Equilibrium Neck Shapes For Initial Stages of Solid-State Sintering Due to Surface Diffusion In a Disk Model of Clays

I. Medved*1,2, J. Moravčíková
1 Department of Physics, Constantine the Philosopher University, 949 74 Nitra, Slovakia
2 Department of Materials Engineering and Chemistry, Czech Technical University, 166 29 Prague, Czech Republic

Abstract:
We study equilibrium neck shapes corresponding to initial stages of solid-state sintering, using a microscopic model of clays in which particles have a uniform disk shape with a microscale diameter R and a nanoscale thickness δ = R/100. Particles are stacked on top of each other, forming vertical piles of various heights ranging from h = δ to h = 10δ. Pores are formed in the spaces between any three touching piles of the same height. Assuming that surface diffusion is the dominant sintering mechanism and considering a simplified form of the neck configuration, we derive equilibrium neck shapes by minimizing a neck surface free energy when a neck volume V fixed. We allow for the anisotropy of the surface free energy, using a single anisotropy parameter q. We discuss the dependence of the obtained neck shapes on the neck volume V, pore height h, and anisotropy parameter q.

Keywords: Solid-state sintering; Surface diffusion; Surface free energy

1. Introduction
Solid-state sintering has been intensively studied from the theoretical point of view (see [1] and references given there) since the classical works of Frenkel [2], Kuczynski [3], Mackenzie and Shuttleworth [4], Kingery and Berg [5], and Coble [6] appeared and proved to provide a successful approach to the understanding of this phenomenon. Models for early sintering stages most often assume particles of a spherical shape, which is usually a good approximation in many applications. However, this is not so for clay minerals like kaolinite in which particles have flat shapes resembling disks [7].

Monteiro and Vieira [8] introduced a more realistic sintering model for clays in which all particles had a disk shape with a thickness δ that was much smaller than the radius R (see Fig. 1(a)). Their model assumes that particles lie in horizontal layers in the close-packed arrangement in each layer as shown in Fig. 1(b). Three sequences of layers were considered: (1) all layers have the same horizontal positions (called the AAA sequence); (2) alternating pairs of layers such that in each pair the lower layer is shifted in the horizontal direction with respect to the upper one by the shift s1 shown in Fig. 1(b) (the ABAB sequence); (3) alternating triples of layers such that in each triple the middle and lower layers are shifted with respect to the upper one by the shifts s1 and s2, respectively, shown in Fig. 1(b) (the
Pores correspond to the empty spaces that are formed between the disk particles (see Fig. 1(c)). Realizing that sintering mechanisms in this disk model are closely related to the nanoscale thickness of particles, it turned out that a faster consolidation occurs for disk particles than for spherical particles [8]. However, rather surprisingly, it was assumed that the neck shape is flat in the horizontal direction and has a finite curvature (set equal to $\delta/2$) only in the vertical direction.

In this paper, we wish to elaborate on the shape of the neck formed during initial stages of sintering for a disk model of clays that takes into account several aspects neglected or not considered in [8]. Namely, we consider a geometric arrangement of disk particles in which pores of various heights can occur, ranging from the nanoscale height $h = \delta$ to the microscale height chosen as $h = 10\delta$. This allows us to compare the neck shapes in nanosized and microsized pores and find out whether there are differences between the two. Moreover, we do not assume that necks have pre-fixed shapes, but we derive equilibrium shapes by minimizing the corresponding surface free energy. To this end, we suppose a simplified geometry of the shapes that, however, allows for the main curvatures to be finite both in the vertical and horizontal directions. The curvature values are evaluated for given pore heights $h$ and neck volumes $V$, considering a surface free energy density, $\gamma_s$, with a weak, medium, and strong anisotropy given by a single parameter, $q$. It will turn out that a single parameter (chosen as the vertical curvature) is sufficient to this end, which is a simplest possible scenario.

The equilibrium neck shapes thus obtained cannot be, in general, expected to coincide with the true neck shapes developed during a sintering process. Nevertheless, they may provide quite a realistic approximation, at least in the limit of a quasistatic regime. In addition, they may describe the final neck shapes evolved after clay samples are heated to and held at a specific temperature lying within the range in which solid-state sintering occurs. Our analysis is limited to initial stages of sintering (until about a half of the total volume of a pore is closed), supposing that surface diffusion is the dominant mechanism of the sintering process [8,9].

2. Model

We consider a model of clays in which (i) disk particles are arranged in close-packed layers shown in Fig. 1(b) and (ii) layers are placed on top of each other with no mutual shift of particles or with a shift $s_1$ or $s_2$. Thus, first few layers may have the same horizontal position, then the next few layers may be shifted by $s_1$ each, then the next few layers may be shifted by $s_2$ each (or not shifted at all), etc. As a result, vertical cylindrical piles of particles with a varying height $h$ are formed (in a given pile, the particles are on top of each other). Pores correspond to the spaces that lie between any three neighboring (and touching) piles (c.f. Fig. 1(c)). We shall consider pores with heights $h = \delta, \ldots, 10\delta$ with $\delta = R/100$. A small value of the height (say, $h = \delta$ and $h = 2\delta$) corresponds to nanosized pores, whereas a larger value of the height (say, $h = 9\delta$ and $h = 10\delta$) to microsized pores.

Using this disk model, we shall study the equilibrium shapes of pores during initial stages of a solid-state sintering process. It is assumed that the dominant sintering mechanism is the surface diffusion [8,9] and that, in initial stages, three equally growing necks of negative curvature are formed in a pore (all the way from its bottom to its top), one neck in each of the three pore corners shown in Fig. 1(c).

The geometrical shape of the necks is in general determined by the mass transport mechanisms occurring during sintering. As a rule, it is a very complex kinetic problem to calculate the shape in a realistic manner (see [10–16], for example). Nevertheless, physically plausible results can be often obtained in a much more straightforward way if approximate
shape geometry is assumed a priori, like in the classical spherical particle model [5] or in a disk model [8].

Fig. 1. (a) A disk particle. (b) The close-packed arrangement of particles in a layer (a view from the top). (c) A pore between three neighboring piles of particles. In initial stages of sintering, necks of the same shape are formed in the three pore corners K1, K2, and K3.

We shall adopt an analogous strategy here, assuming that the neck surface has the following simplified geometry (see Fig. 2):

a) at a given horizontal position, $\lambda$, between 0 (the bottom of the pore) and $h$ (the top of the pore), the neck surface is a portion (an arc) of the horizontal circle of a radius $r_1(\lambda)$ that is tangent to the pore boundary (at two points denoted as $A$ and $B$ in Fig. 2); 
b) the centers, $C_1$, of the segments $AB$ at various positions $\lambda$ form an arc of the vertical circle with a radius $r_2 \geq h/2$ and a center, $C_2$, lying at $\lambda = h/2$ and at a horizontal distance $\ell \geq r_2$ from the pore corner.

Fig. 2. The simplified geometry of the neck surface.

Thus, the neck surface is the set of points $P(\lambda, \alpha) = (X,Y,Z)$ given by two parameters $\lambda$ and $\alpha$ as
where \( x(\lambda) \) is the horizontal distance of \( C_1 \) from the pore corner at the height \( \lambda \), \( \alpha \) is the angle shown in Fig. 1(b) with \( \alpha_0(\lambda) = \arccos[x(\lambda)/R] \) being its maximal value, and \( r_1(\lambda) = R[1/w(\lambda) - 1] \) with \( w(\lambda) = \{1 - [x(\lambda)/R]^2\}^{1/2} \).

Fig. 3. A volume element of the neck between the heights \( \lambda \) and \( \lambda + d\lambda \). The point Q lies on the particle surface at the height \( \lambda \) and has the same \( Y \) and \( Z \) coordinates as \( P(\lambda, \alpha) \).

Obviously, the model form (1) is rather simple to describe the neck shape in initial stages of sintering of disk clay particles with total accuracy because it does not account for several, possibly relevant factors. First, it is generally assumed that surface diffusion conserves the volumes of pores, while the model actually implies that densification is described. However, it may be well supposed that surface diffusion changes primarily the lateral dimensions (the radius \( R \)) of the disk particles rather than their height \( h \leq R/10 \) so that the model should yield reasonable results due to the fact that the changes in the radius \( R \gg h \) (and, thus, in the pore volume) might be neglected in a first approximation, especially in early stages of sintering. Second, in the neck shape (1) the dihedral angle is taken as \( \psi = \pi/2 \) since grain boundary diffusion is neglected \([8,9]\): taking \( \gamma_b \approx 0 \), we have \( \psi = \arccos(\gamma_b/2\gamma_s) \approx \pi/2 \). Finally, the neck surface (1) is not tangential to the horizontal surfaces of the particles. Although this should be the case, the associated corrections to the neck surface (1) should concern only its parts very close to the particles horizontal surfaces, where the vertical curvature should be much larger than \( r_2 \). Since this would change the neck geometry only within a rather small portion of its surface, the corresponding correction to the neck surface is neglected here. In conclusion, in spite of the simplicity of the model shape geometry (1), the latter can be considered to be a reasonable approximation to the true neck shape and, hence, worth of a more detailed analysis.

The equilibrium shape of the model neck surface (1) is such that the surface free energy

\[
F = \int_S \gamma_s dS = 4 \int_{\lambda=0}^{h/2} d\lambda \ r_1(\lambda) \int_{\alpha=0}^{\alpha(\lambda)} d\alpha \ \gamma_s(\lambda, \alpha) \ D(\lambda, \alpha) \quad (2)
\]

is minimal on condition that the neck volume

\[
V = \int_V dV = 4 \int_{\lambda=0}^{h/2} d\lambda \ r_1(\lambda) \int_{\alpha=0}^{\alpha(\lambda)} d\alpha \ H(\lambda, \alpha) \ D(\lambda, \alpha) \cos \alpha \quad (3)
\]
is given. Here $\gamma_s(\lambda, \alpha)$ is a generally anisotropic surface free energy density at the point $P(\lambda, \alpha) = (X, Y, Z)$ on the neck surface, the factor $D(\lambda, \alpha)$ is such that the distance of the points $P(\lambda, \alpha)$ and $P(\lambda + d\lambda, \alpha)$ is $D(\lambda, \alpha)d\lambda$ (up to the first order in $d\lambda$), and $H(\lambda, \alpha)$ is the distance of the point $P(\lambda, \alpha) = (X, Y, Z)$ and the point $Q = (X', Y, Z)$ lying on the pore boundary as shown in Fig. 3. Hence,

$$D(\lambda, \alpha) = [a(\lambda) + b(\lambda) \cos \alpha]^{1/2},$$

$$H(\lambda, \alpha) = \frac{x(\lambda)}{w(\lambda)} - r_i(\lambda) \cos \alpha - \{r_i(\lambda)[2R - r_i(\lambda) \sin \alpha] \sin \alpha\}^{1/2},$$

where

$$a(\lambda) = 1 + \frac{[1 + (x(\lambda)/R)^2][x'(\lambda)]^2}{w^0(\lambda)}, \quad b(\lambda) = -\frac{2[x(\lambda)/R][x'(\lambda)]^2}{w^0(\lambda)}.$$

with $x'(\lambda)$ denoting the derivative $dx(\lambda)/d\lambda$.

Fig. 4. The dependence of the function $g$ on $\lambda$ and $\alpha$. The minimal value of $g$ is equal to $g_{\min} = g(0, \alpha_0(0)) = 1 + (1 - 2\xi_0^2 + 2\xi_0^4)q$ with $\xi_0 = x(0)/R$, while its maximal value is equal to $g_{\max} = g(h/2, 0) = 1 + q$.

Of course, during a real sintering process the shape of a forming neck does not coincide with the equilibrium shape, this can be supposed to be true only if the process is performed in a quasi-equilibrium regime. More properly, the equilibrium neck shape is formed when the temperature in a sample is increased to a fixed value within the range of initial solid-state sintering at which only a small fraction of pores is filled. Assuming such a case, let us now evaluate a minimal value of the surface free energy $F$ for a given neck.
volume $V$. To this end, we shall consider the anisotropic surface free energy density that is often used in the study of crystal growth by surface diffusion [17–19]. Namely, $\gamma(\lambda, \alpha) = \gamma_0[1 + q(n_1^4 + n_2^4 + n_3^4)]$, where $\gamma_0$ and $q$ are constants and $(n_1, n_2, n_3)$ is the normal vector to the neck surface at a point $P(\lambda, \alpha)$. Hence, $\gamma(\lambda, \alpha) = \gamma_0 g(x(\lambda), \alpha)$ with

$$g(x, \alpha) = 1 + q \frac{3 + \cos 4\alpha + 4[\cos \alpha - (x/R)^4(x'/w)^4]}{4 + [\cos \alpha - (x/R)]^2(x'/w)^2}.$$

The parameter $q$ must be chosen positive in order to correspond to a surface diffusion process: then $\gamma_s$ is larger near the center of the neck surface than near its boundary (see Fig. 4), yielding a concave equilibrium surface in agreement with our physical situation.

Given $h$ and $q$, both $F$ and $V$ can be evaluated from Eqs. (2) and (3) as soon as one knows the function $x(\lambda)$; the values of all other involved quantities like $\alpha_0$, $r_1$, $a$, and $b$ then follow. Due to our simple choice of neck geometry, we have $x(\lambda) = \ell - [r_2^2 - (\lambda - h/2)^2]^{1/2}$. Therefore, it suffices to specify $\ell$ and $r_2$ to get $x(\lambda)$ and, subsequently, $F$ and $V$. As a result, the minimization of $F$ with $V$ kept fixed means that $\ell$ and $r_2$ must depend on each other in a unique way (for a given $h$ and $q$), and the equilibrium shape is given just by a single parameter, either $\ell$ or $r_2$. We shall choose the latter one in the following considerations.

3. Results and discussion

3.1 Surface free energy

Since we wish to minimize the surface free energy when the neck volume is fixed, we first use Eq. (3) to evaluate the neck volume, $V_h$, for a given pore height $h$ and various values of $\ell$ and $r_2$. In this way, we obtain the dependence, $V_h(\ell, r_2)$, of the neck volume on $\ell$ and $r_2$ (see Fig. 5). Next, fixing the neck volume, $V_h(\ell, r_2) = V$, we express $\ell$ in dependence on $r_2$, obtaining a function $\ell_h(V, r_2)$. Finally, given $h$, $q$, and $V$, we evaluate the surface free energy $F_{h,q,V}(r_2) = F_{h,q}(\ell_h(V, r_2), r_2)$ with the help of Eq. (2) (see Fig. 6). We set the disk thickness $\delta = R/100$ and consider the heights $h = \delta, \ldots, 10\delta$ and three values $q = 0.3, 0.5, 0.8$.

Fig. 5. (a) The dependence of the neck volume $V_h(\ell, r_2)$ on $r_2$ for fixed values of $\ell/R = 0.15$, 0.20, …, 1.00 (the gray curves from left to right) and for the height $h = \delta$. (b) The first seven of these dependencies for small $r_2$ with the points that are not shown in (a) for clarity.
In numerical calculations, we take values of \( \ell \) ranging from 0.52h to \( R \) and, for a given \( \ell \), we take \( r_2 \) ranging from 0.51h to \( \ell \). In fact, the minimal value of \( r_2 \) is taken as 0.51h only if \( \ell \leq R/2 \), whereas if \( \ell > R/2 \), it is taken as \( [(\ell - R/2)^2 + (h/2)^2]^{1/2} \). This guarantees that \( x(\lambda) \) never exceeds \( R/2 \), i.e., the value when the necks from the three corners of a pore begin to touch each other, initial stages of sintering are over, and a neck geometry different from Eq. (1) should be employed. The maximal neck volume (corresponding to \( x = R/2 \)) is \( V_{\text{max}} = [1/\sqrt{3} + (8\sqrt{3}-17)\pi/18] R^2 h \approx 0.0287 R^2 h \), and we take \( V \) ranging 0.001\( V_{\text{max}} \) to 0.97\( V_{\text{max}} \). The resulting dependence \( V_{\phi}(\ell, r_2) \) is illustrated in Fig. 5 for \( h = \delta \), while the dependence of the surface free energy \( F_{h,q,V}(r_2) \) is illustrated in Fig. 6 for \( h = \delta \), \( q = 0.5 \), and four different values of \( V \).

### 3.2 Equilibrium neck shapes

The equilibrium shape of the neck is obtained by minimizing the surface free energy \( F_{h,q,V}(r_2) \) for a given \( h \), \( q \), and \( V \). The value of \( r_2 \) at which \( F_{h,q,V}(r_2) \) is minimal is denoted as \( r_2^* \). Once \( r_2^* \) is known, the values of the other parameters describing the equilibrium neck shape (i.e., \( \ell^* \), \( x^* \), \( r_1^* \), and \( \alpha_0^* \)) then readily follow. We arrive at these results.

![Fig. 6](image)

**Fig. 6.** The surface free energy \( F_{h,q,V} \) as depending on \( r_2 \) for \( h = \delta \), \( q = 0.5 \), and the values \( V/V_{\text{max}} = 0.001 (■), 0.05 (●), 0.325 (♦), and 0.45 (▲). Given \( V \), the values of \( F_{h,q,V} \) are scaled to its maximal value. For clarity, only every fourth point of evaluation is shown.

For \( q = 0.8 \) and any 0.001\( V_{\text{max}} \) \( \leq V \leq 0.97V_{\text{max}} \), the surface free energy \( F_{h,q,V}(r_2) \) has the shape of a well with a minimum at its bottom (similarly to the two upper curves in Fig. 6). Thus, \( r_2^* \) is finite, and it grows with \( h \) and \( V \). Interestingly, the dependence of \( r_2^*/h \) on \( V \) is almost the same for all \( h \). Indeed, the relative differences between the value of \( r_2^* \) for a given \( h \) and the value averaged over \( h \) are less than 5% for all considered neck volumes \( V \), except for \( V = 0.001V_{\text{max}} \) when it is 12.8% (see Fig. 7(a)).

On the other hand, for \( q = 0.3 \) and all neck volumes \( 0.97V_{\text{max}} \), with an exception of a very small \( V \) (when \( V \leq 0.01V_{\text{max}} \) for \( h = \delta \), \( 7\delta \) and when \( V \leq 0.03V_{\text{max}} \) for \( h = 8\delta \), \( 9\delta \), \( 10\delta \)), the surface free energy \( F_{h,q,V}(r_2) \) is monotonically decreasing (similarly to the two lower curves in Fig. 6). Thus, it attains a minimum at \( r_2^* = \infty \), yielding also \( \ell^* = \infty \) (as the
difference $\ell^* - r^*_2$ must remain finite so that the neck has the desired volume $V$. Consequently, the equilibrium neck surface is flat in the vertical direction.

The case $q = 0.5$ is intermediate. In fact, $r^*_2$ is finite for $0.001V_{\text{max}} \leq V \leq 0.25V_{\text{max}}$ and grows with $h$ and $V$ (see Fig. 7(b)), whereas for $0.3V_{\text{max}} \leq V \leq 0.97V_{\text{max}}$ the value $r^*_2$ is infinite. For neck volumes between $0.25V_{\text{max}}$ and $0.3V_{\text{max}}$, $r^*_2$ rapidly changes from a finite to an infinite value. Again, the dependence of $r^*_2/h$ on $V$ is almost the same for all heights $h$ (see Fig. 7(b)), with the relative differences being less than 10% (except for $V = 0.001V_{\text{max}}$ when the difference is 21.6% and for $V = 0.25V_{\text{max}}$ when it is 16.8%).

Fig. 7. The equilibrium values $r^*_2(h,q,V)$. The markers represent averaged values $\sum_{h=\delta}^{10\delta} r^*_2(h,q,V)/10$ over the ten heights for a given $V$ and (a) $q = 0.8$ and (b) $q = 0.5$ (values of $V$ are limited to $0.25V_{\text{max}}$, then a vertically flat neck shape occurs). For each $V$ and $q$, the interval of actual values of $r^*_2(h,q,V)$ for all ten heights is shown.

Fig. 8. The equilibrium neck shapes for the pore height $h = \delta$, anisotropy factor $q = 0.8$ (top) and $q = 0.5$ (bottom) and selected values of the neck volume $V$ between $0.01V_{\text{max}}$ and $0.5V_{\text{max}}$ (indicated).
Using these results, in Figs. 8–10 we show the obtained equilibrium shapes for a pore of height $h = \delta$, $h = 5\delta$, and $h = 10\delta$, respectively, and the anisotropy parameter $q = 0.8$ and 0.5. (For $q = 0.3$ the equilibrium shapes are not depicted because they have a trivial form – they are vertically flat.) Note that equilibrium neck shapes are different as the pore height changes from the nanoscopic size $h = \delta$ to the microscopic size $h = 10\delta$. Nevertheless, when the vertical radius $r_2^*$ is re-scaled to the radius $r_2^*/h$ relative to the height $h$, the shape differences become rather small and decrease as $q$ (i.e., the anisotropy in the surface free energy) increases. Such a uniform behavior of equilibrium neck shapes is remarkable and does not seem to be obvious a priori.

Fig. 9. The equilibrium neck shapes for the pore height $h = 5\delta$, anisotropy factor $q = 0.8$ (top) and $q = 0.5$ (bottom) and selected values of the neck volume $V$ between 0.01$V_{\text{max}}$ and 0.5$V_{\text{max}}$ (indicated).

Fig. 10. The equilibrium neck shapes for the pore height $h = 10\delta$, anisotropy factor $q = 0.8$ (top) and $q = 0.5$ (bottom) and selected values of the neck volume $V$ between 0.01$V_{\text{max}}$ and 0.5$V_{\text{max}}$ (indicated).
Whether the equilibrium neck surface is flat in the horizontal direction or not is primarily determined by the anisotropy parameter $q$. Indeed, if $q$ is small (the surface free energy density $\gamma_s$ is only weakly anisotropic), then a neck surface that is flat in the horizontal direction occurs in equilibrium for our model in initial stages of sintering (when $V \leq 0.97V_{\text{max}}$). As $q$ grows, the anisotropy of $\gamma_s$ increases, and an equilibrium neck surface becomes curved in the horizontal direction, at least during initial stages of sintering. The pore height $h$ has also an impact on this behavior. Given $q$ and $V$, the values of $r_2^*$ grow with $h$ (see Fig. 7) until, eventually, a neck surface that is flat in the vertical direction occurs in equilibrium. Qualitatively, these conclusions should be expected, and the above numerical results put them on a quantitative footing.

4. Conclusions

We studied the equilibrium shapes of necks created during initial stages of sintering for a disk model of clays. We considered the pore heights $h = \delta, \ldots, 10\delta$ with $\delta = R/100$, where $R$ is the disk particle radius. Assuming a simplified but representative geometry of the neck shape, we derived the equilibrium shape by minimizing an anisotropic surface free energy, provided the neck volume was given. Due to the simple geometry of neck shapes, this minimization problem had a solution fully determined by a single neck shape parameter (taken as the horizontal radius $r_2$). The anisotropy was specified by a parameter $q > 0$ chosen to attain the values 0.3, 0.5, and 0.8, corresponding to a weak, medium, and strong anisotropy. We quantitatively described the dependence of the equilibrium shapes on the height $h$ and the anisotropy parameter $q$, the latter having a more significant impact on the shapes. For the heights $h = \delta, 5\delta, 10\delta$ and $q = 0.5, 0.8$ the resulting equilibrium shapes were depicted.

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5. References


Садржај: Проучаван је равнотежни облик контактних вратова у односу на почетне стадијуме синтеровања у чврстој фази, коришћењем микроскопског модела глине у којој честице имају унiformни цилиндрични облик микропречника $R$ и нанодебљине $\delta = R/100$. Честице су поређане једна на другу, формирајући вертикалне гомиле различитих висина од $h = \delta$ до $h = 10\delta$. Поре су формирани у простору између било које три гомиле исте висине, а које се додирuju. Претпостављајући да је површинска дифузија доминантан механизам синтеровања, и узимајући у обзир поједностављену форму конфигурације контактних вратова, одређен је равнотежни облик контактних вратова минимизирајући површинску слободну енергију, коришћењем параметра анизотропије $q$. Разматрана је зависност добијених облика контактних вратова од запремине контактних вратова $V$, висине пора $h$ и параметра анизотропије $q$.

Кључне речи: Синтеровање у чврстој фази; површинска дифузија; површинска слободна енергија.