Kinetic Monte-Carlo simulations of sintering

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We simulate the sintering of particle aggregates due to surface diffusion. As a method we use Kinetic Monte-Carlo simulations in which elasticity can explicitly be taken into account. Therefore it is possible to investigate the shape relaxation of aggregates also under the influence of an external pressure. Without elasticity we investigate the relaxation time and surface evolution of sintering aggregates and compare the simulations with the classical Koch-Friedlander theory. Deviations from the theoretical predictions will be discussed.

1 INTRODUCTION

One interesting aspect of powder processing is thermal sintering: Due to atomic diffusion solid bridges between particles form and grow. This lowers the surface free energy. If one waits long enough, complete coalescence of the particle aggregate will occur. The typical time scales depend on the particle sizes and shapes, the material type and the prevailing temperature. Here we address open questions concerning the sintering dynamics of large aggregates.

It has long been known, that the time for the sintering of two identical particles is proportional to the 4th power of the radius of the final particle. This is at least true for large particles above the roughening temperature (Nichols 1966). For lower temperatures the equilibration time increases exponentially (Combe et al. 2000).

In earlier investigations elasticity has not explicitly been taken into account, i.e. the atoms were restricted to discrete lattice positions. However, an elastic deformation changes the diffusion constant and hence influences the sintering process. For example, the lattice constant of nano-particles may differ from its bulk value due to surface tension, or particles may be compressed differently in a powder under external load, depending on their position in the contact force network. Therefore we developed a program where the atoms are allowed to be displaced from their lattice sites in order to minimize the total elastic energy of the system.

2 MODEL

We use a three dimensional Kinetic Monte-Carlo (KMC) method to simulate the sintering of aggregates of nano-particles on a fcc lattice. This means that grain boundaries are neglected in this paper. In our simulation the atomic displacements are calculated by finding the nearest local energy minimum by means of a conjugate gradient method (Press et al. 1992). In order to save computing time, we update only the neighborhood of diffusing atoms, and relax the whole system elastically only in the beginning and, if necessary, again after rather large time intervals. The activation energies for the hopping rates then depend on the relaxed real positions of the atoms.

The atoms interact via a Lennard-Jones potential. We calculate the binding energies \( E_{b,i} \) as the sum of the pair interactions up to the fourth nearest neighbor on the underlying fcc-lattice. In a diffusion step an atom hops from its initial position (nominal lattice site \( i \)) to an unoccupied one, which is next to \( i \) on the underlying fcc-lattice. The activation energy for such a move is the difference between the energy at the saddle point and the energy at the initial position of the atom. For the calculation of the saddle point energy \( E_{sp} \) one has to distinguish two cases: The final site may be stable (at least three occupied neighbors) or unstable. In the latter case one can actually not find a local energy minimum at this site (see Fig. 1). Then the atom continues to move from this intermediate site to a randomly chosen stable final po-

Figure 1. 2d illustration for an atom that hops to a stable (a), respectively to an unstable intermediate position (b) from where it immediately continues to one of the neighboring stable sites (c).
Accordingly the saddle point energy for the first case is taken as

$$E_{\text{sp}} = E_{\text{sp},0} + \alpha \frac{1}{2} (E'_{b,i} + E'_{b,f}).$$

(1)

The first term is a constant parameter. The second one describes the strain dependence of the saddle point energy. $E'_{b,i}$ and $E'_{b,f}$ are the strain dependent contributions to the binding energy at the initial (‘i’) and final (‘f’) atom positions. The average is taken to guarantee symmetry and $\alpha$ is an empirical parameter. This ansatz is justified by the finding that the binding as well as the saddle point energy depend approximately linearly on the strain. (Schroeder & Wolf 1996)

If the hop ends in an unstable, intermediate position, this is approximately regarded as the saddle point. We calculate the energy of the atom at the intermediate site giving it the average displacement of the stable atoms on the neighboring sites. This energy is taken as saddle point energy in the second case.

In the KMC simulation every process is selected according to its corresponding rate which is calculated from the activation energy by:

$$q = \nu \exp (-\beta E_a).$$

(2)

$\nu$ is a fixed attempt frequency, $\beta = 1/k_B T$ with the Boltzmann factor $k_B$ and the absolute temperature $T$.

Without elasticity $E_{b,i}$ corresponds to the bond counting model (Newman & Barkema 1999) and the strain dependent terms in (1) vanish.

3 RESULTS

3.1 Relaxation of two clusters

Crystalline particles above their roughening temperature are not faceted but round. If they have equal size, it is well known that the equilibration time, in which the two particles coalesce into a single one, is:

$$\tau \propto N^{4/3},$$

(3)

where $N \propto r^3$ is the total number of atoms.

But what happens if the two diameters differ? In Fig. 2 the equilibration time is plotted versus the number of atoms. If (3) were valid, the double logarithmic plot should give a straight line with slope $4/3$. Instead we find that $\tau \propto r^4$ with the reduced radius of the two particles,

$$r = \left( \frac{1}{R_1} + \frac{1}{R_2} \right)^{-1}$$

(4)

(see Fig. 3).

3.2 Surface evolution during sintering

The surface evolution during the sintering process is usually described by the Koch-Friedlander theory (Koch & Friedlander 1990):

$$\frac{dA}{dt} = -A - A_{\text{eq}} / \tau.$$  

(5)

Here $A(t)$ is the surface of the agglomerate, $A_{\text{eq}}$ the surface in equilibrium, $\tau$ a relaxation time. However, this equation is interpreted and applied in several different ways in the literature. Sometimes $\tau$ and $A_{\text{eq}}$ are viewed as constants, meaning the global relaxation time and the equilibrium surface area the whole aggregate will have after coalescence. In this case Eq. (5) describes an exponential decay.

In many cases $\tau$ and $A_{\text{eq}}$ are regarded as time dependent, local quantities. One assumes that the aggregate coarsens homogeneously by pairwise coalescence of particles. As explained above, the time constant $\tau$ is then determined by the current radius of the constituent particles, which after $n$ pairwise coalescence steps is $2^{n/3}$ times the radius of the initial primary particles. The sintering becomes more slowly.
Using a continuously varying
\[ \tau(t) \propto (V/A(t))^4, \]  
where \( V \) is the constant solid volume of the aggregate and determines \( A_{eq} \), the theory has recently been successfully applied to experimental sintering data of Ni-particles to calculate the activation energy of the relevant diffusion process, whereas the evaluation with a constant \( \tau \) gives unreasonable energy values. (Tsyganov et al. 2004)

What is missing, is a microscopic justification of Eq. (5). Therefore we simulated the sintering of agglomerates and measured the surface area. Typical snapshots are shown in Fig. 4. We fitted the surface area with the analytical solutions obtained for constant \( \tau \) or with Eq. (6), respectively. The constant \( A_{eq} \) was obtained as the average asymptotic surface area for large times.

One can distinguish two different stages in which either a constant or a variable \( \tau \) gives a better description of the surface dynamics. At early times when the particles successively merge together and the average radius increases, the fit with a variable \( \tau \) gives a better description (Fig. 5a). When the average diffusion length does not increase significantly any more, a constant \( \tau \) is a better assumption (Fig. 5b), but surprisingly its value is smaller than at the end of the early time regime with variable \( \tau \).

3.3 Influence of elasticity on sintering
In order to understand the influence of an external stress we allowed elastic displacements of the atoms as described above. We set up a configuration of two particles with periodic boundary conditions in \( x \)-direction.

The strain is controlled by the total system size in \( x \)-direction, which is kept constant during each simulation.

In Fig. 6 an initial and final configuration are shown. One expects that the final configuration is reached faster under compression than under tension. We measure the average squared radius along the \( x \) axis:

\[ R^2(t) = \frac{1}{N} \sum_{i=1}^{N} [(y_i - y_s)^2 + (z_i - z_s)^2] \]  

with

\[ y_s = \frac{1}{N} \sum_{i=1}^{N} y_i \quad \text{and} \quad z_s = \frac{1}{N} \sum_{i=1}^{N} z_i \]  

The value \( R^2(t) \) reflects how far away the system is from the thermodynamic equilibrium state. Its time dependence is plotted in Fig. 7. It is scaled with the initial value, \( R^2(t = 0) \), in order to eliminate the effect of the Poisson ratio for a better comparison of the curves for different initial strains. The initial configuration (upper part of Fig. 5) are two spheres, whose surface is not in thermal equilibrium. Therefore initially the curves raise beyond 1 due to surface roughening.

Looking at the relaxation behaviour we find that both systems evolve asymptotically similarly. How-
ever, the relaxation process is faster for compressive strain which becomes obvious from the larger slope in the beginning of the coalescence. The equilibrium state is therefore reached earlier. The reason is that $\alpha > 1$ in Eq. (1) for hopping diffusion in Lennard-Jones-Systems, and the binding of atoms on the surface becomes weaker under lateral compression of the surface (Schroeder & Wolf 1996). This implies that the activation energy decreases under lateral compression.

The cylindrical configuration reached at the end of our simulation probably is only metastable: Due to the periodic boundary conditions it corresponds to an infinitely long solid cylinder which should undergo a Rayleigh instability and split up into separate spheres. We think that thermal fluctuations in this direction are the reason why $\dot{R}$ increases again for larger times.

4 CONCLUSIONS AND OUTLOOK

We developed a 3d-KMC simulation program to model the sintering of nano-particles. The special feature of the program is that atoms are not fixed at their lattice sites in contrast to common KMC codes. This allows us to analyse the effect of elasticity on the sintering behavior.

The validation of the Koch-Friedlander theory leads to interesting results: The assumption of a constant $\tau$ can only be applied if the characteristic diffusion length does not change. At the beginning of the sintering process of an agglomerate consisting of many clusters the characteristic length scale changes. In this case the assumption of a variable $\tau$ gives a better description of the surface evolution.

We found that the equilibration time for two clusters of different size follows the $r^4$ power law with the reduced radius (4).

The influence of elasticity for our set of parameters is only felt in the case of an external force. There it is found that compressive stress leads to faster relaxation. Without external stress it seems that the influence of the surface tension is negligible. This needs not always be the case, as our potential does not show strong surface tension.

Therefore a next step would be to choose a potential that shows a stronger surface tension. So far grain boundaries were neglected as we used a continuous fcc lattice. In the current development of the code these grain boundaries will be implemented.

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REFERENCES

Combe, N., Jensen, P., & Pimpinelli, A. 2000, 7. Changing shapes in the nanoworld. Phys. Rev. Lett. 85(1): 110.

Koch, W. & Friedlander, S. 1990. The effect of particle coalescence on the surface area of a coagulating aerosol. Journal of Colloid and Interface Science 140(2): 419–427.

Newman, M. E. & Barkema, G. T. 1999. Monte Carlo methods in statistical physics (2. ed.). Oxford: Clarendon Press.

Nichols, F. A. 1966, 6. Coalescence of two spheres by surfacediffusion. J. Appl. Phys. 37(7): 2805–2808.

Press, W. H., Teukolsky, S. A., Vetterling, W. T., & Flannery, B. P. 1992. Numerical Recipes in C - The Art of Scientific Computing. Cambridge University Press.

Schroeder, M. & Wolf, D. 1996. Diffusion on strained surfaces. Surf. Sci. 375: 129–140.

Tsyganov, S., Rellinghaus, B., Kästner, J., Kaufeldt, T., Westerhoff, F., & Wolf, D. 2004. Analysis of Ni nanoparticle gas phase sintering. submitted to PRB.