Journal of Statistical Physics, Vol. 17, No. 4, 1977

A Rigorous Study of Metastability in a Continuous Model

M. Cassandro[1] and E. Olivieri[2]

Received April 12, 1977

We consider the classical continuous Widom and Rowlinson model. We follow the general method for describing metastable states proposed by Penrose and Lebowitz. Suitably restricting the set of the allowed configurations, we construct a nonequilibrium state describing a pure phase. Starting from the natural time evolution of the system, we rigorously prove that when both the activities are sufficiently large and close enough together, the relaxation time per unit volume can be made very large.

KEY WORDS: Phase transitions; metastability; relaxation time.

1. INTRODUCTION

A large class of systems undergoing phase transitions exhibits the phenomenon of metastability. The relevant experimental evidence shows that, given a system in a state within the range of the thermodynamic parameters where different phases are in stable equilibrium with each other, it is possible, by suitable transformations, to reach nonequilibrium states that can be preserved for a time sufficient to allow the measurement of these thermodynamic parameters. The main features of these states are the following:

1a. Only one thermodynamic phase is present.
1b. A system that starts in this state is likely to take a long time to get out of it.
1c. Once the system has gotten out, is unlikely to return.

Nucleation theory[(1)] gives a picture both suggestive and physically sound of metastability, but its quantitative predictions, based on the droplet model and on suitable approximation of a highly nonlinear set of kinetic

[1] Istituto di Fisica G. Marconi, Università di Roma, Roma CNR, GNSM, Roma, Italy.
[2] Istituto Matematico G. Castelnuovo, Università di Roma, Roma CNR, GNSM, Roma, Italy.

equations, are not satisfactory[1] and a rigorous treatment would be very useful also from a phenomenological point of view.

In the van der Waals model of liquid–vapor transitions the static properties of a metastable state can be obtained, extrapolating the free energy from the nearby one-phase states. But this theory does not satisfy the general principles of statistical mechanics and any attempt to extrapolate from stable to metastable states for more realistic systems has to face the lack of information about the analytic structure of the free energy near the critical boundary. For instance, the existence of a singularity in this region for short-range potentials suggested by a general theorem of Lanford and Ruelle[2] seems to deny the very existence of such states and would in any case make any extrapolation very hard.

In this connection Fisher[3] has investigated the analytic properties of the free energy in the droplet model, showing that, in this case, a singularity is actually present, forbidding any real analytic continuation. Langer[4] was able to get around this difficulty by an analytic continuation whose real part can be interpreted as the free energy of the metastable state. But again the droplet model is not a rigorous model and furthermore, due to the very nature of the approximations involved in the definition of the model, a direct dynamical analysis, the only way to check the reliability of these states as metastable states, is impossible.

In this connection it is worth mentioning a recent paper by Binder[5] where the "static" analysis of the Ising model in terms of clusters is implemented from a dynamical point of view by computer simulations.

A fundamental step forward was made in 1971 by Penrose and Lebowitz[6] (PL), who proposed a general method for describing metastable states in statistical mechanics.

They start from what is expected on physical grounds from a metastable state and give a prescription for making these notions precise. Given a finite system K and calling the set of its possible configurations S, the problem is to find a subset R of S such that, if we restrict the allowed configurations of our system as $t = 0$ to R and assume for them the corresponding weights of the Gibbs distribution at equilibrium, then for suitable values of the thermodynamical parameters (i) condition (1a) is satisfied, (ii) the conditional probability $P(t)$ that the system at time t is in a configuration not contained in R is small, and (iii) the relative weight of the configurations contained in R is negligible at equilibrium. In this approach for the first time both the "static" and the dynamical aspects of the problem are coupled in a rigorous way, and, by a simple argument based on the Liouville theorem, the estimate of the relaxation time can be performed without handling the highly nonlinear set of differential equation that any previous approach was forced to deal with.

In their paper PL are able to perform the calculations only for a very special class of potentials (the Kac potentials) in the so-called van der Waals limit where the actual interaction is equivalent to a "mean field." By analytic continuation they get a class of states whose relaxation times go to infinity with the volume. The extension of these results to short-range force systems is by no means trivial. The connection between the range of the forces and analytic properties is expected to reflect an actual difference in the mechanism underlying the condensation phenomena.[4,6,7]

In a previous paper[8] we have studied in the framework of the PL approach a short-range force system: Considering a two-dimensional Ising ferromagnet with (+) boundary conditions and negative external field and assuming the dynamics of a Markovian process, we constructed, suitably restricting the configurations at $t = 0$, a nonequilibrium state with positive magnetization such that when the temperature is sufficiently low (i) only one phase is present, and (ii) the relaxation time per unit volume is finite and can be made very large. This extension of the PL approach to short-range force systems was made possible by the very powerful analysis of the relevant configurations of the Ising system in terms of contours made by Minlos and Sinai.[9]

In the present paper we use a similar technique to study a short-range continuous system—the Widom–Rowlinson model—and we show that the results and their physical interpretation are the same as those previously obtained for the Ising model in spite of the different symmetries and dynamics involved.

In Section 2 we define the model and briefly sketch and discuss a geometrical description of the configurations.[10]

In Section 3 we define the subset of configurations R (our candidate for the metastable state) and discuss the "static" properties of our state. Section 4 is devoted to the evaluation of the relaxation time: We define, following PL, the escape rate (i.e., the probability per unit time for the configurations of the system to move out of R) and work out a rigorous upper bound for it.

In Appendices A, B, and C some useful bounds are derived. In Appendix D we check that our candidate for the metastable state is "far away" from the actual equilibrium state.

2. THE MODEL

The Widom–Rowlinson (WR) model[11] is a classical continuous model with two kind of particles, A and B, in which there is a hard-core repulsion of range r between unlike particles and no interaction between like particles. The activities z_A and z_B and the range r are the only parameters of the model. The physical relevance of this model relies on two facts: (1) its behavior, at

least as far as symmetry properties are concerned, is very similar to that of a real fluid,[3] and (2) it is the only continuous model with short-range forces for which the existence of a phase transition is rigorously proven.[12]

In fact, Ruelle, associating classes of A–B particle configuration to polygons (contours) on a lattice, was able to prove, for suitable boundary conditions, the coexistence of an A-rich phase and a B-rich one.

This section mainly contains a modification of the geometrical description introduced by Ruelle that allows us to transfer to the WR model the results obtained by Minlos and Sinai for the Ising model.

A nice feature of this approach, both in the Ising and in the WR model, is that the introduction of these contours, far from being a purely technical device, allows a more clear and intuitive picture of the microscopic distribution of these particles at equilibrium, giving rise, so to say, to a rigorous version of the droplet model.

Following Ruelle, we introduce a square lattice of $d \times d$ squares with $d = r/(3\sqrt{2})$, so that r is the diagonal of a $3d \times 3d$ square. Our box Λ is a rectangle containing $N = |\Lambda|d \times d$ squares. We introduce the boundary condition that the strip composed of the first four squares adjacent to the boundary of Λ cannot contain B particles (A-boundary conditions). If we consider now an arbitrary configuration in Λ (consistent with the above boundary conditions) and shade all $3d \times 3d$ squares, centered on the small squares containing at least one B particle, the boundary of the union of the shaded areas will be a polygon of various edge "self-avoiding" closed contours.

Among all these contours we will consider the outer ones (i.e., those not embraced by any other contour). We define a chain γ as the smallest set of outer contours such that if two outer contours have a distance less than $8r/(3\sqrt{2})$, they belong to the same chain.

We further say that two chains are compatible if they can be found in the same configuration as disjoint chains.

Given a chain γ, we will call $\Theta(\gamma)$ the (generally disconnected) region that has γ as boundary. $\tilde{\Theta}(\gamma)$ will be the region obtained by adding to $\Theta(\gamma)$ a strip that contains all the square at a distance less than r from the small squares inside but not touching the outer contours belonging to γ, allowed to contain B particles.

It is easy to see[10] that we can write the grand partition function in the following way:

$$\Xi(\Lambda) = \sum_{\{\gamma_1,\dots,\gamma_s\}}{}' \prod_1^s{}_i \frac{\Xi(\tilde{\Theta}(\gamma_i))}{\Xi_0(\tilde{\Theta}(\gamma_i))}\, \Xi_0(\Lambda) \tag{1}$$

[3] If the β particles are invisible, the resulting system of A particles yields a model for liquid-vapor transition. In this case z_A and z_B are related to the temperature and the chemical potential of the system.

where the primed sum is over all the collections $\{\gamma_1,\ldots,\gamma_s\}$ of compatible chains in Λ; $\tilde{\Xi}(\Theta(\gamma))$ is the grand partition sum over all the $A\cdot B$ particle configurations in $\Theta(\gamma)$ compatible with the presence of the chain γ; and $\Xi_0(\cdot)$ is the partition sum of a free gas of A particles (we omit the explicit dependence of Ξ on z_A and z_B unless it is necessary). The nice feature of Eq. (1) is that each contribution to the sum is factorized and each factor is related to a different region of the volume Λ.

Noting now that the probability of finding a given set of chains $\gamma_1, \gamma_2,\ldots, \gamma_m$ in a configuration is

$$\rho_\Lambda(\gamma_1,\ldots,\gamma_m) = \Xi(\Lambda)^{-1} \sum_{\{\gamma_1,\ldots,\gamma_s\}}{}' \prod_1^s{}_i \frac{\tilde{\Xi}(\Theta(\gamma_i))}{\Xi_0(\Theta(\gamma_i))}\,\Xi_0(\Lambda) \tag{2}$$

where $\sum'$ extends over all the collections of compatible chains containing $\gamma_1, \gamma_2,\ldots, \gamma_m$, it can be shown that[10] when $z_A = z_B = z$ is large enough

$$\rho_\Lambda(\gamma_1,\ldots,\gamma_m) \leqslant \exp\left(-\alpha \sum_1^m{}_i\, |\gamma_i|\right) \tag{3}$$

where $|\gamma_i|$ is the total length in units d of the contours belonging to γ_i, and $\alpha = zR^2/72$. That is, the higher the activity, the lower the probability of a given chain; or, better, the small chains are the most relevant objects in the high-activity region. If we recall the class of $A\cdot B$ particles associated with a chain or a given set of chains, the picture of our system in the high-activity region will look like a large sea of A particles with small and rare, uniformly distributed "islands" of B particles.

The picture not only is in agreement, as it should be, with the existence of a phase transition and the breaking of symmetry due to the boundary condition, but it actually gives a detailed account of the microscopic structure of a pure A-rich phase, singling out the most relevant classes of configurations.

To conclude this section, we want to stress that the analysis of these systems in terms of contours goes far beyond this point. The probabilities defined by Eq. (2) satisfy a set of integral equations,[9,10] à la Kirkwood–Saltzburg,[13] and when the activity is sufficiently high, it is possible, by standard techniques,[9,13] to get for these objects analyticity and cluster properties and to check that the system under these conditions is restricted to a single phase.

All the previous arguments can obviously be inverted ($A \leftrightarrow B$) when on the boundaries of the volume Λ we have B particles instead of A particles and the same formalism will describe the B-rich phase.

3.

We start recalling that the very simple and appealing picture given in the previous section arises from Eq. (3) only when $z_A = z_B = z$ is very high and far beyond the critical value. With lower z the picture gets more complicated; for instance, longer chains are not negligible any more: The approach of the critical point is heralded by larger and larger droplets of the opposite phase and influence the convergence properties of the coupled set of integral equations.

A similar and even more dramatic phenomenon should be expected far away from the critical point, when, given, for instance, A-boundary conditions, $z_B > z_A \gg z_{\text{crit}}$. In fact, increasing z_B, we break the symmetry between A and B particles all over the volume Λ, giving rise to a volume effect, opposite to the boundary condition, that naturally leads in the infinite-volume limit to a B-rich pure phase.

In this case Eq. (3) is modified and we get (cf. Appendix A)

$$\rho(\gamma) \leqslant \exp(-\alpha|\gamma| + hz_A 123|\tilde{\Theta}(\gamma)|) \tag{4}$$

where $h = \ln(z_B/z_A)$ and $|\tilde{\Theta}(\gamma)|$ denotes the number of squares in $\tilde{\Theta}(\gamma)$.

The positive volume term in the exponent enhances the weight of large-area droplets and we actually get as an upper bound for the probability of a chain of area c^2 the well-known formula discussed by Fisher[3] in the droplet model. With this in mind it is easy to convince ourselves that to keep the system in a pure A-rich phase when $z_B > z_A$ it is at least necessary to eliminate all the configurations that give rise to chains that are "too large."

We think worth mentioning that the "droplets" we are dealing with (the chains) come out naturally from our geometrical description and any discrimination against configurations associated with droplets of a given size is a well-defined procedure not involving a priori or a posteriori modification of the exact model we started with.

Calling $\{\gamma\}_\eta$ the collection of outer contours associated with the A–B particle configuration η, we define

$$R_\Lambda = \{\eta: \quad |\Theta(\gamma)| \leqslant c^2, \quad \forall \gamma \in \{\gamma\}_\eta\} \tag{5}$$

and eventually define a state by the following probability density:

$$P_\Lambda(\eta) = \begin{cases} K z_A^{N_A(\eta)} z_B^{N_B(\eta)}, & \eta \in R_\Lambda \\ 0, & \eta \notin R_\Lambda \end{cases} \tag{6}$$

where K is a normalization constant.

At this stage c^2 is completely arbitrary, but we expect the metastability requirement listed in the introduction to pin down some sort of "critical size" of the droplets.

The first condition amounts to requiring that our state is a pure A-rich phase.

It is possible to show[10] that the investigation of the static properties of the state described by Eq. (3) goes exactly along the same lines as that of the equilibrium state provided the upper bound given by Eq. (B.1) of Appendix B is used. In other words, our state exhibits the same microscopic picture given in Section 2 typical of a pure A-rich phase provided that $1 - 123hc > 0$ [$h = \ln(z_B/z_A)$] and z_A is sufficiently high (cf. Appendix B). Therefore, given the value of z_A and z_B, we get the following upper bound for c:

$$c < 1/123h = 1/[123 \ln(z_B/z_A)] \tag{7}$$

4.

Following Penrose and Lebowitz,[6] we call $P(t)$ the conditional probability that the system, being in R at $t = 0$, has escaped by the time t. A simple argument based on the Liouville theorem shows that $dP(t)/dt$ has its maximal value at $t = 0$,[6] so it is natural to define the escape rate as

$$\lambda = \left.\frac{dP(t)}{dt}\right|_{t=0^+} = \lim_{\delta t \to 0^+} \sup \frac{P(\delta t)}{\delta t} \tag{8}$$

In order to evaluate an upper bound to λ, we need to estimate the probability for the system to leave R during the time interval $[0, \delta t]$.

Let us introduce some more definitions. Given a chain γ, we define its "interior boundary" to be the boundary of the region consisting of all the small squares that are inside γ but not touching it (i.e., the small squares in $\Theta(\gamma)$ that may contain B particles). We call the "critical boundary" of an $A \cdot B$ configuration $\eta \in R$ the (possibly empty) set of all d-segments belonging to the union of the "interior boundaries" of the chains associated with η such that if a B particle crosses one of these segments, the resulting configuration does not belong to R any more. The simplest example is given by a chain composed of a unique square contour of side c.

In this case the "interior boundary" of γ contains as subsets the "critical boundaries" of all the configurations with outer contour γ.

Consider the event E_b defined in this way: a B particle is approaching a given d-segment b at a distance less than δt times its component $v_\perp$ of velocity perpendicular to b.

Call F_b the following event: at time zero the configuration of the system has a nonempty critical boundary which contains b. Then

$$P(\delta t) = \sum_{b \in \mathcal{B}} \text{prob}(E_b, F_b) + O(\delta t^2) \tag{9}$$

where prob(E_b, F_b) is the joint probability evaluated in the restricted ensemble of E_b and F_b together. $\mathscr{B}$ is the set of all b's in Λ that can be crossed by a B particle. The number of such b's is bounded from above by $|\Lambda|$. Here $O(\delta t^2)$ is the contribution to $P(\delta t)$ of all the events that involve more than one particle.[6]

If a configuration η satisfies the condition stated in the definition of F_b, then, among the chains associated with η, there must exist a set of chains $(\gamma)_b = \{\gamma_1, \ldots, \gamma_v\}$ near b that, after the B particle has crossed b, join together to form a new chain of area $> c^2$.

Of course one of these chains, say γ_1, contains b in its interior boundary (The example mentioned before corresponds to $v = 1$.)

We can write

$$P(\delta t) = \sum_{b \ni \mathscr{B}} \sum_{\gamma_1, \ldots, \gamma_v} \frac{1}{A} \int_0^\infty \exp\left(\frac{-\beta v^2}{2m}\right) dv \int_{\mathscr{M}} \rho_\Lambda{}^R(\gamma_1, \ldots, \gamma_v, \mathbf{r})\, d\mathbf{r} \tag{10}$$

where the second sum is over all the above-mentioned sets of chains $(\gamma)_b = \gamma_1, \ldots, \gamma_v$ and A is the normalization factor of the Maxwell distribution. $\mathscr{M}$ is the rectangle $b \times v\, \delta t$ and $\rho_\Lambda{}^R(\gamma_1, \ldots, \gamma_v; \mathbf{r})\, d\mathbf{r}$ is the joint probability, in the restricted ensemble, of finding the chains $\gamma_1, \ldots, \gamma_v$ in Λ and a B particle in the volume $d\mathbf{r}$ near $\mathbf{r}$. So we have

$$\lambda = \lim_{\delta t \to 0} \sup \frac{P(\delta t)}{\delta t} = \varphi \sum_{\gamma_1, \ldots, \gamma_v} \int_b d\xi\, \rho_\Lambda{}^R(\gamma_1, \ldots, \gamma_v; \xi) \tag{11}$$

where $\varphi = (2\pi\beta m)^{1/2}$ is a kinetic factor and ξ is a generic point of b.

From Appendix C we see that

$$\rho_\Lambda{}^R(\gamma_1, \ldots, \gamma_v; \xi)$$

$$\leqslant z_B \exp\left[121(z_A + z_B)\, d^2 - \alpha(1 - 123hc)\left(\sum_1^v{}_i |\gamma_i| - 121\right)\right] \tag{12}$$

where $\alpha = z_A d^2/4$. Then we obtain

$$\lambda \leqslant |\Lambda| \varphi\, dz_B \exp[121(z_A + z_B)d^2 + \alpha(1 - 123hc)121]$$

$$\times \sum_{\{\gamma_1, \ldots, \gamma_v\}} \exp\left[-\alpha(1 - 123hc) \sum_1^v{}_i |\gamma_i|\right] \tag{13}$$

Now from the definition of the sets $\gamma_1, \ldots, \gamma_v$ that appear in Eq. (13) we see that

$$\sum_1^v{}_i |\gamma_i| \geqslant 4(c^2 - 2)^{1/2} > 4(c - 1)$$

The number of events characterized by the presence of one of these sets of chains $\gamma_1,\ldots,\gamma_\nu$ with

$$\sum_1^\nu{}_i\,|\gamma_i| = 2l$$

is at most $17\cdot 19\cdot 3^{6l}$. (This can be shown by a slight modification of the argument contained in Ref. 12.)

So we eventually obtain

$$\begin{aligned}\lambda \leqslant\ & |\Lambda|\varphi\, dz_B \exp[(z_A + z_B)121d^2 + \alpha(1 - 123hc)121] \\ & \times 17\cdot 19\cdot(27)^{4c-1}\exp[\alpha(1 - hc123)4] \\ & \times \{\exp[-\alpha(4c - 4hc^2123]\}/\{1 - \exp[-\alpha(1 - 123hc) - 3\ln 3]2\}\end{aligned} \tag{14}$$

Then, when $2[\alpha(1 - 123hc) - 3\ln 3]$ is greater than $\ln 2$ we can write

$$\lambda/|\Lambda| \leqslant G(z_A, z_B)\exp[-4cu(z_A, z_B) + c^2 v(z_A, z_B)] \tag{15}$$

where

$$\begin{aligned} G(z_A, z_B) &= \varphi\, dz_B \exp[121d^2(z_A + z_B) + 125\alpha]17\cdot 19\cdot 2/27 \\ 4u(z_A, z_B) &= (123\cdot 125\cdot h + 4)\alpha - 3\ln 3 \\ v(z_A, z_B) &= 4h\cdot 121\alpha \end{aligned} \tag{16}$$

We recall that $\alpha = z_A d^2/4$ and $h = \ln(z_B/z_A)$.

By minimizing with respect to c, we get

$$\lambda/|\Lambda| \leqslant G(z_A, z_B)\exp(-4u^2/v)$$

This bound, as expected, is an exponentially decreasing function of z_A when h is sufficiently small.

We can then conclude that, at least when the activities of the two species of particles are both sufficiently high but close enough together, the relaxation time can be made very large.

As far as a purely theoretical statement is concerned, this would conclude the story, but if we try to get figures out of Eq. (17), the actual values of the activities come out extremely large and the range of metastability very narrow. Whether this is due to the estimates that we have performed or whether it is an actual feature of our candidate for the metastable state is still an open question.

APPENDIX A

In this appendix we will give estimates for the density of B particles We will find a relation between the average number $\langle n_B\rangle_\Lambda$ of B particles in a volume Λ and the average number $\langle s\rangle_\Lambda$ of $d\times d$ squares occupied by B particles.

These estimates will still hold if we impose additional conditions on the configurations (such as the A-boundary condition or the restriction to R of the set of allowed configurations). We have

$$\langle n_B \rangle_\Lambda = \sum_{\{s\}}' P(\mathbf{s}) \langle n_B \rangle_{\mathbf{s}} \tag{A.1}$$

where $\mathbf{s} = s_1, \ldots, s_m$ is a "configuration" of occupied squares. The primed sum runs over all the allowed sets $\{s\}$. (For instance, if we have to evaluate $\langle n_B \rangle_{\Lambda,A}^R$, namely the average number of B particles in the restricted ensemble with A-boundary conditions, then the sum is over all $\mathbf{s}$ compatible with these boundary conditions).

$P(\mathbf{s})$ is the probability of the set of all allowed $A \cdot B$ configurations that give rise to $\mathbf{s}$, and $\langle n_B \rangle_{\mathbf{s}}$ is the average number of B particles in $\bigcup_{1(i)}^m s_i$ with the condition that every s_i is occupied by at least one B particle and every square not in the set $\mathbf{s}$ contains no B particle. We have

$$\langle n_B \rangle_{\mathbf{s}} = \left[\sum_0^\infty \sum_0^\infty z_A^{n_A} z_B^{n_B} n_B \int dX_{n_A}\, dY_{n_B}\, W_{\mathbf{s}}(X_{n_A}, Y_{n_B}) \right] \times \left[\sum_0^\infty \sum_0^\infty z_A^{n_A} z_B^{n_B} \int dX_{n_A}\, dY_{n_B}\, W_{\mathbf{s}}(X_{n_A}, Y_{n_B}) \right]^{-1} \tag{A.2}$$

where (X_{n_A}, Y_{n_B}) stands for an AB particle configuration

$$x_1, x_2, \ldots, x_{n_A}, y_1, y_2, \ldots, y_{n_B}, \qquad dX_{n_A} = \frac{dx_1 \cdots dx_{n_A}}{n_A!}, \qquad dY_{n_B} = \frac{dy_1 \cdots dy_{n_B}}{n_B!}$$

and

$$W_{\mathbf{s}} = W_{\mathbf{s}}(X, Y) \left[\prod_1^m{}_k I_{s_k}(Y) \right] [1 - I_{\Lambda \setminus \cup_1^m s_i}] \tag{A.3}$$

where $W(X, Y) = 0$ if the hard core exclusion is violated by (X, Y) and $= 1$ otherwise.

$I_\Omega(Y) = I_\Omega(y_1, \ldots, y_{n_B}) = 1$ if at least one of the y_i lies in the volume Ω; $= 0$ otherwise.

Writing $Y \setminus y_{n_B}$ for the B-particle configuration, $y_1, \ldots, y_{n_B - 1}$, the following identity holds:

$$\prod_1^m{}_k I_{s_k}(Y) = \prod_1^m{}_k I_{s_k}(Y \setminus y_{n_B}) + \sum_1^m{}_i \left\{ \prod_{k \neq 1} I_{s_k}(Y \setminus y_{n_B}) I_{s_i}(y_{n_B}) [1 - I(Y \setminus y_{n_B})] \right\} \tag{A.4}$$

We write the numerator in Eq. (A.2) as

$$z_B \sum_0^\infty \sum_0^\infty z_A^{n_A} z_B^{n_B} \int dX_{n_A}\, dY_{n_B}\, W_{\mathbf{s}}(x_1, \ldots, x_{n_A}, y, \ldots, y_{n_B}, y_{n_B + 1}) \tag{A.5}$$

and decompose W_s into the two terms suggested by the identity (A.4), using the inequality

$$W(x_1,\ldots,x_{n_A},y_1,\ldots,y_{n_B},y_{n_B+1}) \leqslant W(x_1,\ldots,x_{n_A};y_1,\ldots,y_{n_B})$$

and noting that the range of any variable y_i is md^2, we have

$$\langle n_B\rangle_s \leqslant md^2 z_B + \left[z_B \sum_0^\infty{}_{n_A} \sum_0^\infty{}_{n_B} z_A^{n_A} z_B^{n_B} \int dX_{n_A}\, dY_{n_B}\, W_s'(X,Y)\right] \times \left[\sum_0^\infty{}_{n_A} \sum_0^\infty{}_{n_B} z_A^{n_A} z_B^{n_B} \int dX_{n_A}\, dY_{n_B}\, W_s(X,Y)\right]^{-1} \tag{A.6}$$

where $W_s'(X,Y)$ [see Eq. (A.4)] is such that

$$W_s'(x_1,\ldots,x_{n_A};y_1,\ldots,y_{n_B+1}) \leqslant \sum_1^m W_{s_i}(x_1,\ldots,x_{n_A};y_1,\ldots,y_{n_B}) I_{s_i}(y_{n_B+1})$$

with $\mathbf{s}_i$ obtained by removing the square i from $\mathbf{s}$. Inequality (A.6) then becomes

$$\langle n_B\rangle_s \leqslant md^2 z_B\left(1 + \max_i \frac{Z_{s_i}}{Z_s}\right) \tag{A.7}$$

where

$$Z_s = \sum_0^\infty{}_{n_A} \sum_0^\infty{}_{n_B} z_A^{n_A} z_B^{n_B} \int dX_{n_A}\, dY_{n_B}\, W_s(X,Y) \tag{A.8}$$

and similarly for Z_{s_i}.

Now we are left to the problem of evaluating such a maximum. Writing q for the $11d \times 11d$ square centered at the small square s_i it is evident that

$$\begin{aligned} Z_s &\geqslant \sum_0^\infty{}_{n_A} \sum_0^\infty{}_{n_B} \frac{z_A^{n_A}}{z_A!} \frac{z_B^{n_B}}{z_B!} \int_{(\Lambda\setminus q)^{n_A}} dx_1\cdots dx_{n_A} \int_{\bigcup_1^m (k s_k)} dy_1\cdots dy_{n_B}\, W_s(X,Y) \\ &= \sum_0^\infty{}_{n_A} \sum_1^\infty{}_{p} \sum_0^\infty{}_{l} \frac{z_A^{n_A}}{n_A!} \frac{z_B^{p}}{p!} \frac{z_B^{l}}{l!} \int_{(\Lambda\setminus q)^{n_A}} dx_1\cdots dx_{n_A} \int_{(s_i)^p} dy_1\cdots dy_p \\ &\quad \times \int_{[\bigcup_{k\neq i} s_k]^l} dy_{p+1}\cdots dy_{p+l}\, W_{s_i}(X, y_{p+1},\ldots,y_{p+l}) \end{aligned} \tag{A.9}$$

Then we obtain

$$Z_s \geqslant [\exp(z_B d^2) - 1] \sum_0^\infty{}_{n_A} \sum_0^\infty{}_{n_B} \frac{z_A^{n_A}}{n_A!} \frac{z_B^{n_B}}{n_B!} \times \int_{(\Lambda\setminus q)^{n_A}} dx_1\cdots dx_{n_A} \int dy_1\cdots dy_{n_B}\, W_s(X,Y) \tag{A.10}$$

Considering now Z_{s_i}, we have

$$Z_{s_i} = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} \sum_{0}^{\infty n_B} \frac{z_A^{\,p}}{p!} \frac{z_A^{\,l}}{l!} \frac{z_B^{n_B}}{n_B!} \times \int_{q^p} dx_1 \cdots dx_p \int_{(\Lambda \setminus q)^l} dx_{p+1} \cdots dx_{p+l} \int_{\Lambda^{b_B}} dy_1 \cdots dy_{n_B} W_{s_i}(X, Y) \tag{A.11}$$

Then, using the inequality

$$W_{s_i}(x_1, \ldots, x_p, x_{p+1}, \ldots, x_{p+l}; Y) \leqslant W_{s_i}(x_{p+1}, \ldots, x_{p+l}; Y)$$

we obtain

$$Z_{s_i} = \exp(z_A 121 d^2) \sum_{0}^{\infty n_A} \sum_{0}^{\infty n_B} \frac{z_A^{n_A}}{n_A!} \frac{z_B^{n_B}}{n_B!} \times \int_{(\Lambda \setminus q)^{n_A}} dx_1 \cdots dx_{n_A} \int_{\Lambda^{n_B}} dy_1 \cdots dy_{n_B} W_{s_i}(X, Y) \tag{A.12}$$

Then by (A.7) we obtain the required relations

$$Z_{s_i}/Z_s \leqslant \exp(121 d^2 z_A)/(\exp d^2 z_B - 1) \tag{A.13}$$

and

$$\langle n_B \rangle_s \leqslant z_B d^2 m[1 + \exp(121 d^2 z_A)/(\exp d^2 z_B - 1)] \tag{A.14}$$

In order to get a good estimate from Eq. (A.14), we use the FKG inequalities.[14] Noting that the previously introduced functions $I_\Omega(Y)$ are nondecreasing (in the sense of Lebowitz and Monroe[14]), we find for $z_B < 122 z_A$ that

$$\begin{aligned} \langle n_B \rangle_{s, z_A, z_B} = \left\langle n_B \prod_1^m{}_i I_{s_i} \right\rangle_{z_A, z_B} &\leqslant \left\langle n_B \prod_1^m{}_i I_{s_i} \right\rangle_{z_A, 122 z_A} \\ &\leqslant 122 m z_A d^2 \{1 + \exp(121 z_A d^2)/[\exp(122 z_A d^2 - 1) - 1]\} \\ &\leqslant 123 z_A m d^2 \end{aligned} \tag{A.15}$$

The last inequality holds when

$$\exp(121 z_A d^2)/[\exp(122 z_A d^2) - 1] \leqslant 1/122$$

which is satisfied for sufficiently high z_A.

Finally, Eq. (A.1) implies

$$\langle n_B \rangle_{\Lambda, z_A, z_B} \leqslant 123 z_A d^2 \langle s_B \rangle_{\Lambda, z_A, z_B}$$

APPENDIX B

In this appendix we give estimates for the chain correlation functions. Suppose $z_B > z_A$ and A-boundary conditions. Write $\mathscr{M}(\tilde{\Theta}(\gamma))$ for the set of

all configurations of $A \cdot B$ particles internal to $\Theta(\gamma)$ and having the chain γ as their outer contour. From any configuration $\eta \in \mathcal{M}(\tilde{\Theta}(\gamma))$ we obtain a class of configurations as follows.

1. All A particles interior[10] to some outer contour belonging to γ are changed into B particles and vice versa.

2. Let $G(\gamma)$ be the band consisting of all the small squares that have one side or corner touching the outer contours belonging to γ: A particles are placed in an arbitrary manner in $G(\gamma)$. We write $\mathcal{M}^*(\tilde{\Theta}(\gamma))$ for the collection of all configurations obtained by applying this transformation to configurations in $\mathcal{M}(\tilde{\Theta}(\gamma))$. The following relation holds:

$$\frac{\Xi(\tilde{\Theta}(\gamma), z_A, z_B)}{\Xi^*(\tilde{\Theta}(\gamma), z_A, z_B)} = \frac{\Xi(\tilde{\Theta}, z_A, z_A)}{\Xi^*(\tilde{\Theta}, z_A, z_A)} \exp\left[\int_{z_A}^{z_B} \frac{dz'}{z'} (\langle n_B \rangle_{\tilde{\Theta}, z_A, z'} - \langle n_B \rangle^*_{\tilde{\Theta}_{z_A,z'}})\right] \tag{B.1}$$

where $\Xi(\tilde{\Theta}(\gamma), z_A, z_B)$ [$\Xi^*(\tilde{\Theta}(\gamma), z_A, z_B)$ is the statistical sum over $\mathcal{M}(\tilde{\Theta}(\gamma))$ [$\mathcal{M}^*(\tilde{\Theta}(\gamma))$] and $\langle n_B \rangle_{\tilde{\Theta}, z_A, z'}$ [$\langle n_B \rangle^*_{\tilde{\Theta}_{z_A,z'}}$] is the average number of B particles in $\tilde{\Theta}(\gamma)$ in the ensemble defined by $\mathcal{M}(\tilde{\Theta}(\gamma))$ [$\mathcal{M}^*(\tilde{\Theta}(\gamma))$] with activities z_A and z'.

From Appendix A we see that

$$\langle n_B \rangle_{\tilde{\Theta}(\gamma), z_A, z'} \leqslant 123 d^2 z_A |\tilde{\Theta}(\gamma)| \tag{B.2}$$

where $|\tilde{\Theta}(\gamma)|$ is the number of small squares in $\tilde{\Theta}(\gamma)$.

Now calling $\rho_\Lambda(\gamma)$ the probability of finding the chain γ present, from Ref. 12 we have

$$\rho_\Lambda(\gamma) \leqslant \Xi(\tilde{\Theta}(\gamma))/\Xi^*(\tilde{\Theta}(\gamma)) \tag{B.3}$$

We eventually get

$$\rho_\Lambda(\gamma) \leqslant \exp[-\alpha|\gamma| + 123 h z_A d^2 |\tilde{\Theta}(\gamma)|] \tag{B.4}$$

where $|\gamma|$ is the total length in units of d of the chain γ and $h = \ln(z_B \backslash z_A)$, $\alpha = z_A d^2/h$.

Now let $\rho_\Lambda^R(\gamma_1, \ldots, \gamma_m)$ be the chain correlation function [see Eq. (3) of section 1] in the restricted ensemble defined by (see Section 3). By a simple extension of the arguments used before,[10] we have

$$\rho_\Lambda^R(\gamma_1, \ldots, \gamma_m) \leqslant \exp\left(-\alpha' \sum_1^m |\gamma_i|\right) \tag{B.5}$$

where $\alpha' = \alpha(1 - 123hc)$.

APPENDIX C

In this appendix we evaluate the quantity $\rho_\Lambda^R(\gamma_1, \ldots, \gamma_\nu; \xi)$, namely the joint probability density in the restricted ensemble of finding the chains $\gamma_1, \ldots, \gamma_\nu$ and a B particle in ξ, where ξ is the generic point of a d-segment

belonging to the interior boundary of the chain γ_1. (See Section 4.) Consider the small square $S_b \subset \Theta(\gamma_1)$ from the interior adjacent to the segment b containing ξ.

Consider a rectangle $\epsilon \ni \xi$ strictly contained in s_b. Then

$$\rho_\Lambda{}^R(\gamma_1,\dots,\gamma_\nu;\xi) = \lim_{\epsilon \searrow \xi} \frac{1}{|\epsilon|} \rho_\Lambda{}^R(\gamma_1,\dots,\gamma_\nu;\epsilon) \tag{C.1}$$

where $\rho_\Lambda{}^R(\gamma_1,\dots,\gamma_\nu;\epsilon)$ is the joint probability of having $\gamma_1,\dots,\gamma_\nu$ and a B particle in ϵ. We have

$$\rho_\Lambda{}^R(\gamma_1,\dots,\gamma_\nu;\epsilon) = \left[\sum_{\gamma_1\gamma_\nu\dots,\gamma_s} \tilde{\Xi}'(\tilde{\Theta}(\gamma_1)) \prod_1^s{}_i \tilde{\Xi}(\tilde{\Theta}(\gamma_i)) \Xi_0\left(\Lambda \backslash \bigcup_1^s{}_i \tilde{\Theta}(\gamma_i)/\Xi^R(\Lambda)\right)\right] \tag{C.2}$$

where the sum is over all the sets of compatible chains of area $\leqslant c^2$ containing $\gamma_1,\dots,\gamma_\nu$; $\tilde{\Xi}(\tilde{\Theta}(\gamma_1))$ is the partition function over those configurations belonging to $\mathcal{M}(\tilde{\Theta}(\gamma))$ in which a B particle is contained in ϵ; $\Xi_0(\Omega)$ is the partition function of a free gas of A particles in the volume Ω.

Call q the $11d \times 11d$ square centered at the small square $S_b \supset \epsilon$. We have

$$\tilde{\Xi}'(\tilde{\Theta}(\gamma_1)) \leqslant \tilde{\Xi}(\tilde{\Theta}(\gamma_1)\backslash q)\Xi'(q) \tag{C.3}$$

where $\Xi'(q)$ is the partition function over all $A \cdot B$ configurations in q in which at least one B particle is contained in ϵ. $\tilde{\Xi}(\tilde{\Theta}(\gamma_1)\backslash q)$ is the partition function over all $A \cdot B$ configurations in $\tilde{\Theta}(\gamma_1)\backslash(q \cap \tilde{\Theta}(\gamma_1))$ compatible with the presence of γ_1. We have

$$\Xi'(q) \leqslant z_B|\epsilon| \exp[121d^2(z_A + z_B)] \tag{C.4}$$

Moreover, using the transformation $\mathcal{M}(\tilde{\Theta}(\gamma_i)) \to \mathcal{M}^*(\tilde{\Theta}(\gamma_i))$ defined in Appendix B, we obtain

$$\Xi_R(\Lambda) \geqslant \Xi_R\left(\Lambda \backslash \bigcup_1^\nu{}_i \tilde{\Theta}(\gamma_i)\right) \cdot \tilde{\Xi}^*(\tilde{\Theta}(\gamma_1)\backslash q) \prod_2^\nu{}_i \tilde{\Xi}^*(\tilde{\Theta}(\gamma_i))$$

Now taking into account that the total length of that part of the boundary of $\Theta(\gamma_1)$ that is contained in $\tilde{\Theta}(\gamma_1)\backslash q$ is at least $|\gamma_1| - |q|/d^2$, by Eq. (B.5) of Appendix B we have

$$\rho_\Lambda{}^R(\gamma_1,\dots,\gamma_\nu;\epsilon) \leqslant |\epsilon| z_B \exp\left[121d^2(z_A + z_B) + \alpha' 121 - \alpha' \sum_1^\nu{}_i |\gamma_i|\right]$$

where $\alpha' = \alpha(1 - 123hc)$.

APPENDIX D

In this appendix we prove that the relative weight P_R of the configurations in R is negligible at equilibrium. We may write

$$P_R = \frac{\Xi_R{}^A(\Lambda, z_A, z_B)}{\Xi^A(\Lambda, z_A, z_B)} = \frac{\Xi_R{}^A(\Lambda, z_A, z_B)}{\Xi_R{}^A(\Lambda, z_A, z_A)} \frac{\Xi_R{}^A(\Lambda, z_A, z_A)}{\Xi^B(\Lambda, z_A, z_B)} \frac{\Xi^B(\Lambda, z_A, z_B)}{\Xi^A(\Lambda, z_A, z_B)}$$

where the superscripts A and B label the boundary conditions in Λ and the subscript R means that the partition function is evaluated in the restricted ensemble. It is easily seen that

$$\Xi^B(\Lambda, z_A, z_B)/\Xi^A(\Lambda, z_A, z_B) \leqslant \exp[r|\partial\Lambda|z_B]$$

where $|\partial\Lambda|$ is the perimeter of Λ. So, noting that

$$\Xi_R{}^A(\Lambda, z_A, z_B) = \Xi_R{}^B(\Lambda, z_A, z_A) \leqslant \Xi^B(\Lambda, z_A, z_A)$$

we have

$$P_R \leqslant \exp[r|\partial\Lambda|z_B] \exp\left[\int_{z_A}^{z_B} \frac{dz'}{z'} (\langle n_B\rangle^R_{A,\Lambda,z_A,z'} - \langle n_B\rangle_{B,\Lambda,z_A,z'})\right]$$

with an obvious meaning to the symbols.

Now let $\langle s_B\rangle_{B,\Lambda,z_A,z_B}$ be the expectation value of the number of small squares occupied by B particles in Λ with B-boundary conditions; then, from the FKG inequalities[14] we have

$$\langle n_B\rangle_{B,\Lambda,z_A,z'} \geqslant \langle n_B\rangle_{B,\Lambda,z_A,z_A} \geqslant \langle s_B\rangle_{B,\Lambda,z_A,z_A}$$

Following Ruelle,[12] we see that for sufficiently large z_A

$$\langle s_B\rangle_{B,\Lambda,z_A,z_B}/|\Lambda| \geqslant 1/484 - \varphi(\alpha)$$

where

$$\varphi(x) = \frac{\{3 \exp[3(4 \ln 3 - x)]\}^2}{[1 - \exp(4 \ln 3 - x)]^4}, \qquad \alpha = \frac{z_A d^2}{4}$$

for $\alpha > 4 \ln 3$.

Moreover, from Appendix A we see that

$$\langle n_B\rangle^R_{A,\Lambda,z_A,z'} \leqslant 123 z_A d^2 \langle s_B\rangle^R_{A,\Lambda,z_A,z'} \leqslant 123 z_A d^2 \langle s_B\rangle^R_{A,\Lambda,z_A,z_B}$$

where the last inequality follows from the FKG inequalities (see Appendix A). We have for $\alpha' = \alpha(1 - 123hc)$

$$\langle s_B\rangle_{A,\Lambda,z_A,z_B} \leqslant \varphi(\alpha')$$

We eventually obtain

$$P_R \leqslant \exp[r|\partial\Lambda|z_B + |\Lambda|[\ln(z_B/z_A)](123 d^2 z_A \varphi(\alpha') + \varphi(\alpha) - 1/484)]$$

So that when z is sufficiently large and $\alpha' \geqslant 4 \ln 3$ we have

$$\lim_{\Lambda \to \infty} P_R = 0$$

ACKNOWLEDGMENT

We are greatly indebted to D. Capocaccia for many helpful discussions and criticisms.

REFERENCES

1. J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955), Chapter VII.
2. O. E. Lanford and D. Ruelle, *Comm. Math. Phys.* **13**:194 (1969).
3. M. E. Fisher, *Physics* **3**:255 (1967).
4. J. Langer, *Ann. Phys.* **41**:108 (1967).
5. K. Binder, *Ann. Phys.* **98**:390 (1976).
6. O. Penrose and J. L. Lebowitz, *J. Stat. Phys.* **3**:211 (1971).
7. J. Sewell, *Lett. Nuovo Cim.* **10** (10):430 (1974).
8. D. Capocaccia, M. Cassandro, and E. Olivieri, *Comm. Math. Phys.* **39**:185 (1974).
9. K. A. Minlos and Ya. G. Sinai, *Math. Sb.* **73**:375 (1967) [English tranl., *Math. USSR—Sbornik* **2**:335]; *Tr. Mosk. Math. Obs.* **17**:213 (1967) [English transl., *Trans. Moscow Math. Soc.* **17**, 237]; *Tr. Mosk. Math. Obs.* **19**:113 (1968) [English transl., *Trans. Moscow Math. Soc.* **19**, 121].
10. M. Cassandro and A. Da Fano, *Comm. Math. Phys.* **36**:277 (1974).
11. B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**:1670 (1970).
12. D. Ruelle, *Phys. Rev. Lett.* **27**:1040 (1971).
13. D. Ruelle, *Statistical Mechanics* (Benjamin, New York, 1969).
14. J. L. Lebowitz and J. L. Monroe, *Comm. Math. Phys.* **28**:301 (1972).