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Dynamics Of Particle Removal By Supercritical Carbon Dioxide

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ABSTRACT

We have investigated the possibility of cleaning semiconductor wafers contaminated by particles by flowing supercritical carbon dioxide over them. The hydrodynamics of turbulent flow of supercritical carbon dioxide over a flat plate was calculated. Through these calculations it is proposed that the drag on a particle sitting on a flat plate in the viscous sublayer is capable of rolling submicron-sized spheres off the wafer at sufficiently high velocities.

1. Introduction

Contamination of semiconductor wafers during manufacturing is a common occurrence. Particle adhesion cannot always be prevented in the manufacturing stage, making it necessary to clean the wafer in a subsequent stage. As feature sizes on integrated circuits become smaller, the need for ensuring particle removal increases. In the next generation of semiconductor circuits, it is expected that feature sizes of less than a micron will be attained. It will therefore become imperative that all particles greater than about a tenth of a micron be removed from semiconductor wafers.

Several schemes exist for cleaning wafers, such as an ultrasonic method (1), high pressure jet scrubbing (2) and carbon dioxide snow-jet (3), among others. The use of air to roll away particles has been investigated previously by Bhattacharya and Mittal (4) and by Zimon (5). The dynamics of liquid jets for cleaning has been studied recently by Gim et al (6). Here we investigate the possibility of flowing supercritical carbon dioxide over a dirty wafer in order to roll away spherical particles. There are two advantages of using supercritical carbon dioxide over air. The first advantage is that the density of supercritical carbon dioxide is much larger than that of air, thereby dramatically increasing the drag on the particle. The second is the ability of supercritical carbon dioxide to dissolve organic material. Since some of the contaminant particles are indeed organic in nature, supercritical carbon dioxide will aid in loosening the adhesion between such particles and the surface on which they are located. Furthermore, a liquid such as water is not an option for cleaning semiconductor wafers, as it would tend to hydroxylate the surface of the wafer and damage it in other ways as well.

The basic idea behind using flow to move particles off surfaces is the formation of a boundary layer near the surface. Within this boundary layer, there is a shear in the velocity field, leading to a stress which rolls particles away from any given position. As one might guess intuitively, the wall shear in the case of turbulent flow is much greater than in laminar flow. In laminar flow, the boundary layer is relatively thicker, allowing the velocity to change gradually to its stream value. In the case of turbulent flow, the viscous sublayer which develops right next to the wall is much thinner, causing a

much more abrupt change in the velocity field, thereby setting up a larger wall shear. The velocity profiles for turbulent and laminar flow are compared in Figure 1 as a function of distance from the wall. It can be seen from the figure that laminar flow shows a gradual velocity change while that change is abrupt for turbulent flow. Therefore, turbulent shear is much larger than that present in laminar flow. We must note however, that the viscous sublayer displayed for the case of turbulent flow in Figure 1 must not be interpreted too literally as a laminar sublayer. While this layer may be relatively quiescent compared to the turbulent core of the flow, there is still turbulent motion within this sublayer.

In our treatment of particle removal we shall make a number of simplifying assumptions. We shall assume that the force of adhesion is only due to Van der Waals force of attraction. We shall not consider other possible forces such as electrostatic interactions or gravity. We shall also assume that the surface is smooth. In other words, the roughness of the surface is due to randomness at the atomic level. This means that over the width of the particle, the surface height varies by a few angstroms at most. This assumption allows us to readily determine the force of adhesion of glass particles on a silicon wafer. In this paper, we have not investigated how the particles came to be attached to the wafers (7).

We utilize the physics of rolling particles on a surface as developed by Bhattacharya and Mittal (4). Our treatment differs from that of Bhattacharya and Mittal (4) in that we provide a more detailed description of the turbulent boundary layer which is formed in the steady state when a fluid flows over a flat plate (5). The drag force we use is consistent with the treatment of Gim et al (6).

In section 2 we discuss the properties of turbulent flow and, in particular, the flow velocity as a function of distance from the wall in the turbulent regime—the so-called law of the wall. In this respect we believe our treatment of particle removal is unique. We discuss the magnitude of adhesive forces in section 3. In section 4 we apply our treatment of boundary layer flow to supercritical carbon dioxide and we calculate the requirements for spherical glass particles to be removed from a smooth silicon surface using supercritical carbon dioxide.

2. The Boundary Layer In Turbulent Flow Over A Plate

Turbulent flow over a flat plate is characterized by three regions (8): (a) a viscous sublayer often called the laminar sublayer, which exists right next to the plate, (b) an adjacent turbulent boundary layer, and (c) the turbulent core. Viscous forces dominate inertial forces in the viscous sublayer, which is relatively quiescent compared to the other regions and is therefore also called the laminar sublayer. This is a bit of a misnomer, since it is not really laminar. It is in this viscous sublayer that the velocity changes are the greatest, so that the shear is largest. Viscous forces become less dominant in the turbulent boundary layer. These forces are not controlling factors in the turbulent core.

In the supercritical region, the kinematic viscosity of carbon dioxide is $D \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, (9) so that even for a low flow speed u of 100 cm/s, the Reynolds number $Re = u s/D$ is $\sim 10^5$, s being the typical length scale chosen here to be ~ 1 cm. At such Reynolds numbers we expect the flow of supercritical carbon dioxide over a flat plate to be turbulent at least in the vicinity of the plate. We use standard empirical laws of turbulent flow to get the velocity distribution both near and far from the wall. The velocity in the laminar boundary layer grows linearly and connects in a continuous fashion with a logarithmic velocity profile in the turbulent boundary layer (10):

$$u(y) = \left(\frac{u^{*2}}{D} \right) y; y \leq \frac{D}{u^*}$$

$$u(y) = u^* \left[\frac{1}{\kappa} \ln \left(c \left(\frac{yu}{D} \right)^{7/8} \right) + B \right]; y > \frac{D}{u^*}$$

Eq. (2.1)

$$\tau = \rho u^{*2}$$

$$\kappa = 0.4437; c = 0.15; B = 5.5$$

where τ is the wall shear, ρ is the fluid density at the wall, D is diffusion constant, u^* is a velocity called the frictional velocity, and κ , c and B are empirically determined dimensionless constants.

The transition between the laminar region and the turbulent region is made by demanding continuity, which yields a self-consistent equation to be solved:

$$\text{Eq. (2.2)} \quad R_c^{1/2} = \frac{1}{\kappa} \ln(cR_c^{7/8}) + B$$

where $R_c = y_c u_c / D$. The solution is $R_c = 114$. We can use this value to estimate the stream velocity required to develop a boundary layer of thickness $y_c = \delta$. For $\delta = 100$ microns, we get $u_c \sim 5$ cm/s, using $D \sim 5.4 \cdot 10^{-4}$ cm²/s at T=325°K. From Eq. (2.1), $u^* = u_c / (R_c)^{1/2} \sim 0.5$ cm/s. Now, there exists a relation between the frictional velocity and the stream velocity U viz.,

$$u^* = \left(\frac{f}{2}\right)^{1/2} U$$

$$\text{Eq. (2.3)} \quad f = \frac{0.0791}{\text{Re}^{1/4}}$$

where f is Fanning's friction factor ~ 0.04 which finally yields $U \sim 13$ cm/s. When we examined these values with detailed numerical calculations, it turns out that the estimates of the velocity required to achieve a certain thickness of the viscous sublayer is quite accurate, as long as realistic estimates of the density and diffusion constant are used.

We notice from Eq. (2.1) that the wall shear stress τ is constant within the laminar boundary layer, and for this case is ~ 0.25 dyne/cm². As far as calculation of the wall shear stress for a known stream velocity is concerned, we point out that the use of Fanning's factor alone suffices to determine its value, and we do not need all the formulas stated above.

In order to get the entire velocity profile, we need to use realistic values of the density and diffusion constant as functions of pressure and temperature, and then solve the above equations numerically for the velocity in the two different regions and match them at the edge of the boundary layer. We have given an example of such a calculation in Figures 2 and 3. These two figures are calculations done at 300 bars and 400 bars respectively. What these figures show is basically that there is a greater sensitivity to the stream velocity rather than temperature. We also learn from these figures that for velocities on the order of a few cm/s, the thickness of the boundary layer is about 100 microns.

One might be tempted to conjecture that this layer being turbulent (albeit less turbulent than the regions further away from the plate) will have an eddy swooping down once in a while to somehow “pick” a particle off the surface. We believe this is not very likely, since the sublayer is on the order of a few microns for the velocities under consideration, while the particles we would most like to remove are around less than a micron in radius. In fact, one may use standard estimates for turbulence variables such as the dissipation (loss of kinetic energy per unit time), $\epsilon \sim u_c^3/\delta$ (where u_c is a measure of the typical velocity in that region and δ is the thickness of the viscous sublayer), and the turbulent kinetic energy (mean square velocity fluctuations), $k \sim (\epsilon\delta)^{2/3}$, to obtain a kinetic “pressure” due to turbulence $\rho k \sim 10^{-3}$ dynes/cm², ρ being the characteristic density. Multiplying this pressure by the cross-sectional area of a micron-sized particle yields a force of $\sim 3.14 \cdot 10^{-13}$ dynes. This force due to turbulence may be compared to the force of adhesion (see Eq. (3.2) in the next section), which is ~ 0.0052 dynes for a micron sized particle. It is therefore clear that turbulence cannot scoop up a particle and move it along the surface.

On the other hand, it is in the viscous sublayer that the velocity changes are largest, so that the shear is greatest here. It may be possible for the shear stress in this region will be able to move a particle. We shall develop this idea in the next section.

3. Adhesive Forces

As mentioned in the introduction, in addition to assuming a spherical particle and a smooth surface, we shall assume that electric charges are not present in the problem, and the effects of gravity will be ignored as well.

The adhesive force between a neutral particulate contaminant and the wafer is expected to be due to the attractive Van der Waal's interaction between molecules (11). This is a macroscopic force found by averaging over the force between all the molecules of a particle and the neighboring surface. For a spherical particle sitting on a flat wafer, it is known that surface roughness will cause the mean distance of separation between the particle and the wafer to be nonzero. The attractive force between these two entities acts along the normal between the sphere and the wafer, and is given by:

$$\text{Eq. (3.1)} \quad F_a(r) = -\frac{Ar}{12z^2} = -\frac{hr}{16\pi z^2}$$

where A is Hamaker's constant ($\sim 10^{-19}$ J), r is the radius of the spherical particle, and z is the distance of separation. Experimentally, it is found that $h \sim 10$ eV. In our theoretical study in this paper, A or h need to be considered as empirical parameters which will change depending on the nature of the particle and the surface upon which it is placed. The dielectric properties of the intervening fluid viz., supercritical carbon dioxide will change the strength of the interaction between the particle and the surface. Empirically, the separation distance for a smooth surface is found to be ~ 0.4 nm, because at distances smaller than this the interaction becomes repulsive. Using these numbers, we get:

$$\text{Eq. (3.2)} \quad F_a(r) = -52.1r$$

where the adhesive force F_a is in dynes, r is in cm, and the negative sign indicates an attractive force. For $r = 1$ micron, the adhesive force is 0.00521 dynes.

The force due to the shear in the viscous sublayer on a particle lying on a surface, is analogous to the formula for Stoke's drag (12):

$$\begin{aligned}
 F_s &= 10.2\pi\rho D(P,T)ru(r) \\
 \text{Eq. (3.3)} \quad &= 10.2\pi\rho\left(\frac{f}{2}\right)U^2r^2
 \end{aligned}$$

One sees immediately from this equation that when $U \sim 1000$ cm/s, the shear force will exceed the adhesive force for $r = 1$ micron. This puts movement of the particle due to the shear force in the realm of reality.

In general, for the particles to move, F_s must be greater than the force of friction F_f which is given by the following equation:

$$\text{Eq. (3.4)} \quad F_f = -\mu F_a$$

where μ is the coefficient of friction. The shear force is proportional to the square of the radius of the particle while the force of friction grows only linearly with the radius. Thus, there will be a radius below which the shear force can no longer overcome the force of friction. The radius of the smallest particle which can be moved is therefore given by:

$$\text{Eq. (3.5)} \quad r_{\min} = \left(\frac{\mu A}{12z^2}\right)\left(\frac{1}{5.1\pi\rho fU^2}\right)$$

The idea of utilizing a coefficient of friction is not new, having been proposed and tested for the cleaning of flat plates with air at least two decades ago by Zimon (5). Similar ideas have been proposed for the cleaning of wafers/discs by spinning them (13). If the particles that need to be removed are charged, the force of adhesion may be electrostatic in origin (14).

There appears to be empirical evidence that the approach outlined above is applicable to the sliding of particles (5). For cases of interest to us, the particles appear to roll, rather than slide off the wafer (6). As far as we are aware, well-characterized experiments have not been performed for the case of supercritical carbon dioxide. We now turn to the theory of rolling particles off surfaces. We use the treatment of Bhattacharya and Mittal (4) to compute the radius of the smallest particle that can be moved due to the torque exerted on the particle due to the wall shear. As the particles sit on the surface, there will be a very small deformation x_0 caused by the adhesive force between the particle and the surface. This deformation is given in the following equation:

$$\text{Eq. (3.6)} \quad |F_a| = \pi x_0^2 E$$

where E is the modulus of deformation $\sim 8.0 \cdot 10^{11}$ dynes/cm² for silica. When rolling occurs, we may equate the torques acting on the sphere due to the vertical force of adhesion and the horizontal force of drag to find

$$\text{Eq. (3.7)} \quad |F_a|x_0 = F_s r$$

Using Eq. (3.1), Eq. (3.3) and Eq. (3.6), we obtain:

$$\text{Eq. (3.8)} \quad r_{\min} = \left(\frac{A}{12z^2} \right) \left(\frac{1}{\pi E} \right)^{1/3} \left(\frac{1}{5.1\pi\rho f U^2} \right)^{2/3}$$

Thus rolling yields a $U^{-4/3}$ dependence for r_{\min} . This may be contrasted with the inverse quadratic dependence obtained from Eq. (3.5), for sliding particles. In fact, we suggest that experimental data on r_{\min} could be used to differentiate between the two different mechanisms discussed here, and indeed to verify whether such predictions are correct.

In the next section, we shall specialize these formulas to the case of supercritical carbon dioxide.

4. Supercritical Carbon Dioxide

We pointed out in the introduction that using supercritical CO₂ as a removal agent would be more advantageous than air, and this is borne out by Eq. (3.8). This equation shows that the radius of the smallest particle that will be removed, r_{min} , has a $\rho^{2/3}$ dependence, implying that for a given flow velocity, supercritical CO₂ with a density of ~ 1 g/cc will remove much smaller particles than air. Of course, one could use air and increase its flow velocity appropriately in order to overcome the deficit caused by its low density. One would have to make certain that the air was free of contaminants which could damage the wafer being cleaned. On the other hand, supercritical CO₂ has the inherent advantage of being able to dissolve organic compounds, which should help loosen organic particle contaminants on the wafer surface. Thus, besides flow characteristics, one needs to consider that chemistry could make a difference in this process. The Hamaker constant A which appears in the adhesive force defined by Eq. (3.1) is expected to be smaller for the case of supercritical CO₂ flowing over particles containing organic material and placed on a wafer. Supercritical CO₂ is also a drying agent, and this may be of some use in the cleaning process as well.

The critical temperature of CO₂ is $T_c = 31^\circ \text{C}$, and the critical pressure $P_c = 73.8$ bars. In Figure 4 we plot the viscosity of supercritical CO₂ as a function of temperature (15), varying pressure parametrically. In Figure 5, we plot the density of carbon dioxide over the same range of temperature and pressure.⁹ In order to maximize the force on particles it is desirable to increase the density (see Eq. (3.7)). There is only a weak dependence (see Eq. (3.7)) of the particle removal efficiency on the viscosity, through the Fanning factor. The Fanning factor changes very little as the Reynolds number is changed. In any event, we can optimize the process by choosing to work in a regime where the viscosity is relatively low. Accordingly, we choose a temperature of 325°K , and a pressure of 300 bars based on Figures 4 and 5. Lowering the pressure would not only decrease the density but bring the operating point closer to the critical pressure, which is not desirable. Increasing the pressure would increase the viscosity. Raising the temperature decreases the density, while lowering it would not only increase the viscosity, but again bring us uncomfortably close to the critical temperature. This is due to dramatic density changes as a function of temperature and pressure near the critical

point. We recognize in this manner that there is not a truly optimal operating point. What we obtain is a range of parameters defining an operating regime whose boundaries are defined by the proximity to T_c and P_c , and within which one can perform cleaning experiments.

In Figure 6 we show the thickness of the boundary layer as a function of the stream velocity of supercritical CO_2 for temperatures of 325°K (solid line) and 375°K (dashed line) at a fixed pressure of 300 bars. In this regime the density of CO_2 is ~ 0.94 g/cc and its viscosity is $\sim 7.4 \times 10^{-4}$ g/cm-s. The thickness of the laminar sublayer is seen to depend inversely on the stream velocity. This figure indicates that for a stream velocity of 200 cm/s, the boundary layer thickness is about 2 microns.

In Figure 7, we plot the radius of the smallest particle that can be rolled as a function of the stream velocity for temperatures of 325°K (solid line) and 375°K (dashed line) at a fixed pressure of 300 bars. We notice first of all from this plot that a difference of 25°K in the operating temperature causes a change by almost a factor of two in the radius of the smallest particle which can be moved. It is clear that it is more efficient to work at the lower of the two temperatures that are displayed. Such plots allow us to design experiments with a goal of removing particles larger than some critical value. As pointed out in the introduction, the critical size of particle contaminants is expected to be of the order of 0.1 micron for the next generation of semiconductor wafers. Figure 7 shows that the stream velocity of supercritical CO_2 required to remove particles of this size is about 200 cm/s at 375° K, and the required stream velocity is about 100 cm/s at 325° K. Such velocities are attainable with currently available pumps.

To compare the cleaning characteristics of supercritical carbon dioxide with that of air, we have plotted in Figure 8 the radius of the smallest particle (in the range of a few microns) that can be removed with air at 1 atmosphere and a temperature of 300 K. It shows that even for a relatively high velocity of 1000 cm/s, the minimum radius is ~ 0.2 microns. This may be compared to 0.005 microns for supercritical CO_2 . Requirements of such fast flow for air will probably force the use of jets. This raises an additional complication of having to install a mechanism to “sweep” the wafer

clean. The sweeping motion will most certainly lead to additional contamination from lubricated joints, etc. Such complications do not arise for the case of supercritical CO₂, given the relatively low velocities needed.

5. Conclusions

We have shown that particles can be theoretically rolled off semiconductor wafers using a turbulent flow of supercritical CO₂ over them. Flow speeds of a few hundred cm/s will be required to remove particles less than a tenth of a micron in radius. The relative merits of using supercritical carbon dioxide over air include the use of lower flow velocities with supercritical CO₂, it is pointed as well as an advantage in terms of chemistry over air. Supercritical CO₂ dissolves organic molecules, implying that it can loosen the adhesion between organic contaminants (particles) and the semiconductor wafer.

6. References

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7. Figure Captions

Figure 1. Velocity past a flat plate as a function of distance from the surface of the plate under turbulent and laminar flow conditions using a flow (stream) velocity of 11 cm/s. Notice the gradual change in the laminar flow (dashed line), compared to the turbulent case (solid line). It follows that the shear in the turbulent case, near the plate is much larger than in the laminar case.

Figure 2. Velocity profiles for supercritical CO₂ calculated at 300 bars of pressure. The solid line corresponds to 325°K and a viscous sublayer thickness of 100 microns, the dashed line corresponds to 375°K and a viscous sublayer thickness of 100 microns, and finally the dot-dashed line corresponds to 325°K, but a viscous sublayer thickness 200 microns.

Figure 3. This figure is similar to Figure 2, except that the pressure used is 400 bars. Notice the correspondingly higher velocities required to attain the same viscous sublayer thicknesses (100 microns and 200 microns).

Figure 4. Viscosity as a function of temperature for supercritical CO₂ for three different pressures.

Figure 5. Density as a function of temperature for supercritical CO₂ for three different pressures.

Figure 6. The relation between the stream velocity and the thickness of the viscous sublayer for 325°K (solid line) and 375°K (dashed line) at a pressure of 300 bars. The thickness ranges from about 1 micron for 350 cm/s to 10 microns for 50 cm/s.

Figure 7. The theory of rolling developed for turbulent flow conditions can be used to calculate (at 300 bars) the radius of the smallest particle that can be moved as a function of the stream velocity for 325°K (solid line) and 375°K (dashed line). Notice the sensitivity to temperature. Velocities of 100 cm/s to 200 cm/s are needed to move particles about a tenth of a micron.

Figure 8. In order to compare the cleaning efficiencies of air and supercritical CO₂, we have displayed in this figure the radius of the smallest particle that can be moved with air at one atmosphere and 300°K, for velocities comparable to those used in the previous figure. Notice that the velocities required to move the particles with air are much higher than in the case of supercritical CO₂.

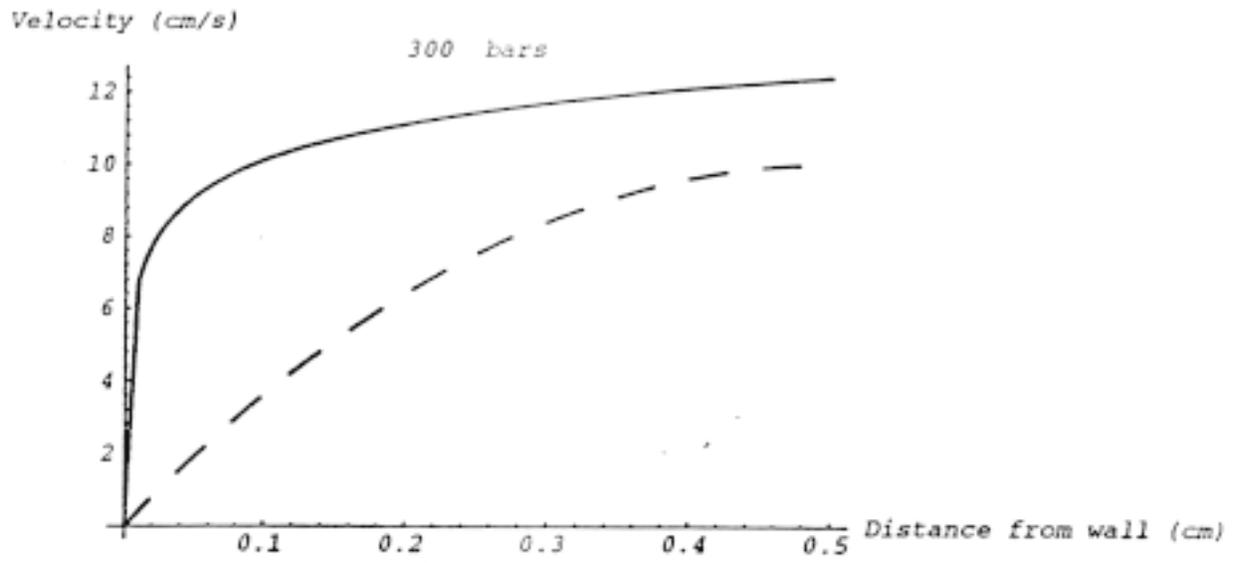


Figure 1

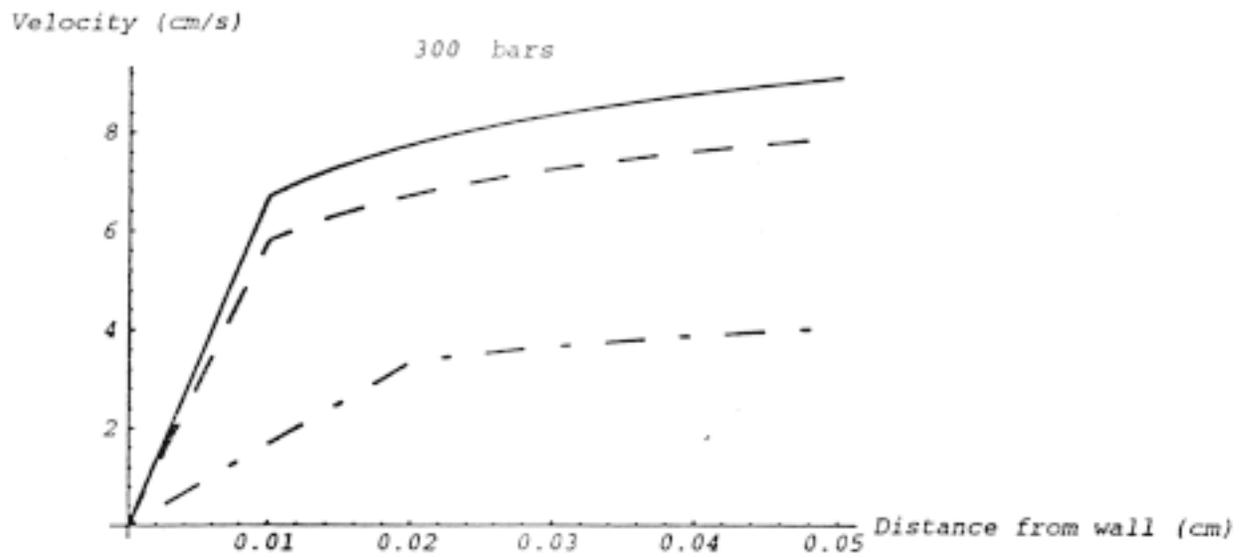


Figure 2

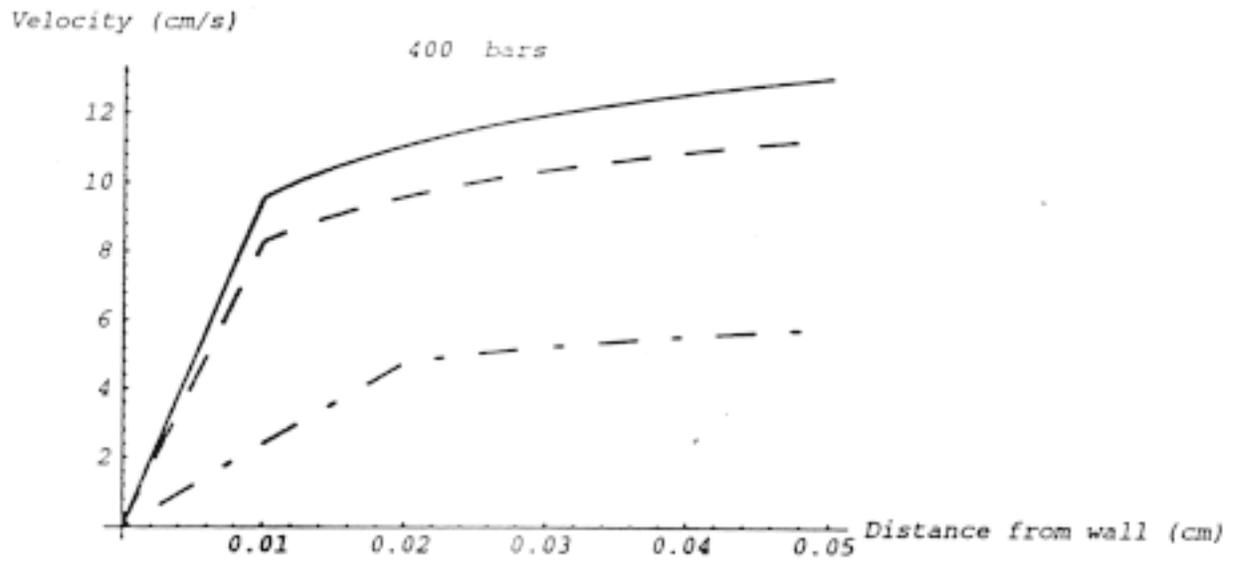


Figure 3

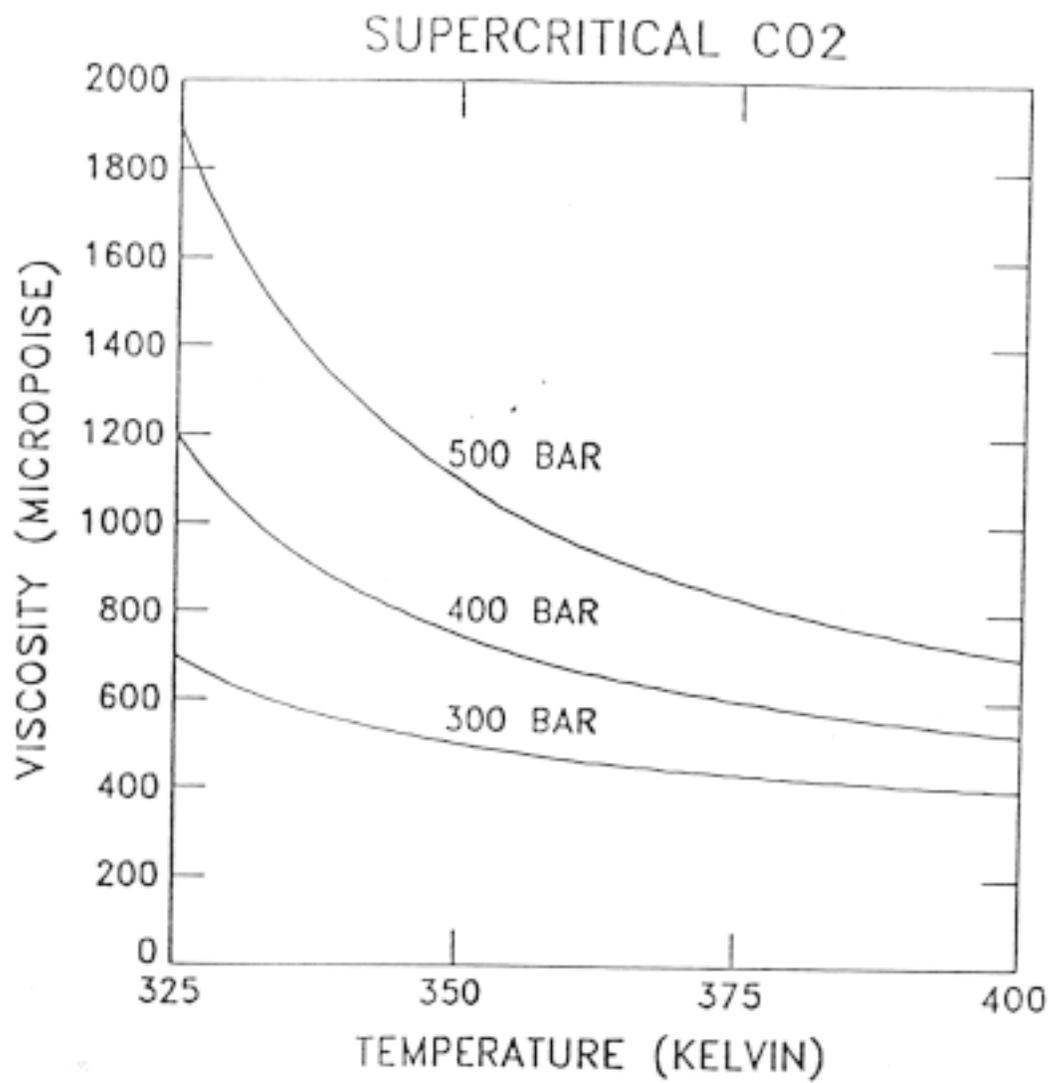


Figure 4

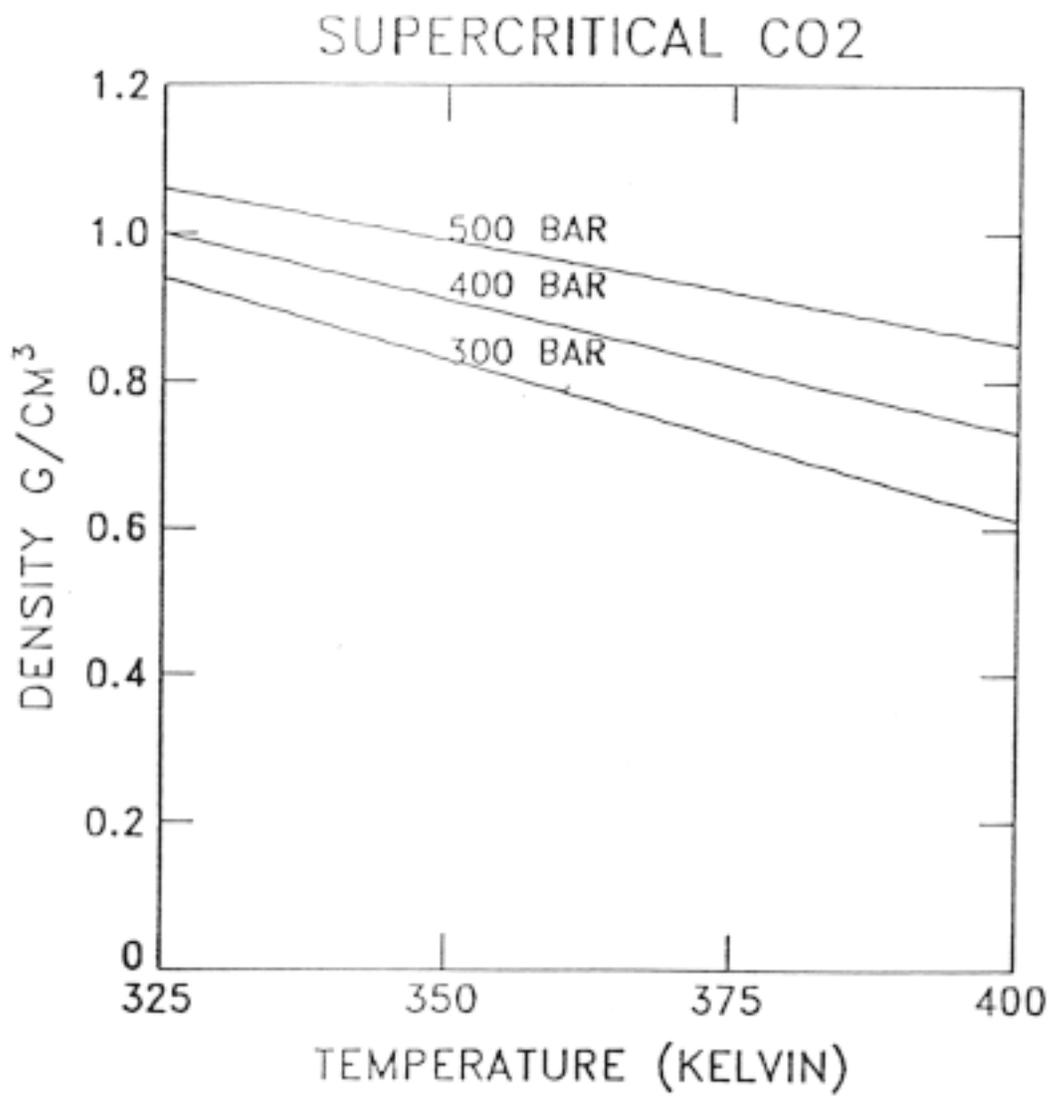


Figure 5

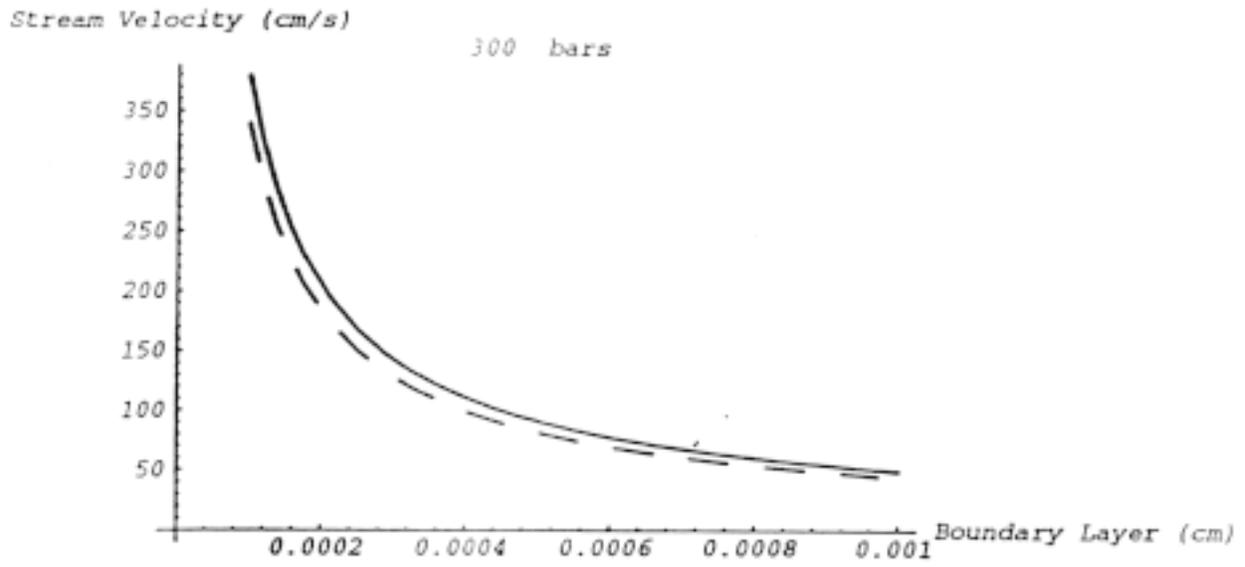


Figure 6

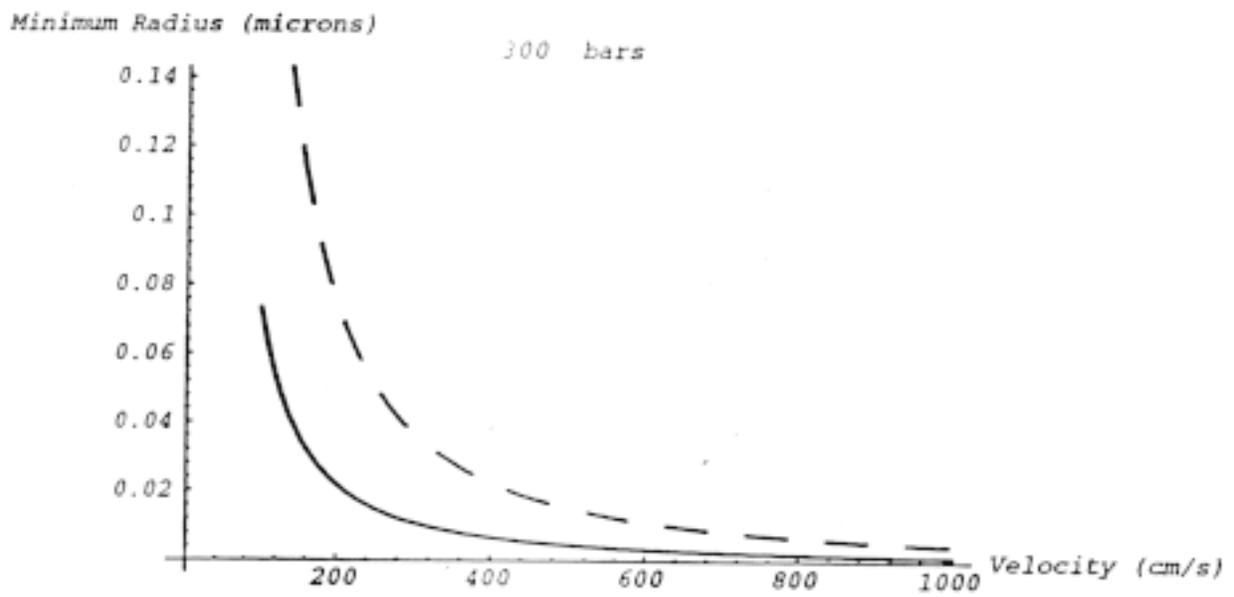


Figure 7

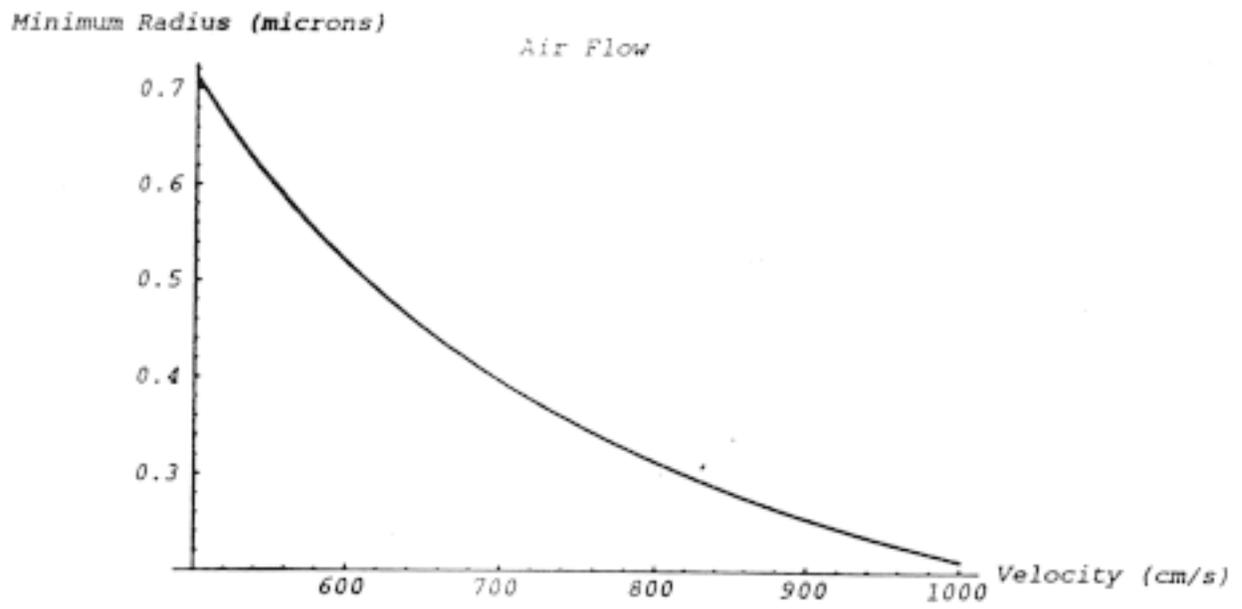


Figure 8