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Modelling Cluster Nucleation and Growth in Alloys

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Modelling Cluster Nucleation and Growth in Alloys

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Abstract

Attempts to understand and describe growth processes in material physico-chemical systems are often made using nucleation theory, which works well in the dilute limit. The range of validity of nucleation theoretical models can be explored using microscopic simulation models in which nucleating clusters can be counted and measured exactly. The Becker-Doring nucleation theory is described and its range of validity is discussed for binary alloy simulations using the Kawasaki exchange model in various concentration regimes. Graph labeling and enumeration techniques are employed to study the range of sizes of clusters present in nucleating systems.

Keywords: mathematical modelling; numerical methods; Monte Carlo simulation; cluster; nucleation; droplet; growth.

1 Introduction

Clusters are found to nucleate and grow in many different systems including sociological models as well as physical and chemical systems. Nucleation and droplet theories such as those based on the Becker-Doring model can be used to study the dynamics of a distribution of different clusters causes some to grow and others to evaporate. These theoretical models are quite general and as expected work very well in the dilute limit but from analysis alone, it is hard to assess to just how high a particle concentration they will continue to give good results.

This paper gives a summary of the general Becker-Doring theoretical approach to studying cluster distributions (sec-

tion 2) and makes some comparisons with simulated data of a binary system of growing clusters (section 3). Some ideas on the validity of the Becker-Doring approach and extensions are given in section 4.

2 Nucleation Theory

A cluster is of size l and the total system has cluster density of $n_l(t)$ per unit volume at time t so that by conservation of mass the volume fraction V_f occupied by all the clusters is: $V_f(t) = \int n(t) d\mathbf{r} = V_{\text{total}} \sum_{l=0}^{\text{inf}} n_l(t)$.

To avoid having infinities around the summation can in fact be up to $n_{l\text{max}}$ providing we can identify the maximum cluster size l^{max} . It is also useful to identify a special cluster size, denoted by l^* which will typically be the mean or median cluster size (or some other moment) in a distribution. We can also specify the different species or phases ϕ in a given system. By conservation we have $N(t) = \sum_{\phi=1}^k N_{\phi}(t)$, if there are k separate phases or species. Generally there will be one majority phase and the other phases form minorities against it as a background. We can choose to treat the background space or vacuum as the majority phase and consider only “actual” particle species as forming clusters, or we can treat the vacancies on a background matrix or lattice as “particles” in their own right. Clusters can be compact or not, but in any case they occupy some space and create an exclusion volume that cannot be occupied by other clusters. The density fractions of phases are therefore highly constrained and not all arrangements and combinations are possible.

There are various processes we can consider for a system of clusters, including both cluster growth and decay. It is con-

venient to consider nucleation theory based on growth and decay of clusters by monomer activation. In theories based on this idea, the cluster size changes by ± 1 for growth and decay. In some systems this may be sufficient to explain all behaviours, but it may be that the probabilities of clusters breaking up or merging is non-zero even when size changes are considerably greater than unity.

The central assumption behind droplet and cluster theories of growth in binary solutions is that it is the heterophase or droplet fluctuations which lead to the decay of metastable states. These theories are generally formulated in the dilute limit, where a small volume fraction of solute material is uniformly distributed in the solvent as a single phase state. Following a quench, droplet fluctuations start the nucleation process, and these droplets then grow or shrink in size according to the condensation and evaporation mechanisms available.

A convenient starting point for this approach is that of [1], whereby a rate equation can be set up to describe changes in the cluster distribution function. Let the number of the minority-phase clusters with a mass of l A-atoms be denoted by $n_l(t)$ per unit volume at time t . The rate equation for condensation and evaporation processes can be written as:

$$\begin{aligned} \frac{dn_l(t)}{dt} &= C_{l-1}^+ n_{l-1}(t) - C_l^+ n_l(t) + \\ &\quad C_{l+1}^- n_{l+1}(t) - C_l^- n_l(t), \quad l \geq 2 \\ \frac{dn_l(t)}{dt} &= C_1^+ n_1(t) + C_2^- n_2(t), \quad l = 1 \end{aligned} \quad (1)$$

The coefficients for condensation or growth of an l -cluster, C_l^+ and for evaporation or decay of an l -cluster, C_l^- are themselves functions of time. Their values must reflect the facts that we are only considering monomer activated processes, that is processes where a cluster increases or decreases its mass by a single atom, and that in a canonical simulation, the monomer population is finite. As clusters grow, the monomer population is depleted, and so C_l^+ will necessarily decrease with time. Equation 1 can be rewritten using the detailed balance condition for growth and decay that states:

$$C_l^+ n_l^{eq} = C_{l+1}^- n_{l+1}^{eq} = W(l, l' = 1) \quad (2)$$

Where $l' = 1$ denotes that we are only considering monomer activated processes, and W is the combined rate factor, and is strictly speaking time dependent itself, although it is treated here as constant in time. The rate equation is now parameterised by n_l^{eq} , the equilibrium or most probable cluster size distribution. The main task for a nucleation theory is to predict a form for this equilibrium cluster size distribution, by

some approximation [2, 3]. It is sufficient here to suppose that the equilibrium cluster distribution can be written as:

$$n_l^{eq} = n_0 e^{-\Delta F_l / k_b T} \quad (3)$$

after Fisher, in which n_0 is a constant, and ΔF_l is the non-classical droplet free energy. This approach is essentially that of an ideal gas law for a non-interacting assembly of droplets, and is correct in the dilute limit [2].

Following [4], the rate equation can now be recast as:

$$\begin{aligned} \frac{dn_l(t)}{dt} &= W(l-1, 1) \left[\frac{n_{l-1}(t)}{n_{l-1}^{eq}} - \frac{n_l(t)}{n_l^{eq}} \right] + \\ &\quad W(l+1, 1) \left[\frac{n_{l+1}(t)}{n_{l+1}^{eq}} - \frac{n_l(t)}{n_l^{eq}} \right] \end{aligned} \quad (4)$$

which is valid for $l \geq 2$, and expanding about l using:

$$\begin{aligned} \frac{n_{l\pm 1}(t)}{n_{l\pm 1}^{eq}} &= \frac{n_l}{n_l^{eq}} \pm \frac{\partial}{\partial l} \frac{n_l}{n_l^{eq}} + \frac{1}{2} \frac{\partial^2}{\partial l^2} \frac{n_l}{n_l^{eq}} + \dots \\ W(l-1, 1) &= W(l, 1) - \frac{\partial}{\partial l} W(l, 1) \end{aligned} \quad (5)$$

to yield:

$$\frac{\partial n_l(t)}{\partial t} = \frac{\partial}{\partial l} \left[W(l, 1) \frac{\partial}{\partial l} \frac{n_l(t)}{n_l^{eq}} \right] \quad (6)$$

which may be used to define a *cluster current* J_l :

$$\frac{\partial n_l(t)}{\partial t} = - \frac{\partial}{\partial l} J_l \quad (7)$$

since this is a continuity equation in cluster-size space $\{l\}$. This can be generalised for the cases where clusters grow and decay by addition and subtraction of more than one atom at a time, by allowing the case $l' \geq 1$.

$$J_l = - \sum_{l'} l'^2 W(l, l') \frac{\partial}{\partial l} \frac{n_l(t)}{n_l^{eq}} \quad (8)$$

This is instructive, but it is expected that the rate coefficients $W(l, l')$ are very small for high values of l' , and furthermore such processes are difficult to simulate using lattice models, since each cluster requires storage, over and above the efficient storage requirements for the lattice sites.

It is convenient to define a cluster reaction rate R_l for processes involving $l \Rightarrow l'$ as:

$$R_l = \frac{1}{n_l^{eq}} \sum_{l'} l'^2 W(l, l') \quad (9)$$

and expanding the derivative in J_l and assuming Fisher's form for n_l^{eq} in equation 3 above we obtain:

$$J_l = - \left[R_l \frac{\partial}{\partial l} n_l(t) - \frac{\partial}{\partial l} \frac{\Delta F_l}{k_b T} R_l n_l(t) \right] \quad (10)$$

This illustrates that J_l contains two terms: a diffusive term: $-R_l \frac{\partial}{\partial l} n_l(t)$ and a drift term: $\frac{\partial}{\partial l} \frac{\Delta F_l}{k_b T} R_l n_l(t)$.

Only the drift term contains explicit dependence on the *form* of the equilibrium distribution. These two terms are of opposite sign, and it is supposed in cluster theories that there is a critical droplet size l^* at which the two terms are equal. For $l < l^*$ the drift term acts against the diffusion so that if a large droplet *does* form, it is likely to *decay* again. However, for the case when $l > l^*$ the drift term acts with the diffusion and hence super-critical droplets can grow steadily.

Following a quench to a metastable state, there is a transient time during which the cluster concentration $n_l(t)$ grows for clusters less than the critical cluster size $l \lesssim l^*$, until clusters saturate weakly at their equilibrium sizes. After this time lag, the nucleation current J_{l^*} around the maximum cluster size, has almost reached a steady state value known as *the* nucleation rate J .

So far the formulation of nucleation theory has only relied on the approximation of taking a specific form for the *unknown* droplet free energy function. Further progress can not be made without building in the restrictions mentioned earlier, of having a large *dilute* system, with a *fixed* monomer population density, and the additional constraint, that large droplets once formed, are removed from the system. This latter prevents all the solute material from precipitating out of solution and allows us to solve the steady state condition for the dilute system. Following Becker and Doring [4], these constraints can be expressed by:

$$\lim_{l \rightarrow 0} \frac{n_l(t)}{n_l^{eq}} = 1 \quad (11)$$

for the requirement that the monomer population density is fixed, and

$$\lim_{l \rightarrow \infty} \frac{n_l(t)}{n_l^{eq}} = 0 \quad (12)$$

for the removal of large droplets. The steady state cluster concentration n_l^{ss} can be obtained using :

$$\frac{\partial n_l^{ss}}{\partial t} = 0 \quad (13)$$

requiring that $J_l \equiv J$ independent of l . Hence:

$$J = n_l^{eq} R_l \frac{d n_l^{ss}}{d l n_l^{eq}} \quad (14)$$

which gives:

$$\frac{n_l^{ss}}{n_l^{eq}} = J \int_l^\infty \frac{dl'}{R_{l'} n_{l'}^{eq}} \quad (15)$$

with

$$J = \frac{1}{\int_0^\infty \frac{dl}{R_l n_l^{eq}}} \quad (16)$$

using the boundary equations 11 and 12. If l^* is large, the free energy term in R_l can be expanded as a quadratic around l^* as:

$$\Delta F_l \approx R_{l^*} - \frac{1}{2} g k_b T (l - l^*)^2 \quad (17)$$

where g is a constant. Equation 15 can be recast as:

$$\frac{n_l^{ss}}{n_l^{eq}} = \frac{1}{2} \left\{ 1 - \operatorname{erf} \left(\frac{l - l^*}{\sqrt{\frac{g}{2}}} \right) \right\} \quad (18)$$

The meaning of the parameter g is then to control the width of the region in which the ratio $\frac{n_l^{ss}}{n_l^{eq}}$ changes from unity to zero. This parameter is known as the Zeldovitch parameter [5].

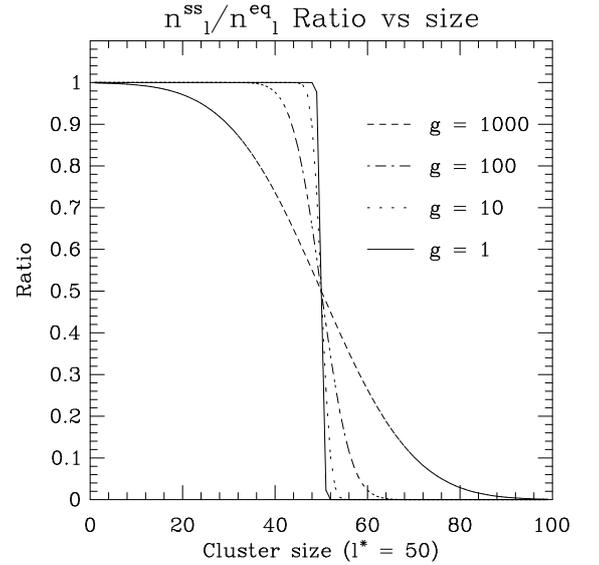


Figure 1: The value of the ratio $\frac{n_l^{ss}}{n_l^{eq}}$ for various values of the Zeldovitch parameter g .

The ratio in equation 18 is illustrated for various values of the Zeldovitch parameter g in figure 1. This implies that $\frac{n_l^{ss}}{n_l^{eq}}$ is close to unity around $l \lesssim l^*$ and goes to zero rapidly, for cluster sizes greater than l^* . This justifies the idea that the critical cluster size is a useful concept and can be employed as a cutoff on the full distribution.

3 Simulation Experiments

Various model systems can be set up to simulate a nucleating and growing system of particle clusters. The Kawasaki or “binary alloy” model is isomorphic to the Ising model [6] on a square lattice. A Monte Carlo procedure is used to evolve a fixed number of “spin-up” or “species-A” sites which can move around the lattice by pair-exchanging with spin-down or species-B sites. The normal nearest-neighbour Ising model coupling is used so that ferromagnetic coupling corresponds to like-like attraction, and unlike-unlike repulsion. This model is a convenient way of producing a set of droplet configurations, parameterised by the quench temperature (expressed as a fraction of the critical temperature) and the volume fraction of species-A sites.

Figure 2 shows that for temperatures well above T_c , there is little phase separation with time, and the configuration is qualitatively similar to that of the nearly infinite temperature, as represented by a completely random start. At the higher concentrations, however, the A-atoms are forced to interact more and there *is* some significant domain formation. This increases dramatically below the transition temperature and the greatest characteristic domain size is for the 50% system just below T_c . In this system there is enough thermal energy for growth to occur quickly, and the process is rapidly dominated by a surface tension driven coarsening mechanism. At lower temperatures, there is insufficient thermal energy available, and while large length scale percolated structures still form, they coarsen much more slowly. The percolation transition is not a fixed property of the lattice, and has been shown to depend on the quench temperature [7]. At high temperatures, it is not significantly modified from 0.59275 [8] for site percolation on the square lattice. This is lowered considerably at temperatures below T_c and percolated structures exist in the 40% configuration, just below T_c .

On further cooling however, the domains coarsen so quickly that they do not percolate. Furthermore, at very low temperatures, the monomer population drops considerably, and since the monomers are the only means of concentration transport, the domains remain smaller and more compact. At such low temperatures, the only mechanism for re-arrangement is that of surface tension, whereby atoms can move along the surface of a domain, without the need for any thermal excitation to break a bond. At low concentrations, growth is even more limited by the size of the monomer populations. Monomers have to travel further between the growing domains, and at low temperatures are much less likely to be able to escape capture by the domains. The diagram shows that the domains at $\frac{T_c}{2}$ are much more compact and symmetric than those at $\frac{T_c}{4}$.

Figure 2 give a qualitative feel for the phase diagram of the binary alloy. There is no evidence to suggest that the mechanisms in a three dimensional system are different from that of the two dimensional system, although the numerical values of the transition temperature and percolation limit are altered [9].

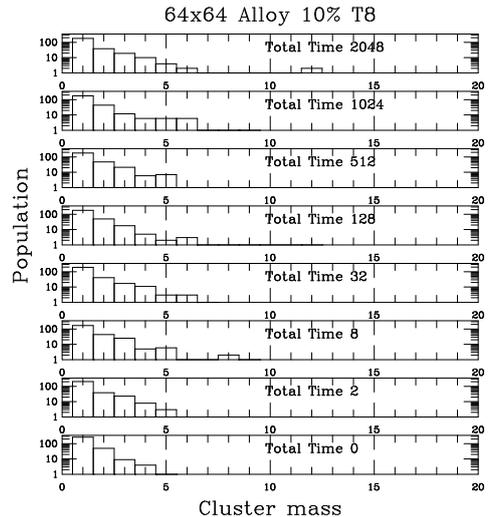


Figure 3: Cluster mass distribution in a simulation of a 64×64 binary alloy with minority phase concentration of 10% and at temperature $T = \frac{T_c}{4}$. The distribution remains well approximated by Fisher’s exponential form.

Using the simulation configurations generated by the Kawasaki model it is possible to apply graph labeling and analysis methods [10] and to exactly enumerate clusters and histogram them by size. Figures 3 and 4 show the cluster distributions as measured from typical model systems. These illustrate that although Fisher’s exponential form for the free energy is useful at high temperatures, it breaks down for quenches to temperatures below the critical temperature. This is attributable to the depletion of the crucial monomers in the simulation, although this would in principle extend to other small mobile clusters, in a real alloy system. There are clearly other deficiencies with the Becker-Doring theory, as it fails to take proper account of the particle interactions.

4 Discussion and Conclusions

The Becker-Doring model appears to provide a reasonable qualitative description of nucleation and growth processes

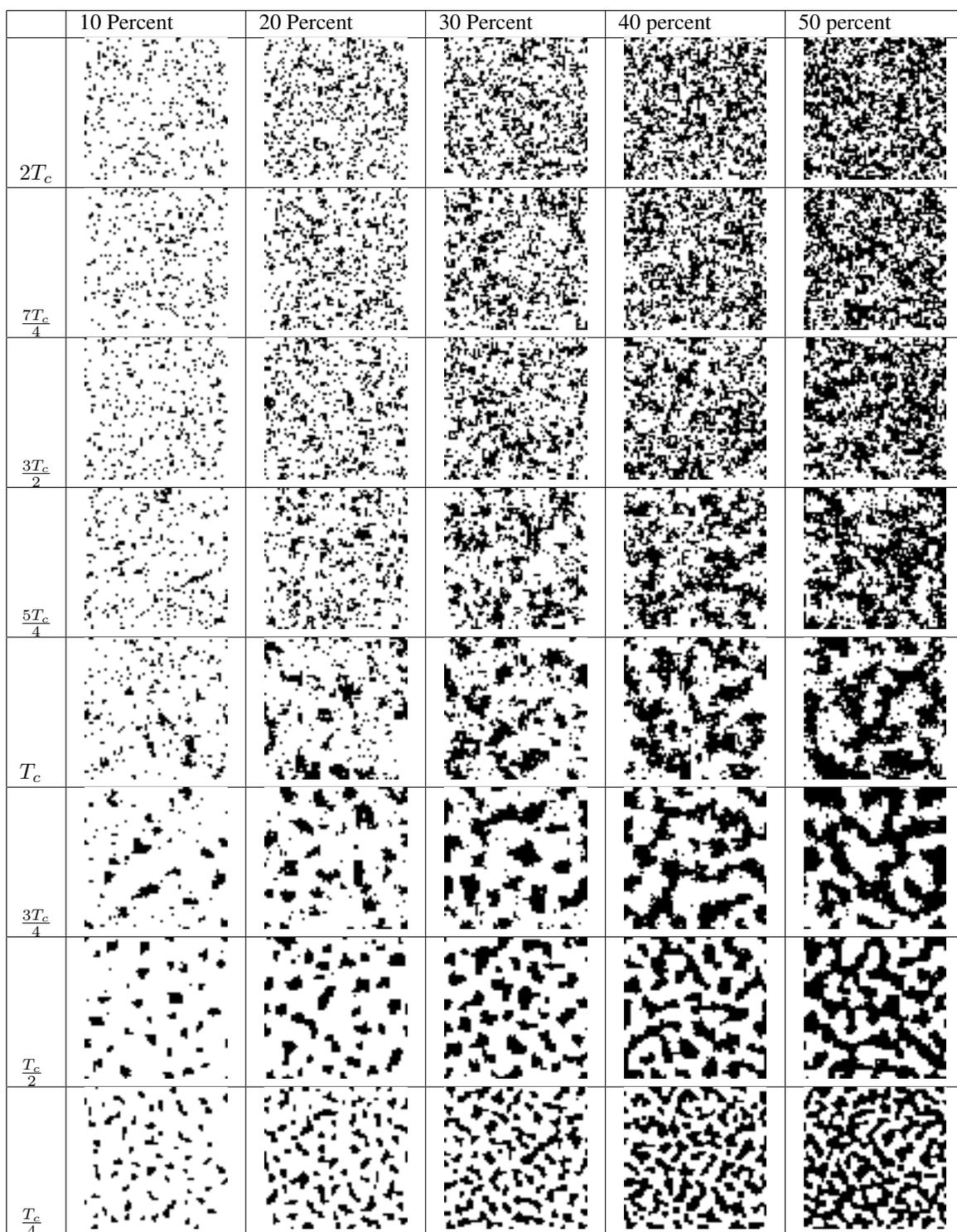


Figure 2: Binary alloy phase diagram showing snapshots of a 64×64 site alloy model at various fractions of the Onsager T_c after 2048 Monte-Carlo time steps following a quench from an initially random configuration. Quench temperature is thus shown vertically with concentration shown horizontally.

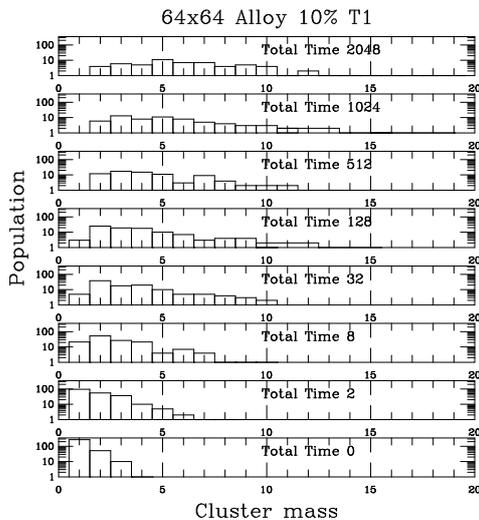


Figure 4: Cluster mass distribution in a simulation of a 64×64 binary alloy with minority phase concentration of 10% and at temperature $T = 2T_c$. The monomer population is depleted and the distribution is no longer approximated by Fisher's exponential form. It is better described by a log-normal distribution or a Maxwellian distribution.

up to the percolation threshold. While this is $f_v \approx 0.59$ for a square lattice with random distribution, for an annealing Kawasaki system it can be much lower – around 0.2 – 0.3 for the model systems shown. Above these values the system definitely does percolate and a single cluster can span almost the whole system.

Some progress has been made in improving the range validity of the Becker-Doring theory [11]. Most notably Binder's cluster theory generalises the cluster distribution to more than one co-ordinate. Other cluster properties such as the cluster surface area and other characteristics of its deviation from sphericity can be employed as additional co-ordinates in cluster space. The problem then becomes one of determining the *vector* nucleation rate, and the critical nucleation co-ordinates in this vector space [12]. This goes some way towards better approximating the interactions amongst sites and clusters, but there is still a need for a more applicable model for the free energy of a droplet than 3. Explicit account needs to be taken of the diminishing population of monomers and other mobile clusters, during the quench. There is also future scope for a comparative study using simulations where clusters can move and aggregate together and cluster-cluster interactions are important.

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