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Cluster kinetics in the lattice gas model: the Becker–Doring type of equations

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Abstract. We discuss the Becker–Doring type of kinetic equations describing the time evolution of the cluster distribution in the lattice gas model, and present the corresponding matrix solution. It is simple to perform analytical or numerical studies and to analyse experimental data using these equations and the results compare well with Monte Carlo results. We also discuss the concept of a time-dependent renormalised fugacity.

1. Introduction

The lattice gas model (see, for instance, Thompson 1972) is defined through the Hamiltonian

$$H = -4J\Sigma' n_i n_j \qquad J > 0 \tag{1.1}$$

where the sum runs over all pairs (i, j) of nearest-neighbour sites in a simple cubic lattice $(i = 1, 2, \ldots, N)$, for instance, and $n_i = 1$ or 0, corresponding to the presence of a particle or hole at site i. The interaction between particles at nearest-neighbour sites is known to favour phase segregation into a liquid and a vapour phase below a given temperature, $T_c k_B/J = 4.5115\ldots$, within some range of density (ρ), where

$$\rho = N^{-1} \sum_i n_i. \tag{1.2}$$

The evolution of a given configuration $\boldsymbol{n} \equiv \{n_i; i = 1, \ldots, N\}$ at temperature T, or the relaxation towards equilibrium at temperature T of a given initial configuration at $T_0 \neq T$, proceeds in the model by a Markov process whose basic step is to move one particle to a neighbouring hole according to a prescribed transition probability (Kawasaki 1966, 1972). More specifically, one assumes that the probability $P(\boldsymbol{n}, t)$ is governed by the following Master equation:

$$\frac{\partial}{\partial t} P(\boldsymbol{n}, t) = \sum_{\boldsymbol{n}'} \left(W(\boldsymbol{n}|\boldsymbol{n}')P(\boldsymbol{n}', t) - W(\boldsymbol{n}'|\boldsymbol{n})P(\boldsymbol{n}, t) \right) \tag{1.3}$$

where $W(\boldsymbol{n}|\boldsymbol{n}')$ is the transition probability per unit time from state $\boldsymbol{n}'$ to state $\boldsymbol{n}$. States $\boldsymbol{n}$ and $\boldsymbol{n}'$ only differ by the interchange of some n_i with a neighbouring n_j, so ρ remains constant during the evolution, and

$$W(\boldsymbol{n}'|\boldsymbol{n}) \equiv W_{ij} = \exp(-\Delta H_{ij}/2k_{\mathrm{B}}T)\, F(\Delta H_{ij}). \tag{1.4}$$

Here ΔH_{ij} is the increase of energy H brought about by the proposed interchange, and F is an even function, e.g.

$$F(\Delta H_{ij}) = [2\cosh(\Delta H_{ij}/2k_{\mathrm{B}}T)]^{-1}.$$

The choice (1.4) satisfies detailed balancing.

Any given configuration of the system can be described in terms of *clusters* defined, for instance, as maximal sets of particles connected by nearest-neighbour bonds; the *size* m of a given cluster may then be defined as the number of particles that belong to it. For equilibrium states, the probabilities for the occurrence of these clusters, C_m^{eq}, i.e. the number of m-particle clusters per lattice site as a function of m, are governed by the corresponding Gibbs distribution (see e.g., Marro and Toral 1983, Toral and Marro 1986). Such a simple picture of the system as a collection of non-overlapping clusters is also convenient in the theory of nucleation for describing the decay of unstable and metastable states (see, for instance, Gunton and Droz 1983). In that case one is interested in $C_m(t)$ which is expected to be related to the droplet or grain distribution at time t observed directly by microscopy or indirectly by other means, e.g. after a sudden quench of the system at $t = 0$ from a very high temperature T_0 to the final temperature T.

Thus the study of kinetic equations for $C_m(t)$ is of a great interest, particularly when the equations are amenable to simple solution. We analyse in this paper (see also Binder *et al* 1975) the assumptions needed to proceed from (1.3) for the configurational probability distribution to an equation for $C_m(t)$ having essentially the structure of the Becker–Doring equations (Becker and Doring 1935). We find in this way a matrix formulation whose solution is rather simple and compares well with some Monte Carlo data on the temporal evolution of the lattice gas model. In particular, as compared with previous work (Penrose *et al* 1978, 1984), the present equations have a simpler structure which is suitable for processing by standard, fast software in many computers; this reduces the computer time needed by more than one order of magnitude and, as a consequence, the formulation is very suitable for analysing experimental data and combining with other analyses of phase separation (see, for instance, Marro and Toral 1986). Moreover, we thus find some interesting formal properties for $C_m(t)$, including a simple dynamical scaling law. As an addendum, we also discuss the concept of a time-dependent renormalised fugacity which can be used to describe $C_m(t)$ very accurately for small values of m.

2. Kinetic equations

The discussion in § 1 suggests that the temporal evolution of the lattice gas model may be investigated, for instance by evaluating the function

$$C_m(t) = \sum_{\boldsymbol{n}} A_m(\boldsymbol{n}) P(\boldsymbol{n}, t) \tag{2.1}$$

where $P(\boldsymbol{n}, t)$ is given by (1.3) and (1.4), and one may write

$$A_m(\boldsymbol{n}) = \sum_K \left(\prod_{i \in K} n_i \prod_{j \in B(K)} (1 - n_j) \right). \tag{2.2}$$

The sum here is over all translationally inequivalent m-particle clusters K, and $B(K)$ represents the border of K (the set of sites that are nearest neighbours of any site of K and do not belong to K). The function $C_m(t)$ can thus be worked out in some simple cases, e.g. one-dimensional systems and/or systems with small values of m. Nevertheless, the evaluation of (2.1) in more general situations is rather difficult because it involves the enumeration of many different clusters and the explicit computation of W in (1.4) as a function of $\boldsymbol{n}$ and $\boldsymbol{n}'$.

Alternatively, one may notice that m-particle clusters corresponding to different terms in the sum contained in (2.2) can be characterised by a set of coordinates, r, representing 'internal' degrees of freedom (surface area etc) such that $C_m(t)$ is the average over r of $C^r_m(t)$, the latter representing a given cluster K, i.e. $C_m(t) = \langle C^r_m(t)\rangle_r$. Now, assuming that clusters can only evolve due to evaporation, condensation, coagulation and splitting processes, one may write, using (1.3) (see also Binder *et al* 1975), that

$$\frac{\partial C_m}{\partial t} = \sum_{m'=1}^{\infty} (C_{m+m'} S_{m+m',m} - C_m T_{m,m'}) + \sum_{m'=1}^{m-1} (C_{m'} T_{m',m-m'} - C_m S_{m,m'}) \tag{2.3}$$

where $T_{m,m'}$ and $S_{m,m'}$ characterise respectively the corresponding growth and shrinking processes, as explained below. This equation contains no processes involving more than two clusters, which should be relatively unimportant in practice, and neglects the actual diffusion of clusters caused by the motion of their centres of mass, which may be included *a posteriori* by an appropriate rescaling (Penrose *et al* 1978). Equation (2.3) also contains a more fundamental hypothesis. Namely, it is assumed here that

$$\langle C^r_m S^{r,r'}_{m,m'} \rangle \simeq \langle C^r_m \rangle_r \langle S^{\bar{r}(m),r'}_{m,m'} \rangle_{r'} \equiv C_m S_{m,m'} \tag{2.4}$$

where $S^{r,r'}_{m,m'}$ is the probability that a cluster splits into clusters (m, r) and (m', r'), and

$$\langle C^r_m C^{r'}_{m'} T^{r,r'}_{m,m'} \rangle_{r,r'} \simeq \langle C^r_m \rangle_r \langle C^{r'}_{m'} T^{\bar{r}(m),m'}_{m,m'} \rangle_{r'} \equiv C_m T_{m,m'} \tag{2.5}$$

where $T^{r,r'}_{m,m'}$ represents the probability that the clusters (m, r) and (m', r') coalesce to form a single cluster. The assumptions (2.4) and (2.5) require essentially that each distribution $C^r_m(t)$ has a very pronounced peak for fixed m around the mean $\bar{r}(m)$, a condition that probably holds for large enough values of m (Binder *et al* 1975). Note also that our assumptions in (2.4) and (2.5) imply a lack of symmetry concerning the coefficients $T_{m,m'}$ and $S_{m,m'}$, which describe inverse processes in some sense; we shall comment below on the consequences of this.

To proceed further we note that it is customary to assume (Becker and Doring 1935, Binder *et al* 1975, Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983) that the most relevant processes occurring during the phase segregation of interest here are single-particle processes—that is, that the evaporation and condensation of clusters occur via the exchange of monomers (e.g. $m \to m+1$ and $m \to m-1$), and that coagulation $(m, m' \to m + m')$ and splitting $(m + m' \to m, m')$ processes are negligible in practice. This assumption, which seems to be well confirmed during the Monte Carlo simulation of the temporal evolution of the lattice gas model in § 1, other than for some very early times during the evolution (Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983), can be stated explicitly by requiring that

$$T_{m,m'} = \alpha_m \delta_{m',1} \qquad S_{m,m'} = \beta_m \delta_{m',1} \tag{2.6}$$

where $\delta_{x,y} = 0, 1$ when $x \neq y$ and $x = y$ respectively. The substitution of conditions (2.6) into (2.3) then leads to

$$\partial C_m/\partial t = J_{m-1} - J_m \tag{2.7a}$$

where

$$J_m = \alpha_m C_m - \beta_{m+1} C_{m+1} \tag{2.7b}$$

represents the net rate (per site) of conversion of m-particle to $(m+1)$-particle clusters. Equation (2.7) has the same structure as the Becker–Doring equations (Becker and Doring 1935, Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983), i.e. $C_m(t)$ changes with time due to processes $m-1 \rightarrow m$, $m \rightarrow m-1$, $m \rightarrow m+1$, $m+1 \rightarrow m$ which correspond respectively to the four terms on the RHS of (2.7*a*). The evolution with time of $C_1(t)$, which is observed to reach a quasi-stationary value in practice after some initial period, is not described by (2.7), but follows the separate equation

$$\frac{\partial C_1}{\partial t} = -J_1 - \sum_{m\geqslant 1} J_m \tag{2.7c}$$

which takes into consideration the processes $2 \rightarrow 1+1$, $1+1 \rightarrow 2$, $m \rightarrow m-1$ and $m \rightarrow m+1$. On the other hand, the finite size of the model we are considering here imposes an upper bound for m, say M, and

$$\partial C_M/\partial t = J_{M-1}. \tag{2.7d}$$

It is then a simple exercise to show that the system density, given by (1.2) or

$$\rho = \sum_{m=1}^{M} mC_m(t) \tag{2.8}$$

remains constant during the evolution described by (2.7).

3. The coefficients α_m and β_m

The utility of (2.7) rests in principle upon the knowledge of the kinetic coefficients α_m and β_m describing respectively the rates at which m-particle clusters absorb and emit monomers. These coefficients may depend on the system density ρ, while they are assumed to be independent of time. The assumption that α_m is independent of time, which is made here for simplicity, is in accordance with the original treatment (Becker and Doring 1935, Frenkel 1955, Zettlemoyer 1969, Abraham 1974) while it is slightly different to what was assumed in some previous work (Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983) where $\alpha_m = a_m C_1(t)$. However, this should only produce small differences given that the system evolution is governed in practice by the behaviour of large clusters. That is, an independent study focusing on the evolution of the correlation functions (Marro and Toral 1986) clearly reveals that $C_m(t)$, $m > 1$, accounts in practice for the whole time evolution of the system, the influence becoming larger as m is increased and as the time progresses. Actually, $C_1(t)$ becomes quasi-stationary after some initial time (Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983). What really seems to matter here are the assumptions about the dependence on m of the kinetic coefficients and the particular treatment one follows to reach an explicit solution of (2.7).

The coefficients α_m and β_m can be related to each other by considering (2.7) at equilibrium—that is, by requiring $\partial C_m/\partial t = 0$ in (2.7*a*), (2.7*c*) and (2.7*d*) one is led to the so-called detailed-balancing condition, $J_m = 0$, for any value of m, which follows here from the consideration of a finite system with constant ρ. The fact that the system is finite also implies that the Becker–Doring equations (2.7*a*), have no stationary solution such as the one that is familiar in classical nucleation theory (Frenkel 1955, Zettlemoyer 1969, Abraham 1974); e.g. C_1 is kept constant there by an artificial mechanism, which moves particles from large to small clusters.

The detailed-balancing condition and (2.7*b*) imply in the present case that

$$\beta_{m+1} = \alpha_m\, C_m^{\mathrm{eq}}/C_{m+1}^{\mathrm{eq}} \qquad (3.1)$$

where C_m^{eq} is the cluster distribution corresponding to the (true) equilibrium state. Thus, one only needs an independent estimation of α_m and C_m^{eq}. The distribution C_m^{eq} is dependent on which model is used; it was studied in the case of the lattice gas model by, for instance, Penrose *et al* (1978) and Marro and Toral (1983). These studies allow us to relate β_{m+1} to α_m by using (3.1). The coefficient α_m, on the other hand, may be affected by the model dynamics; it was first evaluated for the 3D simple cubic Ising model in the low-density limit by Penrose and Buhagiar (1983) (we have used in this work the values given by Buhagiar (1980); see also Penrose *et al* (1984)). Moreover, it also follows from § 2 that

$$\alpha_m = \sum_{j\geq m+1} \frac{\partial C_j}{\partial t}\left[C_m - C_{m+1}\left(\frac{C_m^{\mathrm{eq}}}{C_{m+1}^{\mathrm{eq}}}\right)\right]^{-1}. \qquad (3.2)$$

The available data for $C_m(t)$ are not accurate enough to provide significant time derivatives; it would be well worth generating more Monte Carlo data to check different hypotheses for α_m via the use of (3.2).

4. Solution of the Becker–Doring equations

We shall present here a matrix treatment of the kinetic equations in § 2 that produces simple expressions for $C_m(t)$ in accordance with computer simulation results. The numerical aspects in this treatment are simpler—and thus less computational effort is required than in previous work (see, e.g., Penrose *et al* 1984)—and they are well adapted to the most efficient software in many computers.

Let us define the column vectors

$$\boldsymbol{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_M \end{bmatrix} \qquad \boldsymbol{m} = \begin{bmatrix} 1 \\ 2 \\ \vdots \\ M \end{bmatrix}. \qquad (4.1)$$

It follows that (2.7) may be written as

$$\partial \boldsymbol{C}/\partial t = \mathbf{A}\boldsymbol{C} \qquad (4.2)$$

where $\mathbf{A}$ is a $M \times M$ matrix such that the first row has elements $A_{11} = -2\alpha_1$, $A_{12} = 2\beta_2 - \alpha_2$, $A_{1M} = \beta_M$ and $A_{1j} = \beta_j - \alpha_j$ $(j = 3, \ldots, M-1)$, the principal diagonal is given by $A_{MM} = -\beta_M$ and $A_{ii} = -\alpha_i - -\beta_i$ $(i = 2, \ldots, M-1)$, the nearest diagonal to the left of the principal one is given by $A_{i+1,i} = \alpha_i$ $(i = 1, \ldots, M-1)$, the nearest diagonal to the right of the principal one is given by $A_{i,i+1} = \beta_{i+1}$ $(i = 2, \ldots, M-1)$, and the rest of the elements are zeros; that is, it has the structure

$$\mathbf{A} =$$

where the oblique and horizontal lines represent the only non-zero elements. One also has from (2.8)

$$\rho = \boldsymbol{m} \cdot \boldsymbol{C}. \tag{4.3}$$

It then follows from (4.3) and (4.2) that

$$\partial\rho/\partial t = \boldsymbol{m} \cdot (\mathbf{A}\boldsymbol{C}) = (\boldsymbol{m}^+\mathbf{A})^+ \cdot \boldsymbol{C} \tag{4.4}$$

where the plus sign denotes the transpose: $m^+ = (1, 2, \ldots, M)$; the fact that $\boldsymbol{m}^+\mathbf{A} = 0$ then implies $\rho =$ constant, as required by the model in § 1.

The lack of symmetry shown by the matrix **A** prevents one from using the standard theory for Hermitian operators, yet one may extract some important information from the corresponding eigenvalue problem. Let $P_M(\ )$ denote the characteristic polynomial, i.e.

$$P_M(\lambda) = \det(\mathbf{A} - \lambda\mathbb{1}) \qquad M \geqslant 3 \tag{4.5}$$

where M refers to the dimension† of **A**. It follows after some algebra that

$$P_1 \equiv -(\lambda + \alpha_1) \tag{4.6a}$$

$$P_2 \equiv \lambda[\lambda + (2\alpha_1 + \beta_2)] \tag{4.6b}$$

$$P_3 = -\lambda[\lambda^2 + (2\alpha_1 + \beta_2 + \beta_3 + \alpha_2)\lambda + 2\beta_3\alpha_1 + \beta_2\beta_3 + 3\alpha_1\alpha_2] \tag{4.6c}$$

$$P_M = -(\beta_M + \alpha_{M-1} + \lambda)P_{M-1} - \alpha_{M-1}\beta_{M-1}P_{M-2} + (-1)^M\lambda \prod_{i=1}^{M-1} \alpha_i \tag{4.6d}$$

which are similar to the recurrence relations appearing in the theory of orthogonal polynomials (see, for instance, Nikiforov and Ouvarov 1976); they can be used to prove that the polynomial $P_M(\lambda)$ has simple real zeros. Moreover, one may write

$$P_M(\lambda) = (-1)^M \sum_{k=0}^{M} P_M^k \lambda^k \tag{4.7}$$

where the P_M^k satisfy recurrence relations following from (4.6). The latter allow us to prove that $P_M^k = 0$ for all M and that P_M^k, $k = 1, \ldots, M$, are positive (given that α_m, $\beta_m > 0$ for all m)—that is, the set of M eigenvalues of **A**, which are solutions of $P_M(\lambda) = 0$, are such that one is zero and the rest, different to each other, are all negative, say $0 = \lambda_1 < \lambda_2 < \ldots < \lambda_M$ where λ_i represents the absolute value of the corresponding

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† The upper bound M is introduced here for convenience although it is consistent with the fact that the Monte Carlo data refer to a finite system. The choice should not influence the solution as long as M is larger than the largest cluster size observed in the system.

eigenvalue. The case $\lambda_1 = 0$ should then be associated with the stationary solution of (4.2), and one has

$$C_m(t) = C_m^{\mathrm{eq}} + \sum_{k=2}^{M} d_k^m \exp(-\lambda_k t) \tag{4.8}$$

as a general solution where the constants d_k^m are related to the initial conditions $C_m(0)$. Thus, after some transient, initial time during the system evolution, which probably depends on m, one may expect the dominant behaviour

$$C_m(t) - C_m^{\mathrm{eq}} \simeq d_2^m \exp(-\lambda_2 t). \tag{4.9}$$

If this were the case it would imply that

$$(C_m(t) - C_m^{\mathrm{eq}})/(C_{m'}(t) - C_{m'}^{\mathrm{eq}}) = d_2^m/d_2^{m'} \tag{4.9b}$$

is independent of time except for exponentially small corrections in t. Thus interesting fact, it should be stressed, is a consequence of our assumption that α_m is independent of time. The simplest way to check the scaling prediction (4.9b) is to plot $\ln(C_m(t) - C_m^{\mathrm{eq}})$ versus t; after a transient, relatively small time this should produce straight lines that can be scaled into a single one via simple translations along the vertical axis. This is shown in figure 1, demonstrating both the exponential decay (4.9) towards the equilibrium cluster distribution in the case of some Monte Carlo data and the involved scaling with m. As expected, the time for the onset of scaling, t^*, strongly depends on m; for instance, one has in this case $t_2^* \simeq 2$, $t_3^* \lesssim 250$, $t_4^* < 1000$ and $t_5^* < 1600$ where the sub-index refers

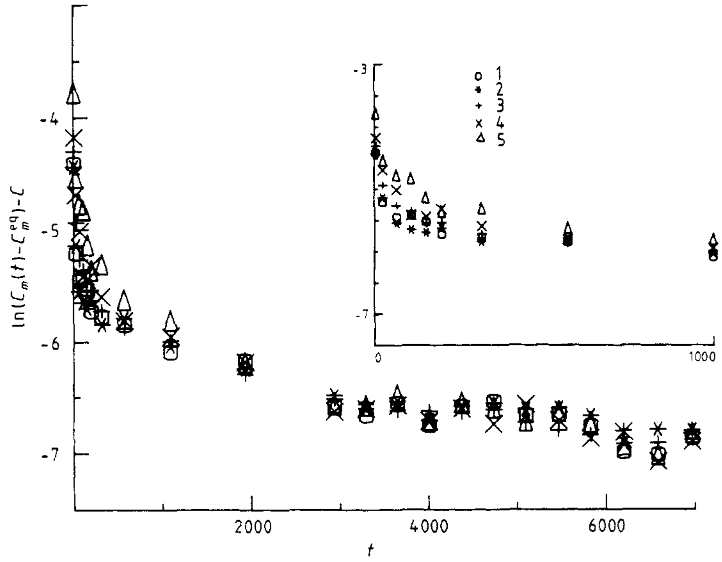

Figure 1. A semilogarithmic plot of $C_m(t) - C_m^{\mathrm{eq}}$ versus time in the case of Monte Carlo data for the lattice gas model for $T/T_c = 0.59$ and $\rho = 0.1$, produced in order to demonstrate the predominant behaviour (equation (4.9)) at comparatively large values of t; different symbols correspond to different values of m as indicated. The inset shows the behaviour at early times where small eigenvalues still play an important role. The scaling parameter for the vertical axis is $c = 0$ ($m = 1$), 1.89 ($m = 2$), 3.71, ($m = 3$), 7.04 ($m = 4$) and 13.04 ($m = 5$). t is in Monte Carlo steps (per lattice site).

to the value of m. The data for large values of m suffer from important statistical errors, preventing inclusion in figure 1; nevertheless, they do seem to be roughly consistent with (4.9).

When the matrix $\mathbf{A}$ is independent of time one simply has

$$C(t) = \exp(t\mathbf{A})C(0) \tag{4.10}$$

which may be diagonalised to

$$C(t) = \varphi\mathbf{E}\varphi^{-1}C(0) \tag{4.11}$$

where $\mathbf{E}$ and $\varphi^{-1}\mathbf{A}\varphi$ have only non-zero diagonal elements $\exp(\lambda_i t)$ and λ_i, respectively. Standard fast software can then be used to compute $\mathbf{E}$ and φ, thus producing the time evolution of the cluster distribution via (4.11). The resulting behaviour for $C_m(t)$ is practically indistinguishable from that obtained by Penrose *et al* (1984), making slightly different assumptions as mentioned above, by using a Newton–Raphson algorithm, while the corresponding computer time may be reduced in the method here by an order of magnitude or more. This stresses the utility of Becker–Doring equations in the analysis of nucleation phenomena, a fact that is not always recognised in the recent literature (see, however, for instance, Penrose *et al* 1978, 1984, Penrose and Buhagiar 1983). In particular, these equations and their numerical treatment given above may be combined with simple relations between $C_m(t)$, the system energy and the structure function to investigate the behaviour of the latter quantities (Marro and Toral 1986).

5. A time-dependent renormalised fugacity

As an addendum to the paper, we analyse here the extension to non-equilibrium phenomena of the concept of a renormalised fugacity, ω, which has proved very useful previously (Lebowitz and Penrose 1977, Kalos *et al* 1978, Marro and Toral 1983). This is defined via the expression:

$$C_m^{\mathrm{eq}} = \omega^m Q_m(1-\rho)^{k_m} \tag{5.1}$$

where

$$Q_m \equiv \sum_k \exp[-E(K)/k_\mathrm{B}T]$$

is a 'cluster partition function' (Lebowitz and Penrose 1977) where the sum runs over all the translationally different clusters K of size m, $E(K)$ represents the energy of cluster K, and $k_1 = 3.25$, $k_2 = 4.5$, $k_m = 5$, $m \geqslant 3$ (Marro and Toral 1983). This may be generalised in principle to

$$C_m(t) = \omega(t)^m Q_m(t)(1-\rho)^{k_m} \tag{5.2}$$

where we shall assume that k_m remains the same as before. It thus follows that

$$\begin{aligned}\omega_m(t) &\equiv (C_m(t)C_1(t)/C_{m+1}(t))(1-\rho)^{k_{m+1}-k_1-k_m}\\ &= Q_m(t)Q_1(t)/Q_{m+1}(t).\end{aligned} \tag{5.3}$$

As shown by figure 2, the Monte Carlo data for $C_m(t)$ reveal that $\omega_m(t)$ almost stabilises very early to a constant value, at least for m not too large. Let us then assume that $Q_m(t)$ soon becomes almost independent of t, and equal to the equilibrium value Q_m when the initial state is unstable (for metastable states the stationary value may differ from Q_m). On this assumption, the time-dependent renormalised fugacity defined in (5.2) may be found in practice from the equation

$$\rho(t; m_c) = \sum_{m \leqslant m_c} mC_m(t) = \sum_{m \leqslant m_c} m\omega(t)^m Q_m(1-\rho)^{k_m} \tag{5.4}$$

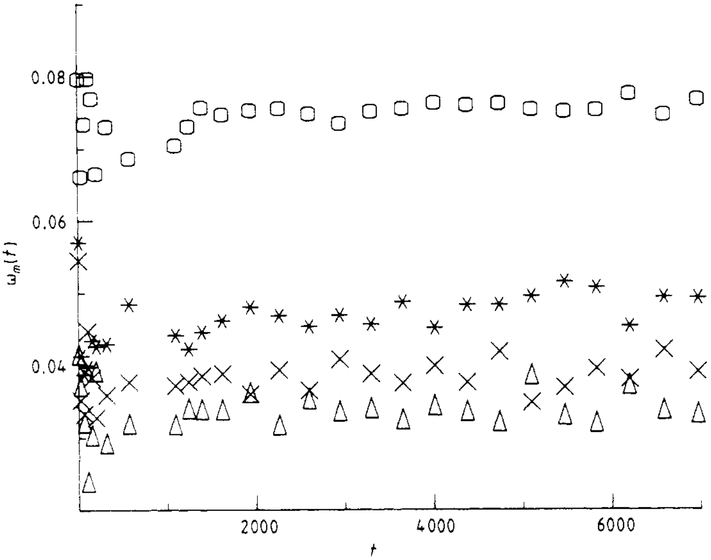

Figure 2. The parameter $\omega_m(t)$ as defined in (5.3) as a function of time for the same data as in figure 1. The symbols are as follows: circles, $m = 1$; stars, $m = 2$; crosses, $m = 3$; and triangles, $m = 4$.

where m_c is the cut-off defining for the vapour phase, e.g. $m_c \simeq 10$ at $T = 0.6T_c$ (see Marro and Toral (1986) for other cases), $\rho(t; m_c)$ represents the corresponding vapour density (see Toral and Marro (1985) for the behaviour of this quantity), and Q_m is known exactly for $m \leqslant 10$ and rather accurately for $m \leqslant 20$ (Sykes (1975), Perini *et al* (1984); see also Marro and Toral (1983)). The fact that (5.2), with $Q_m(t)$ independent of time and equal to the equilibrium value, and (5.4) may be very useful in practice is demonstrated by table 1. Notice, however, that one cannot extrapolate the validity of (5.4) to include the liquid phase where $m > m_c$, i.e. the series resulting from (5.4) as $m_c \rightarrow \infty$, $\rho(t; m_c) \rightarrow \rho$ can be seen to diverge; as a consequence, one may not combine (5.2) for all m with a Becker–Doring description such as that in earlier sections.

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Table 1. The temporal evolution of the renormalised fugacity, $\omega(t)$, is obtained from (5.4) by combining the exact values for the cluster partition functions Q_m and experimental data for $\rho(t)$, the evolution with time of the vapour-phase density. The time variation of the cluster distribution is then predicted from

$$C_m(t) = \omega(t)^m Q_m (1-\rho)^{k_m}.$$

The first row for each time gives the Monte Carlo data for $T/T_c = 0.6$ and $\rho = 0.1$; the second row gives our prediction. The agreement is good, except at early times as expected.

t	$C_1(t)$	$C_2(t)$	$C_3(t)$	$C_4(t)$	$C_5(t)$	$C_6(t)$	$C_7(t)$	$C_8(t)$	$C_9(t)$	$C_{10}(t)$	$\omega(t)$
11.6	2168	608	296	205	171	128	97	91	60	47	0.023904
	2050	558	274	182	137	112	98	89	84	81	
25.5	1939	562	282	175	104	98	61	64	38	38	0.022073
	1959	510	239	152	109	86	71	62	56	52	
55.1	1766	488	228	145	84	45	53	46	38	31	0.021052
	1868	464	207	126	86	64	51	42	36	32	
108.1	1814	408	199	91	79	43	40	28	30	23	0.020223
	1795	428	184	107	71	51	39	31	25	21	
440.9	1662	388	145	76	39	32	22	15	13	9	0.018660
	1656	364	144	78	47	31	22	16	12	10	
1238.3	1550	325	128	59	31	18	12	10	6	5	0.017433
	1547	318	118	59	34	21	14	9	7	5	
2595.3	1455	280	96	43	20	11	7	4	3	2	0.016140
	1432	272	93	43	23	13	8	5	3	2	
4373.9	1433	267	85	36	18	10	5	3	1	1	0.015654
	1389	256	85	39	20	11	6	4	3	2	
5468.4	1421	266	78	34	17	9	4	2	2	1	0.015487
	1374	251	83	37	19	10	6	4	2	1	
6969.7	1391	250	75	30	15	7	3	2	2	1	0.015131
	1343	240	77	34	17	9	5	3	2	1	

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