few degrees of freedom
and on some numerics for the 2D Ising model. It would be most interesting if one could establish these connections in a convincing and understandable fashion.

The analytic properties of the free energy function for the nearest-neighbour Ising ferromagnet have been investigated by Isakov (1984) in a deep paper. His main result is that, for sufficiently large $k$,

$$\lim_{h \to 0^+} \frac{1}{k!} \frac{\partial^k F}{\partial h^k} = \left[ A_k^{-kd} k! \right]^{1/(d-1)}, \quad d \geq 2$$

where $F$ is the thermodynamic energy, $h = 2H/k_B T$ with $H$ the magnetic field, $k_B$ Boltzmann's constant and $T$ the temperature, $d$ is the number of dimensions, and $A_k$ has, for small enough temperatures, positive upper and lower bounds independent of $k$ at fixed $T$ and $d$. This result shows that the Maclaurin series for $F$ in powers of $h$ has zero radius of convergence, so that the function $F(h)$ has a singularity at $h = 0$; but it does not preclude an analytic continuation using the complex $h$-plane as envisaged in the papers by Schulman and others mentioned earlier. Isakov also investigates the relation between the free energy of a metastable state (defined using a restricted ensemble) and the free energy function extrapolated from negative to positive values of $h$ by treating the divergent series

$$\sum_{k=0}^{\infty} \frac{1}{k!} \left( \frac{\partial^k F}{\partial h^k} \right)_{h=0} h^k$$

as an asymptotic series (i.e. by truncating at the smallest term). This
procedure is shown to give a valid approximation, but there is an inevitable uncertainty which increases with \( h \).

A variety of papers bear on the question of how to define metastable states, or what ensembles to use to represent them. For a deterministic dynamical system, we are interested in the rate at which systems escape from a suitably defined metastable region \( R \) in phase space, and in whether those systems that have not yet escaped from \( R \) can be said to approach an "equilibrium ensemble" in the same way as they would if there were no escape. A theorem of Pianigiani and Yorke (1979) shows that under certain conditions they can (this theorem is also relevant to the study of the Lorenz model – see Yorke and Yorke 1979). For stochastic dynamical systems described by a Markov chain (such as those defined by the Glauber or Kawasaki stochastic dynamics) the question of defining metastability has been investigated for the Ising ferromagnet by Davies and Martin (1981) and by Davies (1982a); the idea is to find not a metastable region but a metastable probability distribution over the states of the process – i.e. one that changes very slowly in comparison to the relaxation of a small perturbation of the equilibrium (Gibbs) probability distribution. The simplest way for this to be possible is for the smallest non-zero eigenvalue of the time evolution to be much smaller than any of the others. The relevant mathematical results about Markov processes have been explored further by Davies (1982b, c, d).

Another way of looking at stochastic dynamical models has been used by Cassandro, Galves, Olivieri and Vares (1984, also Galves, Olivieri and Vares 1984). Here metastability is characterized by the convergence
of time averages, under a suitable re-scaling, to a measure-valued Markov jump process. That is to say, if $X(t)$ is a dynamical variable of the model, the time average

$$\bar{X}_{T, \tau}(s) = \frac{1}{T} \int_{s\tau}^{s\tau+T} X(t) dt$$

converges, under a re-scaling in which $T \to \infty$, $\tau / T \to 0$, to a random variable $\bar{X}_\infty(s)$ whose probability distribution is concentrated at one value for scaled times $s < S$ and at another for $s > S$, and the scaled time $S$ at which the jump occurs is itself a random variable with exponential distribution (i.e. $\text{Prob}(S > \sigma) = e^{-\sigma}$). Further work along these lines was done by Kipnis and Newman (1985), Schonmann (1985) and by Galves, Olivieri and Vares (1986).

A different approach to the study of metastable states has been developed by Sewell (1977a, 1977b, 1980; see also Vanheuverzwijn 1979), using the infinite-system formalism. A virtue of this approach is that it extends easily to quantum mechanics and can therefore be applied to essentially quantum-mechanical metastability phenomena such as superconductivity. In the infinite-system formalism, equilibrium states are defined as those which minimize the free energy functional and also satisfy the Kubo-Martin-Schwinger condition

$$\langle AB(t) \rangle = \langle B(t+\beta)A \rangle$$

where $A$, $B$ are observables, $\beta = 1/k_B T$ and $B(t)$ is the time translate of $B$. Metastable states are now defined as ones that minimize the restriction of the free energy density to some reduced state space. If in addition they satisfy the KMS condition,
they are found to be infinitely long-lived even in the presence of localized perturbations, but this case can occur only for special models involving long-range forces. If the metastable states do not satisfy the KMS condition they may still have long lifetimes against a suitably wide class of local perturbations; this is essentially the case considered in sections 5–6 of the body of this present article.

One the most fruitful ways of studying metastability is the cluster approach described in sections 7–9 of the body of the article, which is coupled with the use of the Becker-Döring kinetic equations derived there. Static properties of clusters for the nearest-neighbour Ising model have been investigated by Dickman and Schieve (1983, 1984), and Huiser et al. (1982) have looked at a simplified dynamical model of the behaviour of such clusters. It is possible to make a "first-principles" calculation of the first few coefficients \( a, b \) in the Becker-Döring kinetic equations for the Kawasaki dynamics of a lattice gas at very low densities on a simple cubic lattice (Penrose and Buhagiar 1983). The resulting values, together with a suitable extrapolation to large values of \( \ell \), can be used in a numerical integration of the Becker-Döring equations (Penrose, Lebowitz, Marro, Kalos and Tobochnik 1984); although the extrapolation method used is not very accurate, as shown by the Monte Carlo work of Perini et al. (1984), the results of the numerical integration agreed quite well with computer simulations at low densities, though less well at high densities. Some mathematical results about the Becker-Döring equations have been proved by Ball, Carr and Penrose (1986); in particular the existence and uniqueness of the solutions was proved (not a trivial matter, since there are infinitely
many equations) and their limiting behaviour as \( t \to \infty \) was rigorously established.

There has been very little progress in improving theoretically on the Becker-Doring calculation of the nucleation rate for a metastable state, described in section 9 of the body of this article and often referred to as "classical nucleation theory". Computer simulations bearing out some of the detailed predictions of this theory have, however, been carried out by Stauffer, Coniglio and Heerman (1982) and by Heerman, Coniglio, Klein and Stauffer (1983); see also Heerman and Klein (1983). For a discussion of the relation between this theory and experimental work, the reader is referred to the article by Langer (1980).

There has been some improvement in the theoretical understanding of systems for which the range of interaction, denoted by \( 1/\gamma \) in the main body of this article, is large but finite. In the limit of \( \gamma \to 0 \) the theory outlined in section 6 predicts a sharp spinodal transition between metastable and unstable states. For finite \( \gamma \), the nucleation rate near this spinodal curve has been studied analytically (Klein and Unger 1983), by simulations (Heerman and Klein 1983) and by phenomenological arguments (Binder 1984). Such systems are relevant to the theory of polymer mixtures, since an increase of the range \( 1/\gamma \) corresponds to an increase of the molecular weight of the polymer (see Binder 1984).

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