Modification of Frenkel's Model for Sintering

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The coalescence of two equal spherical droplets of a Newtonian fluid is studied. Coalescence of particles under the action of surface tension is commonly referred to as sintering. Sintering has been studied in processing of ceramics, metals, and polymers. In a first attempt to model sintering, Frenkel (1945) used an asymptotic approximation to describe the initial stage of the process. Frenkel's model, which is based on Newtonian viscous flow under the action of surface tension, was corrected by Eshelby (1949) to satisfy the continuity equation and will subsequently be referred to as the Frenkel-Eshelby model. More recently, a model was developed by Hopper (1984, 1990, 1991) which is based on using the Kolosoff-Muskhelishvili equations and complex function theory. Hopper's analytical solution is hence limited to two-dimensional and Newtonian flow problems only. Numerical simulations of the sintering process have also been developed to predict the coalescence kinetics (Jagota and Dawson, 1988; Van de Vorst, 1994; Martínez-Herrera and Derby, 1994, 1995). These simulations also include the effects of various geometric and physical arrangements on the coalescence rate.

Qualitative assessments of Frenkel's theory have been made by some authors (Kuczynski, 1949; Kingery and Berg, 1955; Rosenzweig and Narkis, 1980, 1981). A recent study showed the validity of Hopper's model in the prediction of sintering rate for rotomolding grade polyethylene resins (Bellehumeur et al., 1996). In an earlier study, Hornsby and Maxwell (1992) found that the Frenkel-Eshelby model combined with the use of the Trouton viscosity was in good agreement with their experimental results for polypropylene. However, experiments performed with acrylic resins, ultrahigh molecular weight high density polyethylene and copolymer resins showed that mechanisms other than viscous flow may be important in polymer sintering (Siegmann et al., 1996; Mazur and Plazek, 1994; Vlachopoulos et al., 1996; Bellehumeur, 1997).

The objective of the present work is to develop a sintering model which describes the complete sintering process of two spherical particles. The emphasis of this work is on the development of a simple but yet general model which further could be adapted in simulating industrial processes, such as rotational molding, in which sintering is involved. The approach is similar to that of Frenkel (1945) and Eshelby (1949) but goes beyond the description of the initial stages. Similar simplifications are used in order to reduce the number of parameters in the model. The flow is approximated to be viscous extensional and the evolution of the particle shape is restricted, so the number of parameters is reduced. However, unlike Frenkel (1945), the variation of the particle radius with time in the coalescence process is considered. The resulting model is relatively simple and compares relatively well to experimental data.

Derivation of the Model

The model is based on the balance of the work of surface tension and the viscous dissipation. All other forces, including gravity, are neglected. We assume that the shape of two spheres evolves as shown in Figure 1. At time $t = 0$, two equal sized spheres of radius a_o, centered at points A and B, have only one contact point O. At time t, both centers have moved towards point O and a shape of two intersecting spheres of radius $a(t)$ has been created. The angle of the intersection and the radius of the neck are denoted by $\theta(t)$ and $x(t)$, respectively. In the final stage, only one sphere of radius a_f remains and all three points A, B and O coincide. The following relation for $a(t)$ vs. $\theta(t)$ is obtained from the conservation of mass with the assumption of a constant density

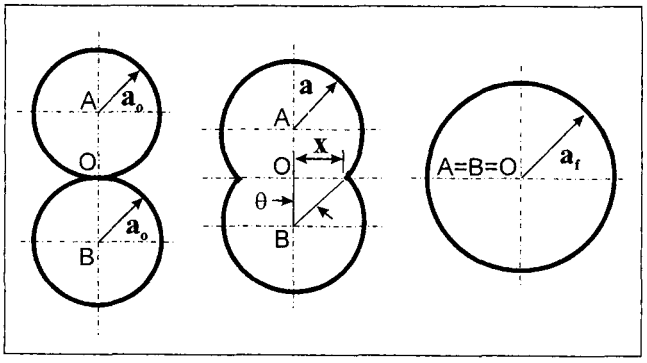

Figure 1. Shape evolution.

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$$a(t) = a_o\left(\frac{4}{\{1+\cos[\theta(t)]\}^2\{2-\cos[\theta(t)]\}}\right)^{1/3} \quad (1)$$

For simplicity, the functions $\theta(t)$, $a(t)$ and $x(t)$ will be subsequently denoted θ, a and x. Thus, the total surface of particles varies with the angle θ according to the following formula

$$S = 4\pi a^2[1+\cos(\theta)] = \frac{8\pi a_o^2 2^{1/3}}{[1+\cos(\theta)]^{1/3}[2-\cos(\theta)]^{2/3}} \quad (2)$$

whereas Frenkel assumed the particle radius to be constant [that is, $a(t) = a_o$] and made an approximation for small angles [that is, $\cos(\theta) = 1 - \theta^2/2$]. The work of viscous forces W_v for a Newtonian fluid can be expressed as

$$W_v = \int\int\int_V \eta\nabla u:(\nabla u + \nabla u^T)dV \quad (3)$$

η being the viscosity, ∇u the gradient of velocity, and V the volume of the sintering system. Following Eshelby, the flow field is assumed to be extensional and can be described by

$$\nabla u = \begin{bmatrix} \frac{\dot\epsilon}{2} & 0 & 0 \\ 0 & -\dot\epsilon & 0 \\ 0 & 0 & \frac{\dot\epsilon}{2} \end{bmatrix} \quad (4)$$

where $\dot\epsilon$ is the strain rate and consequently

$$W_v = \int\int\int_V 3\eta\dot\epsilon^2 dV \quad (5)$$

Following Frenkel, the strain rate $\dot\epsilon$ is assumed to be constant throughout the complete domain and is approximated by

$$\dot\epsilon = \frac{\partial u_y(A)}{\partial y} \approx \frac{u_y(A) - u_y(O)}{a} \quad (6)$$

where $u_y(A)$ is the velocity with which point A moves towards point O (Figure 1). The term $u_y(O)$ is the velocity of the fluid at the plane of contact of the two particles and is equal to zero. The term $u_y(A)$ is defined as follows

$$u_y(A) = \frac{d}{dt}[a\cos(\theta)] = -\frac{2^{5/3}a_o\sin(\theta)}{[1+\cos(\theta)]^{5/3}[2-\cos(\theta)]^{4/3}}\theta' \quad (7)$$

where $d\theta/dt$ is denoted as θ'. Consequently

$$\dot\epsilon = \frac{u_y(A)}{a} = -\frac{2\sin(\theta)}{[1+\cos(\theta)][2-\cos(\theta)]}\theta' \quad (8)$$

which leads to the formula for dissipated energy

$$W_v = 32\pi a_o^3\eta\frac{1-\cos(\theta)}{[1+\cos(\theta)][2-\cos(\theta)]^2}(\theta')^2 \quad (9)$$

The work of surface tension W_s is defined as

$$W_s = -\Gamma\frac{dS}{dt} \quad (10)$$

where Γ is the coefficient of surface tension and S is the surface of the sintering system. Applying the chain rule on Eq. 2, the term dS/dt can be derived and the expression for the work of surface tension becomes

$$W_s = \Gamma\frac{8\pi a_o^2 2^{1/3}\cos(\theta)\sin(\theta)}{[1+\cos(\theta)]^{4/3}[2-\cos(\theta)]^{5/3}}\theta' \quad (11)$$

Under the assumption that θ' is always positive, by equating the work of surface tension to the viscous dissipation, we obtain

$$\theta' = \frac{\Gamma}{a_o\eta}\frac{2^{-5/3}\cos(\theta)\sin(\theta)[2-\cos(\theta)]^{1/3}}{[1-\cos(\theta)][1+\cos(\theta)]^{1/3}} \quad (12)$$

with the initial condition

$$\theta(0) = \theta_o = 0 \quad (13)$$

Equation 12 has a trivial solution $\theta \equiv 0$. It is singular near zero and a special numerical treatment is necessary to solve it. There is a unique solution of Eq. 12 since its righthand side is locally Lipschitz continuous in θ. For $\theta \to 0$, the following approximations are made: $\sin(\theta) = \theta$ and $(1-\cos(\theta)) = \theta^2/2$, respectively. Hence, the asymptotic behavior of Eq. 12 is

$$\theta' = \frac{1}{2}\frac{\Gamma}{\eta a_o\theta} \quad (14)$$

Considering that $\theta > 0$ and applying the initial condition (Eq. 13), the solution of Eq. 14 is

$$\theta(t) = \left(\frac{t\Gamma}{\eta a_o}\right)^{1/2} \quad (15)$$

which corresponds to the Frenkel-Eshelby model. Thus, a solution for $\theta(t)$ is obtained solving Eq. 12 numerically using an automatic step size Runge-Kutta-Fehlberg integration method (Burden and Faires, 1985). To overcome numerical instabilities when $\theta = 0$, the initial boundary condition is fixed at a time value slightly different than zero and the corresponding value of θ_o is determined from Eq. 15. Once a solution for the evolution of the sintering angle with time is obtained, the evolution of the neck radius with time can easily be derived

Table 1. Modified Frenkel Model Predictions

$t\Gamma/\eta a_o$	x/a	$t\Gamma\eta a_o$	x/a
0.0001	0.0100	—	—
0.01	0.0979	0.40	0.5736
0.02	0.1396	0.50	0.6242
0.03	0.1713	0.60	0.6721
0.04	0.1984	0.70	0.7062
0.05	0.2210	0.80	0.7403
0.06	0.2419	0.90	0.7666
0.07	0.2609	1.00	0.7910
0.08	0.2786	1.50	0.8767
0.09	0.2949	2.00	0.9241
0.10	0.3109	4.00	0.9872
0.20	0.4274	6.00	0.9976
0.30	0.5060	8.00	0.9995

$$\frac{x}{a} = \sin(\theta) \tag{16}$$

$$\frac{x}{a_o} = \sin(\theta)\left(\frac{4}{[1+\cos(\theta)]^2[2-\cos(\theta)]}\right)^{1/3} \tag{17}$$

$$\frac{x}{a_f} = \frac{x}{a_o}2^{-1/3} \tag{18}$$

or

$$\frac{x}{a_f} = \sin(\theta)\left(\frac{2}{[1+\cos(\theta)]^2[2-\cos(\theta)]}\right)^{1/3} \tag{19}$$

Numerical results of the present modified Frenkel model are presented in Table 1. The initial condition was set at the value for dimensionless time $t\Gamma/\eta a_o = 0.0001$ instead of zero and from Eq. 15 $\theta_o = 0.01$.

Results and Discussion

A comparison between various models is shown in Figure 2. It can be seen that the predictions are similar in the early stage of sintering. It should also be noted that the present model is asymptotically identical to the Frenkel-Eshelby model. Hopper's model is for cylinders and the completion of coalescence occurs for $x/a_o = 1.4142$, while for spheres it occurs for $x/a_o = 1.2599$. The numerical predictions by Jagota and Dawson (1988) compare rather well to the present modified Frenkel model despite the simplifying assumptions.

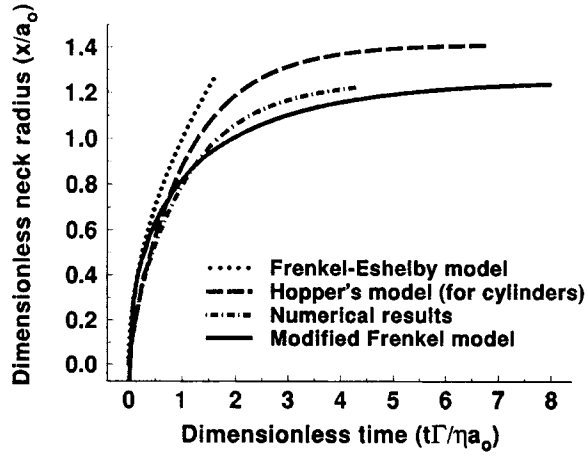

Figure 2. Modified Frenkel model vs. Frenkel-Eshelby model, Hopper's model (1984), and numerical results by Jagota and Dawson (1988).

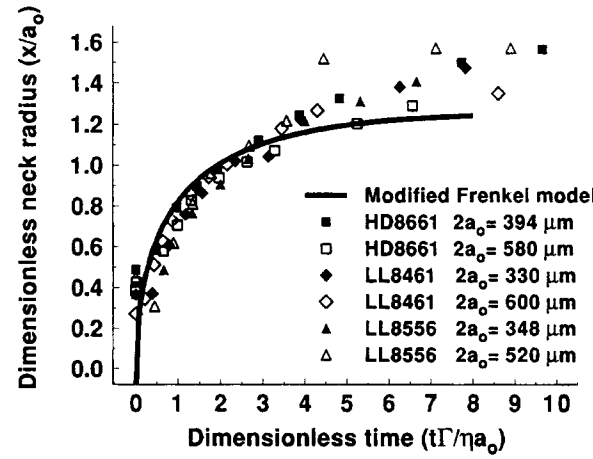

Figure 3. Modified Frenkel model predictions vs. experimental data (Bellehumeur et al., 1996).

A comparison between the present model and representative experimental data (Bellehumeur et al., 1996; Bellehumeur, 1997) is shown in Figure 3. These experiments were carried out using rotomolding grade polyethylene resins. The deviations in the late stage of coalescence are primarily due to the destruction of the sphericity of the particles as they spread on the observation surface. Plots of x/a vs. time show a much better agreement (Bellehumeur, 1997), because both the neck and the particle spread simultaneously on the observation surface during the experiment. Experiments with copolymers (Bellehumeur, 1997) showed a less satisfactory agreement with the model, apparently due to contributions of the elastic resin properties.

The main advantage of the present model over others is that the mathematical theory is simple enough to enable possible generalization with consideration of viscoelasticity or inclusion into more general formulations of industrial processes, such as rotational molding or powder coating.

Acknowledgments

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