Nucleation theory versus cluster aggregation

1993 J. Phys. A: Math. Gen. 26 L655

(http://iopscience.iop.org/0305-4470/26/15/007)

J. Phys. A: Math. Gen. 26 (1993) L655–L659. Printed in the UK

LETTER TO THE EDITOR

Nucleation theory versus cluster aggregation

Z Alexandrowicz

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Received 19 April 1993

Abstract. According to classical nucleation theory (CNT), clusters are produced with the help of a reversible gain of single molecules, with no cluster–cluster aggregation. Simulations at $T \cong T_c$ seem to disagree. We show that, when a growing embryo cluster aggregates with clusters of any size $d \geq 1$, the dominant contribution is of $d = 1$ (single molecules). Production of the biggest clusters obeys, therefore, CNT. Production of other clusters, however, is modified by their slow *rate determining* aggregation with the biggest. The theory fits excellently the simulations and for the first time combines aggregation with CNT.

Classical nucleation theory (CNT) associates the onset of a homogeneous phase transition with production of clusters (Becker and Doring 1935). It derives a rate equation dn_s/dt, where n_s is the number of clusters of size s at time t. Thus

$$(dn_s/dt)_{CNT} = d\,[R_s n_s(\infty)(d\Phi_s/ds)]/ds. \tag{1}$$

Here $n_s(\infty)$ is the equilibrium value of n_s, $\Phi_s = n_s/n_s(\infty)$ and R_s is a rate constant. The derivation of (1) assumes a back and forth variation of cluster size, in steps of one molecule, $s \leftrightarrow s \pm 1$. The possible occurence of cluster–cluster aggregation and fragmentation is ignored, but no supporting argument has ever been offered. Stauffer (1992*a*) has recently proposed a test of (1): Integration from s to ∞, gives

$$R_s = S(s)/(d\Phi_s/ds) \qquad \text{where } S(s) = n_s(\infty)^{-1} \int_s^\infty (dn_{s'}/dt)ds'. \tag{2}$$

Both $S(s)$ and $d\Phi_s/ds$ can be measured directly in a simulation (unfortunately only for small clusters). Simulations of Ising lattices at $T \gg T_c$ and $T \ll T_c$ show that the rate constants R_s indeed settle down to reasonable constant value. At $T \cong T_c$ however, R_s appears to decrease with t indefinitely (Stauffer 1992a, Stauffer 1992b, Behrens and Stauffer 1993). Also, the deviations Φ_s decay to equilibrium, not as expected exponentially $\Phi_s \propto \exp(-\text{const}^* t)$, but as a power law $\Phi_s \propto t^{-p}$. What comes to mind of course is to blame the neglect of cluster–cluster aggregation by CNT. The present letter studies a reversible aggregation of a growing embryo s-cluster with 'dust' clusters of any size $d \geq 1$, and shows that it occurs mainly with smallest dust $d \to 1$. This justifies the CNT assumption that growth proceeds in $s \leftrightarrow s \pm 1$ steps. However, except for the biggest clusters, dn_s/dt is modified by the aggregation with clusters larger than s.

Let us consider a reversible growth of 'critical' clusters, resulting from thermal motion at $T \cong T_c$. Taking the Ising model as an example, the clusters represent regions

of *completely correlated* up (down) spins (Fortuin and Kasteleyn 1972, Coniglio and Klein 1980, Swendsen and Wang 1987). Thermal spin-flips (Glauber dynamics), cause a back and forth variation of the regions' boundaries, causing a reversible aggregation of neighbour clusters with rate k_0 per spin. We focus on the growth of a given embryo cluster, whose size s' increases with the help of these reversible aggregations, from 1 to s. An average relaxation time needed for such growth is denoted by $\tau(s)$. (It should not be confused with the relaxation time τ of the entire system, during which *all* n_s attain their equilibrium value!). We first restrict ourselves to the case that s' aggregates with neighbour 'dust' clusters of a fixed size d ($1 \leqslant d \leqslant s-1$); the corresponding relaxation time is denoted by $\tau(s; d)$. The occurence of an s'-d aggregation requires that a d-cluster adjoins the boundary of the s'-cluster. The probability for that is proportional to $n_d(A_{s'}/A_d)$, where $A_{s'}$ and A_d denote the boundary's area (whose nature is discussed later on), for s' and d, respectively, while n_d is the number of clusters of size d. The rate growth of s', due to its aggregation with neighbour d-clusters in unit time, is therefore $(k_0 A_d) n_d (A_{s'}/A_d) d$. The aggegation however alternates with fragmentation. The relaxation time $\tau(s; d)$ is proportional to the sequence of such back and forth time-steps. But near to equilibrium only the square root of these (random walk-like) steps contributes to the *net* growth from 1 to s. Hence $\tau(s; d)^{1/2} k_0 n_d A_s d \propto s$ (omitting variation of $A_{s'}$ which is of the order d/s smaller). We pause to point out a cardinal difference from Katz *et al* (1966), who derive (in our notation): $[\tau(s; d) k_{s,d} n_d A_s]^{1/2} d \propto s$. They associate the s'-d aggregation, with a back and forth diffusion of the d-clusters, towards the cross-section A_s. We however associate it with an aggregation of the *boundary as a whole unit, with* $n_d A_s$ *stationary neighbours*, alternating with a fragmentation in a succession of time-steps. Returning, we write

$$\tau(s; d) \propto (s/A_s)^2 (n_d d)^{-2} \tag{3}$$

and in particular, $\tau(s; 1) \propto (s/A_s)^2 n_1^{-2}$. The rate growth of s' with the help of dust of a fixed size d, is proportional to $\tau(s, d)^{-1}$. However s' grows with the help of d ranging from 1 to $s-1$. Assuming an approximately linear superposition, we get

$$\tau(s)^{-1} \propto \tau(s; 1)^{-1} n_1^{-2} \sum_{d=1}^{s-1} (n_d d)^2 \cong \tau(s; 1)^{-1}. \tag{4}$$

The last result on the right utilizes standard cluster theory (Stauffer 1979); At equilibrium $n_d \propto d^{-y}$, where y (usually denoted by τ), is larger than two, so that the sum in (4) converges on the lower limit, $d \to 1$. It is worth noting that a down-convergent distribution of total mass $\Sigma n_s s$, is to be generally expected, if scaling holds while s increases indefinitely. Far from equilibrium, the back and forth steps become forward-alone, but this does not invalidate the sum's convergence on the lower limit. Furthermore, n_d decreases even faster than d^{-y}. Finally, (4) does not depend on whether the clusters are fractal or not. Summing up, although an s-cluster may aggregate with any dust d, the process is dominated by the single step growth, $s \leftrightarrow s \pm 1$. On the face of it therefore, CNT is vindicated. Let us, however, take a closer look at the problem. In an absence of aggregations involving s, the production $\mathrm{d}n_s/\mathrm{d}t$ may be expected to be 'local'; that is, determined by the flows from $s-1$ and $s+1$, and attaining equilibrium after a time in the order of $\tau(s)$. In the presence of cluster–cluster aggregation, however, we cannot expect $\mathrm{d}n_s/\mathrm{d}t$ to attain equilibrium *before all the clusters with which it aggregates attain equilibrium as well*. The slowest to do so are

the biggest. Let, therefore, B_t denote an appropriately defined size, which typifies the big clusters at time t (second moment of cluster distribution at t, for example). Referring to our definition of $\tau(s)$ in (3) and (4), $\tau(B_t)$ denotes the relaxation time needed to grow an embryo cluster from size 1 to B_t. The present counterpart of the 'local' alternative of before, is the following: At each instant the production, dn_s/dt behaves as if it would attain equilibrium only after the growth of embryo B_t-clusters is essentially completed; that is, after the relaxation time $\tau(B_t)$. Let us consider the production of clusters of a given size s. Suppose that the nucleation is such that, during initial time B_t is relatively small, so that $s \geqslant B_t$ (B_t is a typical, not a maximal size). The attainment of equilibrium by dn_s/dt need not then await the B_t-clusters. At some later time, however, the typical big clusters B_t have grown larger, so that $s \ll B_t$ (unless $s = B_\infty$). In that case a 'source and sink' scenario determines the actual production, $(dn_s/dt)_{\text{actual}}$. Assuming first that the sink is absent (i.e. neglecting the aggregation), we have a production determined by the local $s \leftrightarrow s \pm 1$ growth; that is, equal to $(dn_s/dt)_{\text{CNT}}$ of (1). Taking for simplicity $n_s(0) = 0$, we obtain $n_s(\infty) = \int (dn_s/dt)_{\text{CNT}}\, dt$, where t increases from 0 to $\cong \tau(s)$, during which a cluster grows from 1 to s. We now evaluate the effect of the sink, and first treat B_t as a fixed size. The equilibrium $n_s(\infty)$ is attained only after the time $\tau(B_t)$. To describe the stretching of the time, we introduce a scaled variable $t' = t[\tau(B_t)/\tau(s)]$, and write $n_s(\infty) = \int (dn_s/dt)_{\text{actual}}\, dt'$, where t' increases from 0 to $\tau(B_t)$. In order to restore the previous upper limit we return to t, substituting $dt' = d(dt'/dt)$. Our integral reads $n_s(\infty) = \int (dn_s/dt)_{\text{actual}} (dt'/dt) dt$, where t increases from 0 to $\tau(s)$, like before in the sink's absence. On the left-hand side too, $n_s(\infty)$ remains as before, being only slightly affected by the presence of $B_t \gg s$ clusters (see standard theory quoted after (4)). Hence scaling implies that the expressions under the integral sign, with and without the sink, are equal. Thus

$$(dn_s/dt)_{\text{actual}} = (dt'/dt)^{-1} (dn_s/dt)_{\text{CNT}}. \tag{5}$$

We now allow B_t to vary with t. B_t represents the typical cluster size, which the nucleation process produces after time t (prior to equilibrium). Therefore(!).

$$\tau(B_t) \cong \; t \to t' = t^2/\tau(s). \tag{6}$$

Equation (5) and (6) give

$$(dn_s/dt)_{\text{actual}} = (2t)^{-1} \tau(s) d[R_s n_s(\infty)(d\Phi_s/ds)]/ds \qquad \text{for } s \ll B_t. \tag{7}$$

Equation (7) differs cardinally from (1) in the presence of t^{-1} on the right-hand side. Therefore, if an actual rate 'constant' $R_{s,\,\text{actual}}$, is calculated with the help of (2) under the $s \ll B_t$ regime, we obtain,

$$R_{s,\,\text{actual}} \propto t^{-1} \tau(s) R_s \qquad \text{for } s \ll B_t. \tag{8}$$

Equation (1), with the help of a scaling argument, leads to the classical exponential decay of the deviation to equilibrium, $\Phi_s \propto \exp(-t/\tau)$ (Binder *et al* 1975, Stauffer 1992*a*). Equation (7), however, because of the extra t_{actual}^{-1} factor on the right-hand side, leads instead to a power law decay. Let us work this out in detail. Since Φ_s must also depend on s, a natural guess is that it constitutes a function of our scaling factor $\tau(B_t)/\tau(s) = t/\tau(s)$. We propose

$$\Phi_s = 1 - c_0 [t/\tau(s)]^{-p} \qquad \text{for } s \ll B_t. \tag{9}$$

In order to evaluate the new critical exponent p from (7), we need to substitute the scaling dependence of $n_s(\infty)$, $\tau(s)$ and R_s. The first, as mentioned already, is

$n_s(\infty) \sim s^{-y}$, with y known from standard theory. The second, $\tau(s)$, has been calculated by a recent theory of critical slowing-down (Alexandrowicz 1992, 1993), giving

$$\tau(s) \sim s^{\theta} \qquad \text{where } \theta = 2\rho/[1-0.295(2\rho-1)]. \tag{10}$$

Here ρ is a 'geometric' exponent, describing the typical *connected length* l_s l_s of an s-cluster (also called chemical distance); it is defined through $l_s \sim s^{\rho}$ (Alexandrowicz 1980). Values of ρ of Ising clusters at equilibrium can be easily measured with the help of computer simulation (Alexandrowicz 1990). The last scaling dependence needed, is evaluated with the help of the following argument. The constant R_s in the CNT equation (1), and in our modified equation (7), represents a factor increasing dn_s/dt. The increase is due to the surface A_s allowing $n_1 A_s$ molecules ($d=1$ clusters) to aggregate with s *simultaneously* in a unit time. As has been shown in (3), the consequent increase in the rate, that is in $\tau(s)^{-1}$, is proportional to A_s^2 which in turn is proportional to $s^2/\tau(s)$ (see (3) again). Hence

$$R_s \propto A_s^2 \propto s^2/\tau(s). \tag{11}$$

The result shows that R_s is proportional, not to the boundary's area (as commonly assumed in CNT), but to its square! We have, however, already commented on the reason, in connection to (3): R_s does not represent a cross-section of an s-cluster accessible to back and forth diffusing molecules; the back and forth variation is attributed instead to the τ(s) steps moving the boundary as one whole. Combining (10) with (11), gives $R_s \sim s^{2-\theta}$. Introducing $n_s(\infty)$, $\tau(s)$, R_s and (9) into (7), and performing the differentiations, we find that the powers of t and of s on the two sides of the equation cancel out. This shows that (9) constitutes a valid solution of (7). The remaining coefficients lead to

$$p = (y - 1 + \theta - 2/\theta)/\theta. \tag{12}$$

Thus our new critical exponent p, describing the power law decay of cluster numbers towards equilibrium, can be calculated from (12), with the help of the critical slowing-down equation (10), and utilizing simulation results for ρ.

Let us recapitulate the behaviour of a nucleation at $T \cong T_c$ predicted here. The size B_t of our typical big clusters at time t increases monotonically towards B_∞. The evolution of clusters of a given size $s(\ll B_\infty)$, is this: Initially they are absent $n_s = 0$. Their creation requires $t \cong \tau(s)$. At this stage the $s \geqslant B_t$ regime applies, that is $(dn_s/dt)_{\text{actual}}$ is unaffected by the t-dependent B_t clusters. Consequently R_s is constant, and $1-\Phi_s$ decreases exponentially with t. As time goes on, however, we inevitably run into the $s \ll B_t$ regime. Equation (8) and (9) take over, i.e. $R_{s,\text{actual}} \propto t^{-1}$ and $1-\Phi_s \propto t^{-p}$. This agrees excellently with the puzzling recent simulation results (Stauffer 1992*a*, Stauffer 1992*b*, Behrens and Stauffer 1993). These indicate that $R_{s,\text{actual}}$ is initially constant but ultimately tends to an asymptotic decrease almost attaining t^{-1}. (The slight discrepancy is presumably explained by the following: CNT treats a binary reaction between s and $d=1$. Hence growth rate should be made proportional to n_s *and* to n_1, like in our equation (3). The omission of n_1 from (1) implies that it is absorbed into R_s as a constant. But in the actual simulations, n_1 still increases by about 10%, offsetting somewhat the decrease of $R_{s,\text{actual}}$). The deviations Φ_s too, ultimately decrease as $\Phi \propto t^{-p}$ with a constant p, as expected. More than that; the simulation data at $d=2$ (Stauffer 1992*b*) give, for the dynamic deviation exponent, $p = 0.60(1)$. The (implicit) result for θ (Alexandrowicz 1992, 1993) is $\theta = 1.23(4)$, predicting a remarkable fit $p = 0.60(6)$! At $d=3$ and 4 the results are $\theta(3) = 1.037(25)$

and $\theta(4)=1$, respectively, predicting $p(3)=0.305(50)$ and $p(4)=1/3$; corresponding simulation data for p are not yet available.

In summary, the present theory of homogeneous nucleation generalizes the small-step $s \leftrightarrow s \pm 1$, assumption of CNT, by allowing a cluster of size s to grow with the help of 'dust' clusters of an arbitrary size d. A scaling argument shows that the main contribution comes from smallest d (4), so that indeed growth proceeds in $s \leftrightarrow s \pm 1$ steps. Consequently the conclusions of the rate equation (1) of CNT hold true, for the typical big clusters at a given time t, called here B_t. However CNT errs in neglecting the effect of aggregation altogether: If we focus on clusters whose size s is fixed, the behaviour is different. In a nucleation at $T \cong T_c$ which produces increasingly large B_t we inevitably attain an $s \ll B_t$ regime [unless $s \cong B_t(\infty)$]. Under this regime $(\mathrm{d}n_s/\mathrm{d}t)_{\text{actual}}$ is determined by a source and sink scenario: The s-clusters are produced by the $s \leftrightarrow s \pm 1$ growth; simultaneously however they are consumed when they participate as dust in the growth of embryo B_t clusters. The latter (much slower) process sets the pace with which n_s attains equilibrium. This scenario turns out to be amenable to a very simple scaling description, which leads to $(\mathrm{d}n_s/\mathrm{d}t)_{\text{actual}}$ of (7), radically different from $(\mathrm{d}n_s/\mathrm{d}t)_{\text{CNT}}$ of (1). It predicts that a rate 'constant' $R_{s,\text{actual}}$ derived from simulation data, should in fact decrease as t^{-1} (8). The deviation $\Phi_s \equiv n_s/n_s(\infty)$ too should behave in a surprising manner, notably to decay as a power law $1-\Phi_s \propto t^{-p}$ (9), instead of the expected $1-\Phi_s \propto \exp(-t/\tau)$. Both predictions are in a quantitative agreement with the puzzling results of recent simulations (Stauffer 1992*a*, Stauffer 1992*b*, Behrens and Stauffer 1993). Furthermore, combination with a recent theory of critical slowing-down (Alexandrowicz 1992, 1993), enables us to calculate the new dynamic exponent p, in excellent agreement with the simulations. We conclude that the present theory for the first time reconciles nucleation with cluster–cluster aggregation. It also proposes a joint description of irreversible nucleation, and of critical relaxation at equilibrium.

I wish to thank Dietrich Stauffer, whose relentless questioning of the $s \leftrightarrow s \pm 1$ assumption stimulated this study, and Janos Kertesz for valuable advice.

References

Alexandrowicz Z 1980 *Phys. Lett.* **80A** 284
Alexandrowicz Z 1990 *Physica* **167A** 322
Alexandrowicz Z 1992 *Physica* **189A** 148; *Physica* 1993 **194A** 154
Becker R and Doring W 1935 *Ann. Physik* **24** 719
Behrens M and Stauffer D 1993 *Ann. Physik* **2** 105
Binder K, Stauffer D and Muller-Krumbhaar H 1975 *Phys. Rev.* B **12** 5261
Coniglio A and Klein W 1980 *J. Phys A: Math. Gen.* **13** 2775
Fortuin C M and Kasteleyn P W 1972 *Physica (Utrecht)* **57** 536
Katz J L, Saltsburg H and Reiss H 1966 *J. Coll. Sci.* **21**, 560
Stauffer D 1979 *Phys. Rept.* **54** 1
Stauffer D 1992*a* *Ann. Physik* **1** 56
Stauffer D 1992*b* *Physica* **186A** 192 More accurate D = 2 data are quoted in Alexandrowicz Z and Stauffer D 1992 *Physica* **191A** 195
Swendsen R H and Wang J S 1987 *Phys. Rev. Lett.* **58** 86