# NUMERICAL MODELING FOR COMBUSTION OF THERMOPLASTIC MATERIALS IN MICROGRAVITY*

KATHRYN M. BUTLER
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland

## Objectives

A time-dependent, three-dimensional numerical model is under development to predict the temperature field, burning rate, and bubble bursting characteristics of burning thermoplastic materials in microgravity. Model results will be compared with experiments performed under microgravity and normal gravity conditions. The model will then be used to study the effects of variations in material properties and combustion conditions on burning rate and combustion behavior.

## Relevance

A clear understanding of fire spread mechanisms in microgravity is critical to the proper assessment of fire hazards from the wide variety of materials used in spacecraft. In early studies, combustion was thought to be less hazardous at low gravity due to the decreased convection of combustion products away from the flame and of oxygen into the flame. Microgravity experiments in a quiescent environment on paraffin, neoprene, foam rubber, and other combusting solids [1] showed that the flames did not reach steady-state conditions but gradually darkened and shrank in size, with some samples self-extinguishing. Such experiments supported the assumption that fire hazards in low gravity could adequately be assessed by tests of materials at normal gravity.

More recent studies have demonstrated that certain thermoplastic materials present a fire hazard unique to microgravity. During combustion, chemical reactions within the bulk of these materials generate internal bubbles, which grow and migrate until they burst at the surface. Burning fuel vapor and occasionally molten fuel are forceably ejected, potentially spreading the fire in random directions. In experiments in normal gravity, Kashiwagi and Ohlemiller [2] observed vapor jets extending a few centimeters from the surface of a radiatively heated polymethylmethacrylate (PMMA) sample, with some molten material ejected into the gas phase. In combustion experiments on Velcro fasteners made of nylon [3], the ignition of flammable gases from a bursting bubble resulted in flamelets spurting from the flame zone. Occasionally, burning liquid droplets were expelled from the sample with velocities higher than 30 cm/sec. These droplets burned robustly until all fuel was consumed, demonstrating the potential for the spread of fire in random directions over an extended distance. The Wire Insulation Flammability Experiment (WIF) [4] studied the burning properties of polyethylene insulation covering a nichrome wire in both quiescent and flowing air. Bursting fuel vapor bubbles were observed, causing pulsations of the flame and ejection of small particles of molten polyethylene. The combustion behavior of PMMA spheres in microgravity, including the bursting bubble phenomenon, is currently being studied by Yang and Hamins [5] in a set of experiments being flown on the NASA Lewis DC-9 Reduced-Gravity Aircraft.

Besides investigating an important mechanism for fire spread in microgravity, the numerical model under development will contribute to the understanding of the role of in-depth generation of bubbles in the transport of heat and volatile gases. This is a problem of considerable interest for a variety of ground-based applications. In their study of degrading PMMA, Kashiwagi and Ohlemiller [2] observed that in addition to enhancing the transport of volatiles to the surface, bursting bubbles also leave holes that increase the depth of the surface layer affected by oxygen. A steady-state regression rate for PMMA that takes bubble nucleation, growth and convection into account was computed by Wichman [6]. The development of bubbles in a melting solid is also of importance in the field of softening coal pyrolysis. When coals that

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exhibit plastic behavior are heated, they swell to a much larger volume until a critical final swelling temperature is reached. During the swelling, the coal behaves like a highly viscous liquid, and bubbles from gas-producing chemical reactions are generated. A mathematical model of softening coal pyrolysis to predict volatile yields, plasticity, and swelling was developed and compared with experimental results by Oh [7]. This model treats the coal particles as spherical and isothermal, with a spatially uniform bubble concentration. Bubbles grow due to chemical reactions, gas diffusion, and coalescence until they contact the particle surface, at which time they are assumed to rupture.

Intumescent fire-resistant materials protect an underlying surface through the development of a thick foam char in the presence of a high heat flux. In these materials, an endothermal gasification reaction generates bubbles in the molten thermoplastic, and the gas trapped in the final swollen char provides an insulating barrier to the transport of heat. By improving our understanding of the effects of bubble growth and migration on heat transfer, and of the conditions under which a bubble near the surface will burst, the three-dimensional model will also provide insight into intumescent behavior [10], [11].

Microgravity simplifies the combustion behavior to be modelled. Bubbles are not subject to buoyancy forces, and therefore migrate under the influence of temperature gradients only. A simple spherical geometry may be considered, and the combustion process can be modelled and compared to microgravity experiments without worrying about gross distortions of the melting sample due to gravity. Experience with this model may suggest new directions for solid combustion experiments in microgravity.

Research Approach – Burning Thermoplastics Model

A time-dependent, three-dimensional numerical model of polymeric materials that melt and bubble upon exposure to heat is under development. Both rectangular and spherical geometries are available. The behavior of burning thermoplastic materials is studied by observing the combined effects of a large number of randomly distributed bubbles as they nucleate, grow, and distort the surrounding velocity and temperature fields. Hydrodynamic, thermal, and chemical mechanisms are included, and an adjustable buoyancy term allows investigation of gravity effects from 0G to 1G. The model will eventually include condensed phase chemistry specific to PMMA, the mass transport of fuel vapor and fuel by bursting bubbles, and gas phase coupling. PMMA is a relatively simple fuel that has been well studied, and physical parameters necessary for model input are readily available from the literature.

Initially, the thermoplastic material is represented by a volume of highly viscous material with randomly distributed bubble nucleation sites. Under microgravity conditions, the initial volume is spherical for comparison with microgravity experiments on combusting PMMA spheres. The volume is represented by a grid of points in $(r, \theta, \phi)$ space. Appropriate boundary conditions are applied to the outer surface, and the energy equation is solved to determine the temperature field throughout the volume. When the local temperature at a bubble nucleation site exceeds the degradation temperature of the polymer, bubble growth is initiated. The bubble growth rate is currently determined by a simple diffusion-controlled growth relation [8]. Another approach that includes the time-dependent production of gaseous degradation products by chemical reactions is being developed. This approach is based on cell models of bubble growth that have been developed for studying foam fabrication [9], and which incorporate several important factors, including variations in gas concentration, finite thickness walls, and properties of the melt such as viscosity, surface tension, and viscoelastic properties.

A temperature gradient in the surrounding fluid induces migration of a bubble toward the region of higher temperature. Two mechanisms are potentially responsible. Thermocapillary motion is driven by surface tension gradients along the surface of the bubble, which create a tangential stress that causes fluid motion both inside and outside the bubble. The bubble is thus propelled toward warmer regions where the surface tension is lower. This force requires a fluid free from surface-active contaminants. In the presence of contamination, which is likely in the chemically active PMMA melt, internal circulation in the bubble is eliminated and thermocapillary motion is prevented. The second mechanism derives from viscosity gradients, which will drive a growing bubble toward increasing temperature if the bubble growth rate $\dot{R}$ is much larger than the resulting translation speed $U$ [11]. With buoyancy included, and assuming the presence of contamination, the expanding bubble migrates with terminal velocity

$$\mathbf{U} = \frac{2}{3} R \dot{R} \left( -\frac{d \ln \mu}{dT} \right) \nabla T - \frac{2}{9} \frac{\triangle \rho R^2}{\mu} \mathbf{g} \quad . \tag{1}$$

In this equation, $R$ is the bubble radius, $\mu$ viscosity, $\nabla T$ the temperature gradient, $\triangle \rho$ the difference between melt and bubble density, and $\mathbf{g}$ the gravity vector. The buoyancy force is set to zero for microgravity.

The expansion and migration of each individual bubble causes movement in the surrounding fluid that is transmitted to the other bubbles in the melt. Even for a small PMMA sphere whose diameter is on the order of a centimeter, the bubbles generated in-depth during combustion number in the tens to hundreds. This makes it impossible for today's computers to solve the equations of continuity, momentum, and energy while meeting the boundary conditions on the surface of each bubble. The approach taken in this model is to first solve the problem at hand in the local region around a single bubble. If the bubbles are far apart compared with their size, the flow around one bubble induced by all other bubbles can be obtained to lowest order as the sum of the individual flow fields [10] The path of an individual bubble through the surrounding melt is therefore determined by its own expansion rate, the local temperature gradient, and the sum of the velocity fields from all of the other bubbles. A description of bubble motion that is more accurate for bubbles in close proximity will be pursued.

The flexible outer surface of the thermoplastic material feels the forces from all bubbles within the volume and swells accordingly. The points of the grid representing locations within the melt also translate according to the sum of bubble velocity fields. Bubble size and location and the locations of surface and grid points are incremented in time using a Runge-Kutta scheme.

Through migration and growth, the bubbles will eventually reach the outer surface of the volume. The model currently treats this in a simple way by allowing two options. The first option assumes that the bubble is trapped by the sample material. The position of the outer surface is set to the surface of the bubble that would otherwise escape, and the bubble is contained. The second option considers the bubble to have "burst" upon breaking the outer surface. The bubble is then eliminated from further calculations. Merging of bubbles within the volume is treated in a similar way. Overlapping bubbles may either be left alone or merged, in which case one of the bubbles is eliminated and the other assigned a radius consistent with the combined volumes of both bubbles and located at their center of mass.

The model treatment of nucleation and growth of bubbles within a spherical thermoplastic sample is illustrated in Figure 1. To demonstrate the sequence of events, two hundred bubble nucleation sites are randomly located on a plane through the center of the sphere. A steady heat flux is applied to the upper surface. As the temperature within the sphere increases with time, bubbles at increasing depths begin to grow. The bubbles move toward the hot surface where the viscosity is lower (no buoyancy has been included in this calculation), and tend to separate due to the expansion of other bubbles. The outer surface swells to contain the bubbles, and merging of bubbles has been prevented. In this set of illustrations the effect of the bubbles on heat transfer has not been taken into account. Since the ratio of the thermal conductivity of the gas contained within a bubble to the melt is about 0.1, this effect will be significant.

The solution of the energy equation for this problem poses some difficulties. As the in-depth bubbles grow, the outer surface is distorted, and the outer boundary condition no longer applies along a geometrically simple interface. The bubbles vary considerably in size and grow with time, complicating the solution in their vicinity. These difficulties are addressed by dividing the problem to be solved into two: an equation of the entire melt that satisfies the outer boundary conditions, and a separate set of problems that satisfy the local boundary conditions at each bubble. The variations in heat flux contributed by the bubble fields at the surface of the melt are subtracted from the boundary conditions of the melt problem to maintain the accuracy of the total temperature field. The summation of the melt solution with the individual bubble solutions then gives a reasonable approximation to the total temperature field, at least under the condition that the bubbles are far apart relative to their size.

A Lagrangian approach to the melt problem, which modifies the energy equation to maintain the initial simple geometry for calculations, has run into computational problems due to singularities in velocity near the growing bubbles. If the timescale for thermal diffusion is much shorter than the timescales for bubble expansion and translation, then the solution to the transient energy equation in the local neighborhood around a single bubble is well approximated by the sum of a dipole singularity plus a source:

$$T = \mathbf{r} \cdot \nabla T \left[ 1 - \frac{R^3}{r^3} \frac{(\alpha - 1)}{(\alpha + 2)} \right] + \frac{R^2}{kr} \dot{q}'' \quad . \tag{2}$$

In this equation, $T$ is the melt temperature, $k$ is the thermal conductivity of the melt, $\alpha$ is the ratio of the thermal conductivity of the bubble to that of the melt, and $\dot{q}''$ is a heat source that represents the heat evolved in the chemical gasification reactions. The strengths of the source and dipole singularities vary with time and the local temperature gradient. The difficulty here is in the determination of the value of the temperature gradient at the bubble site, due to the effect of its neighbors. The best approach for the determination of the temperature field is under review.

In the current model, a constant heat flux is applied to the outer surface of the thermoplastic sample, and the heat transfer is through conduction only. Although the condensed phase phenomena are of primary interest in this research project, the behavior of the gas phase must also be included to properly simulate a burning solid. Initially, a simple description consisting of the Shvab-Zel'dovich formulation [12], which assumes that heat and mass diffuse at equal rates in the gas phase, and the flame-sheet approximation will be added to the model. Finite-rate kinetics [13] and radiation heat transfer from the flame [14] will be considered for refinement of the coupling between gas phase and condensed phase.

Research Approach – Bubble Bursting Model

Of particular interest in this modeling effort is the behavior of bubbles generated within the combusting thermoplastic material as they reach the surface. The rate of bursting and the force with which burning fuel and volatile gases are expelled from the bursting bubble will determine the fire spread hazard in microgravity, as well as having a large impact on heat and mass transport.

In their experiments on burning PMMA samples, Kashiwagi and Ohlemiller [2] observed that the bubble frequency increased and bursting was less violent with increasing levels of oxygen. They hypothesized that this behavior was due to substantially lower viscosity in the near-surface region. Experiments currently being flown on the NASA Lewis DC-9 Reduced Gravity Aircraft by Yang [5] are investigating the combustion behavior of PMMA spheres in microgravity. Spheres of diameters 2, 2.5, and 3 millimeters are attached to thin wires for support and ignited by heater wires under various conditions of pressure and oxygen level. Preliminary observations show that although in-depth bubbling begins immediately upon ignition, the flame front around the PMMA spheres is roughly spherical and relatively undisturbed for the first few seconds of burning. This calm period is followed by the sudden onset of rapid spurting of flamelets in random directions, which continues until the fuel is used up. Figure 2 contains representative images from both the early and late stages of burning from this set of experiments.

To understand what drives the bursting process, a separate numerical model will be developed to investigate in detail the behavior of a single bubble as it reaches the surface of a melted thermoplastic object. This is a multiphase fluid flow problem involving complex time-dependent three-dimensional boundaries. Two potential modeling techniques have been identified for this task: the lattice Boltzmann method [15] and an interface-capturing two-phase fluid model recently developed by Nadiga and Zaleski [16] that uses finite differences. The lattice Boltzmann method is well suited to following the development of complex interfaces in multiphase fluids in three dimensions. For example, Martys and Chen [17] have successfully modeled the displacement in a porous medium of one fluid by a second fluid that is immiscible with the first. The finite difference model is also designed to model complex fluid interfaces, and additionally incorporates correct thermodynamic relationships in the model formulation. In either case, development work will be necessary to include the thermodynamic quantities for the bubble bursting problem.

Variables thought to be influential on the bursting behavior include bubble size and internal pressure, bubble growth rate and velocity, and the viscosity, surface tension, and viscoelastic properties of the melt at the surface. These factors will be incorporated into the bubble bursting model as the modeling technique allows.

The results from the bubble bursting model will be used in the burning thermoplastics model to determine whether a bubble is retained or released when it reaches the surface, based on the material properties of the surface and the characteristics of the bubble. If the bubble bursts, the vapor contained within will be released, decreasing the size of the melted thermoplastic sample.

Research Plans

In this three-dimensional, time-dependent model, the behavior of bubbling thermoplastics is studied from first principles. The basic geometry and framework for the model has been completed. The next steps in development include satisfactory treatment of heat transfer and the incorporation of a submodel of bubble growth that takes into account chemistry, diffusion, finite thickness walls, and properties of the melt. Values representing PMMA will be assigned to the input parameters, and the chemistry of decomposition of PMMA into its gaseous monomer will be incorporated into the equations for heat transfer and bubble growth rate. Calculations of gas phase mechanisms will then be added in sufficient detail to adequately represent the coupling between the flame and the surface of the burning thermoplastic sample.

A separate model of the bubble bursting process will be developed to determine the conditions under which burning fuel vapor and droplets are expelled from the surface. Results from this model will be incorporated into the burning thermoplastics model.

Once the model has been adequately developed, its predictions will be compared to experiments. The comparisons will be used to improve and validate the model. Finally, a parametric study will investigate the effects of combustion conditions and material properties on the burning behavior of thermoplastic materials.

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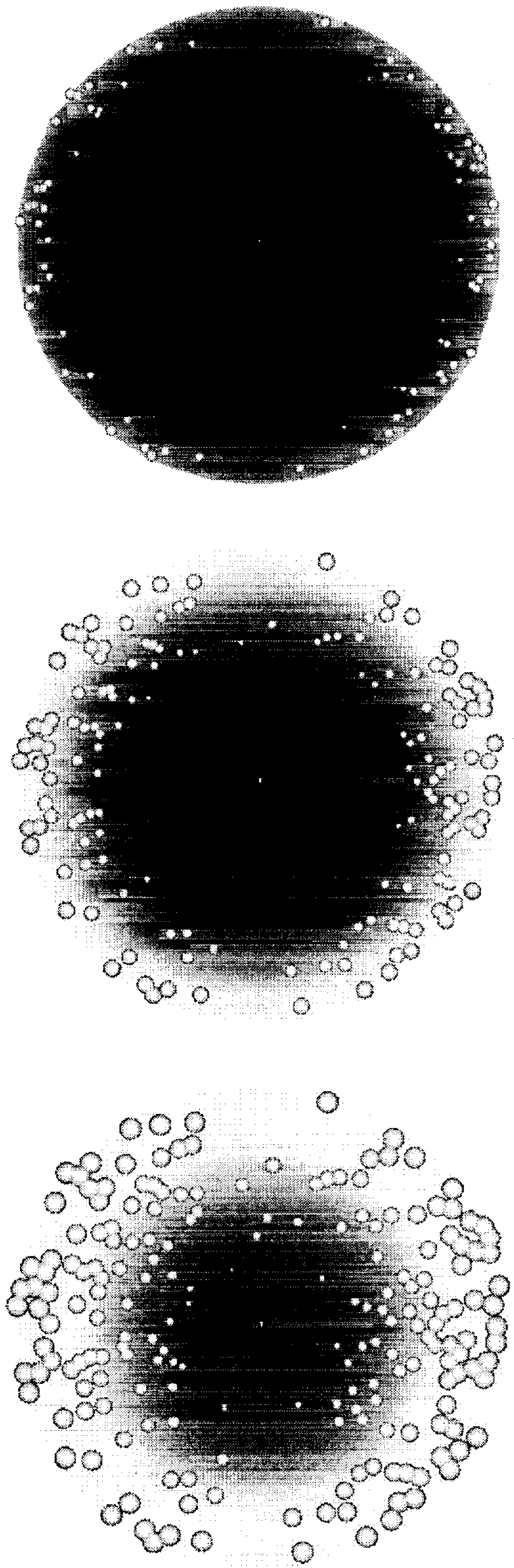

FIGURE 1: Development of bubbles in the interior of a sphere with time as a steady heat flux is applied to the outer surface. Darker regions indicate lower temperatures.

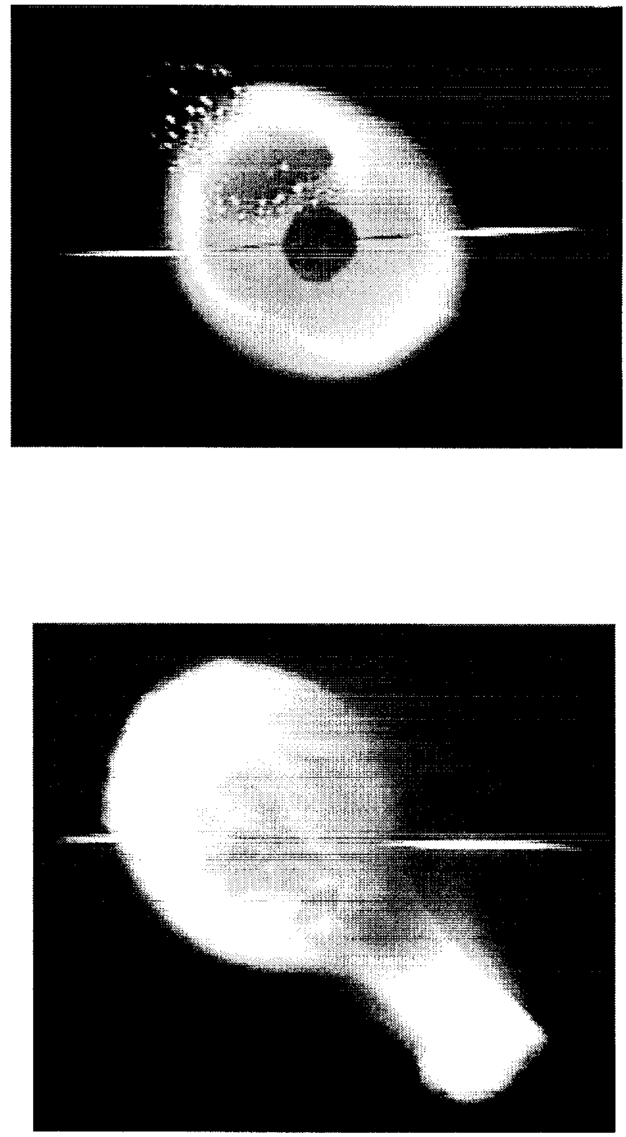

FIGURE 2: Images from combustion of a PMMA sphere in microgravity. The top image shows a sphere in the first few seconds after ignition, with a relatively undisturbed spherical flame front. Later in the burning process (after about ten seconds), sputtering occurs, with multiple flamelets shooting in random directions. One of these flamelets is captured in the bottom image.