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## FAST TRACK COMMUNICATION

# Non-self-averaging nucleation rate due to quenched disorder

**Richard P Sear**

Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK

E-mail: [r.sear@surrey.ac.uk](mailto:r.sear@surrey.ac.uk)

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Online at [stacks.iop.org/JPhysCM/24/052205](http://stacks.iop.org/JPhysCM/24/052205)**Abstract**

We study the nucleation of a new thermodynamic phase in the presence of quenched disorder. The quenched disorder is a generic model of both impurities and disordered porous media; both are known to have large effects on nucleation. We find that the nucleation rate is non-self-averaging. This is in a simple Ising model with clusters of quenched spins. We also show that non-self-averaging behaviour is straightforward to detect in experiments, and may be rather common.

(Some figures may appear in colour only in the online journal)

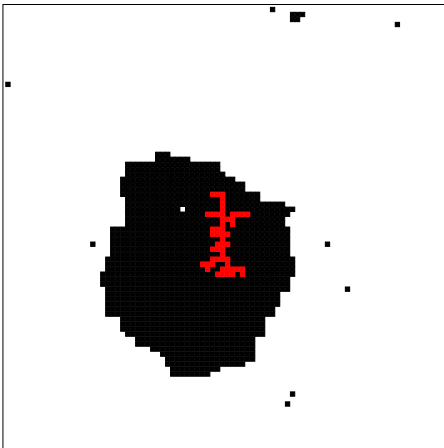
Nucleation of a new phase often occurs in the presence of quenched disorder. Examples of sources of quenched disorder are impurities [1–3] and deliberately added disordered porous media [4–7]. For example, a porous polymer microgel can induce nucleation [6] and quenched disorder is clearly an appropriate description of such a microgel. The microgel is disordered in the sense that it is formed by random crosslinking that creates pores with a range of sizes and shapes, and this disorder is quenched as the crosslinks are irreversibly formed covalent bonds. Here we perform essentially exact computer simulations of nucleation in the presence of quenched disorder, in a very simple model. We find that quenched disorder can result in a nucleation rate that is non-self-averaging. This has the important and easy-to-observe consequence in experiments that, in a set of nominally identical samples, the spread of nucleation times can be very large—much larger than they would be if the nucleation rate was self-averaging. This prediction is a generic consequence of quenched disorder and should apply to nucleation rates in many systems.

Consider the following situation. An experimentalist wishes to measure a nucleation rate, for example for a crystal in solution. Nucleation is slow because it is an activated process with a substantial free energy barrier and so is a rare event. Let us assume for simplicity that only one nucleation event is required for crystallization, and that growth is

sufficiently fast that the time for a crystal to grow large enough to be observed is negligible. These conditions are met for some [6, 7] but not all [4, 5] experimental systems. Then the probability  $P$  that a single sample has not crystallized is  $P(t) = \exp(-rt)$ , where  $r$  is the nucleation rate in the sample.

Now, estimating the rate  $r$  cannot accurately be done with one sample so  $N_{\text{SAM}} \gg 1$  samples are required. For a set of  $N_{\text{SAM}}$  samples the number at time  $t$  that have not crystallized,  $N_{\text{NX}}(t)$ , can be obtained. Then  $P(t)$  is approximated by the fraction  $f(t) = N_{\text{NX}}(t)/N_{\text{SAM}}$ , for  $N_{\text{SAM}} \gg 1$ . Then, if the nucleation rate is the same in all samples,  $f(t)$  will be a simple exponential function of time and it gives the nucleation rate  $r$  directly. However, Diao *et al*'s [6, 7] plots of  $f(t)$  are not all simple exponentials. As they note [7] this implies that the rate varies between one sample and another. Earlier work by Kabath *et al* [8] on the nucleation of ice also found two slopes and hence possibly two rates in a plot of the same type. Deviations from simple exponential behaviour are also seen in work by Murray *et al* [9], also on ice.

Deliberately added disordered porous media are not the only source of quenched disorder that affects nucleation. Parmar *et al* [3] studied the crystallization from solution of the protein lysozyme. They found that irreversibly formed clusters of the protein itself could significantly perturb nucleation. These clusters were around a few tens of lysozyme



**Figure 1.** Snapshot of nucleation of the up-spin phase on a quenched cluster, at  $J/kT = 0.8$  and  $h/kT = 0.03$ . Free up spins are black, the quenched up spins of the cluster are red and lattice sites with down spins are left white. The quenched cluster is of 53 fixed spins and has a radius of gyration  $R_G = 5.35$ . The simulation box is  $90 \times 90$  lattice sites. The snapshot is taken from a nucleation run and is a configuration (with 1228 up spins) that is near the top of the barrier.

diameters across. In Parmar *et al*'s experiments each sample contains some relatively small number (in comparison to the number of protein molecules) of clusters, which are produced via a random irreversible aggregation process.

As these clusters form irreversibly via a random process they are an example of what in statistical physics is known as quenched disorder. See [10, 4] for previous work on the effect of quenched disorder on nucleation. The microgel particles of Diao *et al* [6] are another example. Both are disordered and, as they form irreversibly, this disorder is not dynamically fluctuating at thermal equilibrium, it is 'frozen' in and hence is referred to as quenched. Thus, here the nucleation rate is affected by quenched disorder. Quenched disorder, such as irreversibly formed clusters, vary from one sample to another nominally identical sample. This can cause properties, such as the nucleation rate, to vary from sample to sample. If a property varies from one sample to another nominally identical sample then it is said to be non-self-averaging.

Here, we will study nucleation in a very simple model with quenched disorder, explore the consequences of the quenched disorder and show how experiments can reveal the affect of quenched disorder on nucleation rates. We want a model that is simple in order to make the generic physics as clear as possible and we need a simple model in order to be able to sample many different realizations of the quenched disorder. For these reasons we pick perhaps the simplest possible model: the two-dimensional Ising model [11].

We assume that there is a separation of timescales between the timescale of the process that produces the quenched clusters and the timescale for a nucleus to grow over the barrier. Note that the timescale for a nucleus to grow over the barrier is typically around 100 times the timescale of the microscopic dynamics, it is not one over the nucleation rate, which is much slower [1]. Nucleation rates are low when the barrier is large because the nucleation fluctuation is a rare

event, i.e. it is highly infrequent, not because the intrinsic dynamics of the nucleus are very slow. When the nucleus dynamics are much faster than cluster growth, the cluster does not grow significantly during nucleation and our calculations separate out into two parts. In the first part we generate the clusters. In the second we calculate the nucleation rate on the cluster.

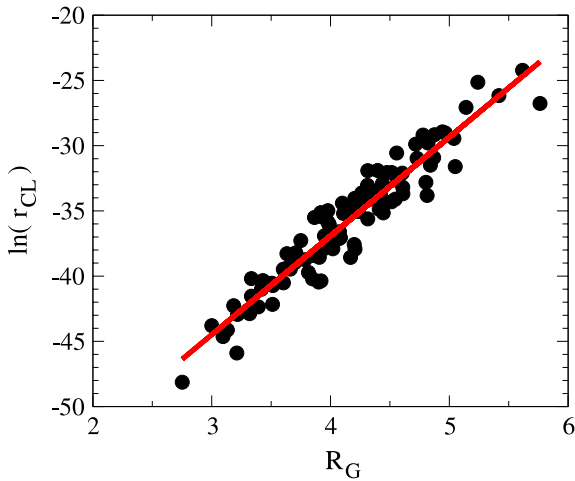
Our quenched clusters are generated using a simple form of diffusion-limited aggregation (DLA) [12]. Our algorithm is as follows. We start with a square lattice of  $L \times L$  sites; here  $L = 90$  always. This is chosen to be large enough to accommodate both the quenched cluster and the nucleus without finite size effects from the periodic boundary conditions. A sample in an experiment will have many clusters that are widely spaced because they are very dilute. We will model this by a set of many clusters but we simulate each cluster individually in a simulation box.

The spin on each site is then randomly set to be either an up spin, with probability  $\phi = 0.005$ , or a down spin with probability  $1 - \phi$ . The spin in the centre of the simulation box is then set to be a quenched up spin. This quenched spin forms the nucleus of the cluster. A simulation is then performed in which the unquenched up spins freely diffuse until they encounter a quenched spin, then this up spin itself becomes a quenched spin. Although two unquenched spins cannot occupy the same site this is the only interaction, if two unquenched spins occupy neighbouring sites then they do not quench; this ensures only one quenched cluster is produced.

Quenched spins are never moved. Periodic boundary conditions are used. The simulation is run until all the up spins are quenched, at which point we have a single cluster of quenched spins, that has grown from the original quenched spin. On average, the clusters have 41.5 spins, although this number varies from cluster to cluster. Note that our algorithm is not that used in the original DLA work of Witten and Sander [12] so the scaling at large  $R_G$  will not be that in the standard DLA model. Here we just use a simple DLA-like process to produce the quite small disordered clusters we require.

Nucleation itself is then of the Ising model's up-spin phase from its down-spin phase. The dynamics are the standard spin-flip (Glauber) Metropolis Monte Carlo dynamics [11]. The freely flipping spins see the cluster as a fixed set of up spins. A nucleus of the up-spin phase forming in the down-spin phase is shown in figure 1. For a given quenched cluster we calculate the nucleation rate using the forward flux sampling (FFS) algorithm of Allen and co-workers [13–15]. This is the same model and method as used in earlier work [16, 17]. We work at the temperature  $J/kT = 0.8$  and field  $h/kT = 0.03$ . Here  $J$  and  $h$  are the conventional Ising model parameters [11].  $J$  is the coupling between neighbouring spins and  $J/kT = 0.8$  is large in the sense that at this temperature the transition is strongly first order. The supersaturation in the Ising model  $= 2h = 0.06kT$  here. At this temperature and supersaturation the concentration of up spins in the metastable phase is 0.0021.

In figure 2, we show the nucleation rates for a set of 100 clusters. Note that the clusters have radii of gyration from a



**Figure 2.** Nucleation rates,  $r_{CL}$ , on a set of 100 quenched clusters. The rates are plotted as a function of the radius of gyration of the quenched cluster. The rates are per cycle, where a cycle is one attempted spin-flip per lattice site. Simulation data for  $J/kT = 0.8$  and  $h/kT = 0.03$  are shown as black circles, and the red line is the linear fit to this data:  $\ln(r_{CL}) = -67.20 + 7.57R_G$ . Each circle is a single rate from a single run, but repeated independent runs on a single cluster find that the statistical uncertainty in each rate is approximately the same as the symbol height.

little below three to almost six, and that the nucleation rates vary over a range of ten orders of magnitude. As expected, the nucleation rate is much larger on the larger clusters. The variation in nucleation rate is so large that just one of the hundred clusters contributes 58% of the total nucleation rate.

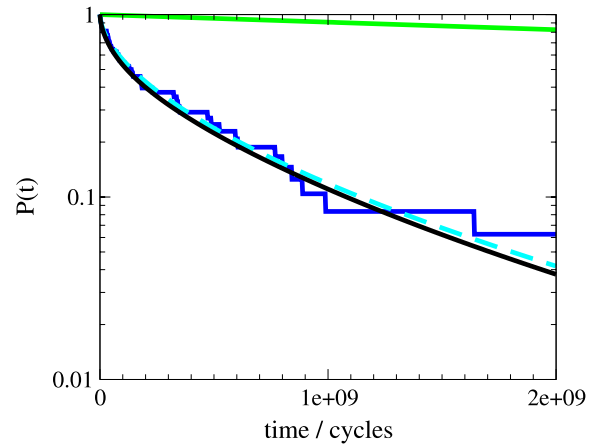
Experiments are done on a set of small vials of solution [6, 7]. Each vial contains many clusters or pores. We mimic a vial which will contain many pores or clusters with a set of  $N_{CL} = 1000$  clusters. We refer to a system of  $N_{CL}$  independent clusters as a sample. This is not a very large number of clusters but the computational cost of larger values of  $N_{CL}$  is prohibitive. Then the nucleation rate in sample  $i$ ,  $r_{SAM}(i)$ , is given as the sum over the nucleation rates on its  $N_{CL}$  clusters:

$$r_{SAM}(i) = \sum_{j=1}^{N_{CL}} r_{CL}(i, j), \quad (1)$$

where  $r_{CL}(i, j)$  is the nucleation rate on cluster  $j$  of sample  $i$ . We neglect homogeneous nucleation as its rate per lattice site is  $3.1 \times 10^{-40} \pm 2.2 \times 10^{-40}$ /cycle, which is 18 orders of magnitude smaller than even the smallest nucleation rate on a cluster. By averaging over many samples, we can obtain an expression for the probability  $P(t)$  that a randomly selected sample has not nucleated, as a function of time:

$$P(t) = \langle \exp[-r_{SAM}t] \rangle, \quad (2)$$

where  $\langle \rangle$  denotes an average over  $N_{SAM}$  samples. To get good statistics for the behaviour of samples we average over  $N_{SAM} = 150$  samples. This requires a large total number ( $N_{SAM}N_{CL} = 1.5 \times 10^5$ ) of clusters. We cannot calculate this many nucleation rates directly, so although we do generate  $1.5 \times 10^5$  clusters explicitly using the algorithm described



**Figure 3.** Probability  $P(t)$  that a sample with size such that it has  $N_{CL} = 1000$  clusters has not nucleated, as a function of time. The black curve is obtained by averaging over many ( $N_{SAM} = 150$ ) samples to obtain a good approximation to the true ( $N_{SAM} \rightarrow \infty$ )  $P(t)$ . The dark blue curve is  $f(t)$  for 48 samples, where the time at which nucleation occurs in each sample is taken from an exponential distribution with the rate for that sample. The dashed cyan curve is the stretched exponential,  $\exp[-(t/2.67 \times 10^8)^{0.57}]$ , fit to  $f(t)$ . The green curve is the  $P(t)$  that is obtained if all clusters larger than  $R_G = 5.5$  are removed.

above, for each cluster we use its radius of gyration and the fit in figure 2 to estimate the nucleation rate on this cluster. The resulting  $P(t)$  is plotted in figure 3.

We see that the time dependence of the fraction of samples crystallized is very far from an exponential function of time.  $P(t)$  is very far from a straight line in the linear-log plot in figure 3. It is, however, fitted almost perfectly (fit not shown) by the stretched exponential  $\exp[-(t/2.36 \times 10^8)^{0.55}]$  [18]. The large spread in the values of  $r_{SAM}$  results in a qualitative change in the behaviour of  $P(t)$ .

In systems where nucleation occurs on quenched clusters the nucleation rate varies dramatically from one sample to another, and so some samples crystallize rapidly while others do not crystallize even after much longer times. This prediction should be generic and is easy to test. If a set of, say, 10–100 nominally identical systems are set up and the fraction where nucleation has occurred plotted as a function of time, then it is easy to distinguish the exponential dependence on time in the absence of disorder, from the stretched exponential dependence that quenched disorder can cause.

To compare with Diao *et al's* work [6, 7], we also took a set of  $N_{SAM} = 48$  samples, each with  $N_{CL} = 1000$  quenched clusters. Then we calculated the fraction,  $f$ , of samples that have not nucleated, which is what is obtained in experiments. To do that we generated nucleation times for all 48 samples. We used the appropriate nucleation rate for each sample, and in each case generated a random number from an exponential distribution. The resulting  $f(t)$  is the dark blue curve in figure 3. We have fitted a stretched exponential function ( $= \exp[-(t/\tau)^\beta]$ ) to this data (dashed cyan curve) and obtain a good fit with an exponent  $\beta = 0.57$ , which is far from one. Thus fitting stretched exponentials to experimental data and obtaining a value for  $\beta$  that is significantly less than one would

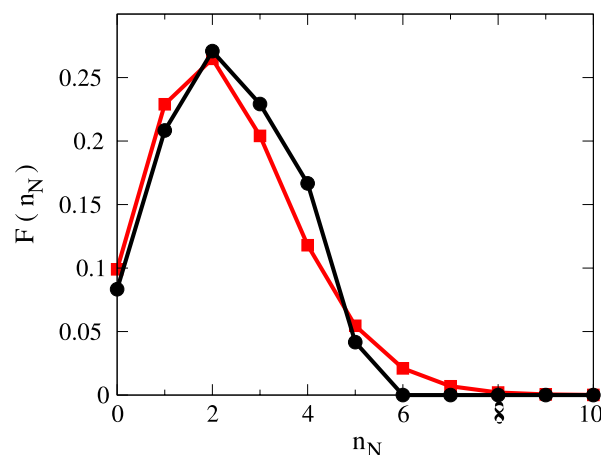
suggest that quenched disorder is causing the nucleation rate to be non-self-averaging in the experiments [18].

Nucleation is dominated by the largest clusters, in the sense that nucleation in a sample will almost certainly occur on one of its largest clusters. Thus, removing the largest clusters, for example by filtration as Parmar *et al* [3] did in lysozyme solutions, will dramatically slow nucleation. To see this we took our samples, removed all clusters with  $R_G \geq 5.5$  and then recalculated  $P(t)$ . The result is shown as the green curve in figure 3. Clearly the nucleation behaviour is dramatically different when the largest clusters are removed. This is just what Parmar *et al* found and, based on the findings here, it may well be a rather general result. Also, allowing a sample to ‘age’ in some way by allowing time for clusters to form and grow will result in larger clusters and dramatically faster nucleation. As the nucleation rate is so sensitive to cluster size, it is possible that in some systems the time to observe nucleation may be largely the time for clusters to grow and aggregate until they are large enough to support nucleation at an appreciable rate. ‘Ageing’ samples to change the crystallization behaviour is quite common in crystallization experiments from solution, see, for example, [19, 20].

An alternative way to quantitatively study nucleation is to measure not the time until nucleation, but the probability distribution function of the number of crystals that have formed at a given time. Both Galkin and Vekilov [21] and Selimović *et al* [22] count the number of (lysozyme) crystals in a number of samples and compare the result to a Poisson distribution. If nucleation is occurring at the same rate in each sample, if each nucleation event is independent, and if the time to grow large enough to be visible can be neglected, then the number of crystals should follow Poisson statistics. We have plotted a histogram of the number of crystals in the samples at a time  $t = 10^9$  cycles; assuming nucleation on one cluster does not affect nucleation on another cluster. The result deviates from Poisson statistics but not by a large amount. It appears that histograms of the number of crystals may be relatively insensitive to even the very large deviations from self-averaging that we have in our samples.

To calculate the data in figures 3 and 4 we averaged over  $N_{\text{SAM}} = 150$  and 48 samples. By comparing the data with that obtained using smaller values of  $N_{\text{SAM}}$  we have determined that the  $P(t)$  plots in figure 3 are close to the  $N_{\text{SAM}} \rightarrow \infty$  limit. We also varied  $N_{\text{CL}}$  and found that our finding that  $P(t)$  is well fitted by a stretched exponential with  $\beta \approx 0.5$  is robust with respect to variations in the system size (specified here by  $N_{\text{CL}}$ ). Changing  $N_{\text{SAM}}$  or  $N_{\text{CL}}$  does change figure 4 but the qualitative form is insensitive to the values of  $N_{\text{SAM}}$  and  $N_{\text{CL}}$ , the data is always reasonably close to, but not identical to, a Poisson distribution. So, we conclude that varying the size of the sample ( $N_{\text{CL}}$ ) over a large range does not alter our central finding that the sample-to-sample nucleation rate varies by orders of magnitude in this model, and hence  $P(t)$  is close to a stretched exponential. However, we leave a systematic study of scaling with system size  $N_{\text{CL}}$  to future work.

In conclusion, we have studied the effect of quenched disorder on nucleation in a simple model. We found that



**Figure 4.** Plot of the fraction of samples  $F(n_N)$ , where nucleation has occurred on  $n_N$  clusters, as a function of  $n_N$ . This is for  $N_{\text{SAM}} = 48$  samples after a time  $1 \times 10^9$  cycles, at which time the mean number of nucleation events per sample is 2.31. The data is the black circles and lines, which are compared to a Poisson distribution with the same mean, which is the red squares and lines.

quenched disorder has a large effect on an easily measurable experimental observable [6, 7]. This observable is the fraction of a set of nominally identical samples that have crystallized. We found that quenched disorder caused the fraction not crystallized to decay as a stretched exponential function of time. Our results are for a simple model but we believe that this result is generally applicable. This is because nucleation is known to be extremely sensitive to the details of the surface nucleation is occurring on [1, 2]. Here we found that varying the size of a cluster could change the rate by a factor of  $10^{10}$ , while work on crystallization has found nucleation rates that change by many orders of magnitude when the size of a pit [23] or the angle of a wedge [24] is varied. As the rate varies so widely from cluster to cluster, or from pit to pit, the total nucleation rate in a sample can be dominated by the rate on outliers such as unusually large clusters, or surface pits whose size and shape is just right for a crystal nucleus. Of course, properties that are dominated by a few outliers are those properties where self-averaging breaks down. As the number and exact dimensions of these rare clusters or pits vary randomly between one nominally identical sample and another, so does the nucleation rate, with consequences that are both important and straightforward to observe in experiment. Thus, we believe that quenched disorder may be generally useful in modelling and understanding the important problem of the nucleation of a new phase.

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