presented as Fig. 5. The authors gratefully acknowledge the finanical support of the National Research Council of Canada (Grant No. A8668).

References

[1] Arnold, R.N. and Warburton, G.B., "Flexural Vibration of the Walls of Thin Cylindrical Shells Having Freely Supported Ends," *Proceedings of the Royal Society (London), Series A*, Vol. 197, June 1949, pp. 238-256.

[2] Karimbaer, T.D., Koroler, V.P., and Epanov, V.G., "Experimental Investigation of Frequencies and Forms of Natural Vibration of Glass-Fibre Reinforced Plastic Shells," *Problemy Prochnosti*, Vol. 6, May 1974, pp. 31-33 (in Russian).

[3] Dong, W.N. and Muggeridge, D.B., "Vibration Characteristics of Reinforced Plastic Pipe in a Fluid Medium," IEEE Ocean International Conference, Halifax, Nova Scotia, Aug. 1974, pp. 418-424.

[4] Jain, R.K., "Vibration of Fluid-Filled, Orthotropic Cylindrical Shells," *Journal of Sound and Vibration*, Vol. 37, No. 3, 1974, pp. 379-388.

[5] Weingarten, V.I., Masri, S.F., and Lashkari, M., "Free Vibration of a Partially Submerged Cylindrical Shell," *Hydromechanically Loaded Shells, Proceedings of the 1971 Symposium of the International Association for Shell Structures*, Honolulu, University Press of Hawaii, 1973, pp. 591-601.

Screening of Liquids for Thermocapillary Bubble Movement

William R. Wilcox* and R. Shankar Subramanian†
Clarkson College of Technology, Potsdam, N.Y.
John M. Papazian‡
Grumman Aerospace Corporation, Bethpage, N.Y.
and
Harry D. Smith§ and Douglas M. Mattox¶
Westinghouse R&D Center, Pittsburgh, Pa.

Nomenclature

C_p = heat capacity of melt, kJ/kg·K
D_b = diameter of bubble, m
Gr = Grashof number, $g\alpha\beta h^4/\nu^2$
h = thickness of layer of liquid, m
k = thermal conductivity of liquid, W/m·K
ℓ = length of layer of liquid, from hot wall to cold wall, m
Pr = Prandtl number, ν/κ
q = rate of heat loss from cell, W/m^2
Ra_h = horizontal Rayleigh number, $\alpha\beta g h^4/\kappa\nu$
T = temperature at point in liquid, K
V = velocity of movement of melt due to buoyancy and surface tension, m/s
V_b = velocity of movement of bubble under influence of ΔT, m/s
y = vertical distance from bottom of liquid to any point, m
α = coefficient of thermal expansion of liquid, $(\partial \ln\rho/\partial T)$, K^{-1}
β = longitudinal temperature gradient, K/m
γ = surface tension between liquid and gas, N/m
κ = thermal diffusivity, $k/\rho C_p$, m^2/s
μ = dynamic viscosity, kg/m·s
ν = kinematic viscosity, m^2/s
ρ = density of melt, kg/m^3

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*Professor and Chairman, Dept. of Chemical Engineering.
†Associate Professor, Dept. of Chemical Engineering. Member AIAA.
‡Senior Research Scientist, Materials and Structural Mechanics, Research Dept.
§Senior Scientist, Ceramic Systems.
¶Manager, Ceramic Systems.

THE objective of this work was to develop a technique for ascertaining thermocapillary movement of gas bubbles in a liquid. Gas bubbles have been found to be incorporated much more often in space-processed materials than in those processed on Earth.[1-6] The behavior of gas bubbles is expected to be especially important in containerless processing of glasses in orbit. Although buoyancy would no longer provide appreciable migration rates, gas bubbles are predicted to move in a temperature gradient due to the dependence of surface tension on temperature, with a velocity equal to[7,8]

$$V_b = -\frac{D_b}{4\mu}\frac{\partial \gamma}{\partial T}\nabla T \tag{1}$$

Thus one might expect that if $\partial\gamma/\partial T \neq 0$, a bubble in a liquid would always move in an imposed temperature gradient. However, surfactants may prevent the bubble from moving, as apparently happened in SPAR experiments on molten CBr_4.[1,9] Volatile constituents may also cause movement in the opposite direction.[10-12]

For flight experiments, some method is required to pretest the qualitative behavior of a gas bubble. We have chosen to use horizontal tubes or layers. Unfortunately, experiments done on Earth are complicated not only by the buoyant rise of the bubble but also by natural convection of the liquid itself. With a bubble in a tube or sheet, the prime concern is that any bulk movement of the liquid be much slower than the expected bubble movement. Fortunately there are existing theoretical results on similar systems, namely flat sheets of liquid with vertical end walls at different temperatures. We expect these to be approximtely true for our experimental arrangements, and Eq. (1) to provide an order-of-magnitude estimate for thermocapillary bubble movement rates in a horizontal channel or tube.

In the derivation of Eq. (1), it was assumed that steady-state conditions are valid, that the properties are constant, that there are no interactions with system boundaries or other bubbles, and that the liquid is pure.[7] Since in real situations these conditions are not satisfied, we seek here only semiquantitative tests of the usefulness of proposed experimental techniques.

Theory

It may be shown that the bubble always moves slower than the liquid if the upper surface is free.[13] Thus the liquid film must be enclosed on all sides. At the upper and lower horizontal surfaces, two types of boundary conditions on the temperature field are typically used to represent limiting cases. In one case, the boundaries are assumed to be insulated so that the normal heat flux through them is set equal to zero. In the other extreme, the temperature field is prescribed as being linear from one end of the channel to the other. This latter case is commonly referred to as that of "conducting" boundaries. In both cases, the parallel flow velocity field in the liquid film in a region away from the end walls (for a constant axial temperature gradient β) is given by[14-17]:

$$\frac{V\nu}{\alpha\beta g h^3} = \frac{(y/h)^3}{6} - \frac{(y/h)^2}{4} + \frac{y/h}{12} \tag{2}$$

for $\ell/h \gg 3.5 \times 10^{-6}\ Ra_h$. The maximum value of V in the upper part of the channel is reached at $y = 0.79$, with the movement in a direction opposite to that of the thermocapillary migration of the bubble for $\partial\gamma/\partial T < 0$. The relative movement rates are thus

$$\left| \frac{\text{Maximum axial velocity in liquid}}{\text{bubble movement rate}} \right| \approx \left| \frac{0.032\ \alpha g h^3 \rho}{D_b(-\partial\gamma/\partial T)} \right| \tag{3}$$

Let us estimate the ratio of film movement to bubble movement for typical properties of molten glass in a thick cell ($\alpha = 10^{-4}$/K, $\partial\gamma/\partial T = -0.06$ mN/m·K) $\rho = 3000$ kg/m^3, $D_b = 1$ mm, $h = 10$ mm). From Eq. (3) we find that the liquid would move about 50% faster than the bubble. For a thin film, say with $D_b = 0.1$ mm and $h = 1$ mm, we find that bubbles move 64 times faster.

For water, on the other hand, a 10-mm-thick cell with 1-mm-diam bubbles gives a bubble movement rate twice that of the bulk convection. While not entirely satisfactory, successful screening could be carried out in such a thick cell. Nevertheless, thin cells are clearly more advantageous.

There is another concern with layers of liquid, i.e., that multiple cells or instabilities may develop. A linear stability analysis has been performed by Hart[14] in the extreme cases of conducting and insulating horizontal boundaries. Hart assumes the basic flow to be given by Eq. (2) and indicates that this is true when $Gr \leq 800\ \ell/h$ with the Grashof number defined by $Gr = g\alpha\beta h^4/\nu^2$. Hart's stability analysis indicates that the critical Grashof number Gr_c for the onset of instability depends strongly on the Prandtl number of the fluid and on the nature of the boundary conditions at the horizontal surfaces. In the case of conducting boundaries, when the critical Grashof number is plotted against the Prandtl number for $Pr \gtrsim 1$ (liquids), the neutral stability curves exhibit a negative slope. That is, for large Prandtl number fluids such as glasses, the critical Grashof number is very small (e.g., for $Pr \sim 100$, $Gr_c \sim 100$). In the case of insulating boundaries, Hart presents a neutral stability curve for longitudinal modes which indicates that Gr_c increases steeply with increasing Prandtl number for liquids. Unfortunately, due to computational restrictions, results for transverse modes (which become unstable at lower Gr_c) are presented only for $Pr \lesssim 0.02$. Based on Hart's results, it would appear that insulating boundaries are desirable to prevent the onset of instabilities.

If the cell loses heat to the surroundings, a temperature minimum can occur, leading to a flow reversal (doubly circulating flow).[13] For uniform heat flux q from a free surface with zero surface stress, this is predicted to occur for $q > 2kh\beta/\ell$. Interestingly, in Ref. 18 this result is derived from an analysis which ignores convective heat transfer and treats simple one-dimensional conduction.

Experimental

From the foregoing we expect a horizontal cell to be useful for screening for thermocapillary bubble movement provided Eq. (3) gives a result significantly less than one and that the heat loss q from the cell is less than $2kh\beta/\ell$. Three experimental variations on this concept were employed and are briefly described.

Horizontal Sheets of Molten Glass Heated From Below

Heat was provided by passage of electric current through a horizontal platinum sheet, cut with a taper in order to generate a temperature gradient on the order of 30 K/mm.[19] Initial experiments were performed with a thin layer of molten glass containing many small bubbles on the top of the platinum sheet. No cover was used. Zirconia particles were added as a tracer for bulk motion. The anticipated circulation in the presence of a free surface was observed. Thus, all subsequent experiments were performed with a silica cover slip containing an inverted channel about 0.5 mm deep.

Bubbles in 85 PbO-15 SiO_2, 85 PbO-7.5 B_2O_3 – 7.5 SiO_2, and 79 PbO-11 B_2O_3-8 SiO_2 – $2Al_2O_3$ melts were observed to move slowly in the "wrong" direction, i.e., away from the heat source. At first this was thought to be indicative of an error in our experimental technique, but later it was found that these systems exhibit a surface tension that increases with increasing temperature[20]—a very unusual phenomenon. Experiments done with molten borax gave semiquantitative agreement with Eq. (1), i.e., the bubbles moved faster as the bubble diameters increased and as the viscosity decreased (temperature increased). Bubbles tended to rise due to buoyancy, but not severely because of the vertical temperature gradient which partially counteracted buoyancy. Bubbles with diameters approaching the channel thickness (0.5 mm) moved slower than one would expect by extrapolation of velocities for smaller bubbles, clearly due to wall effects. A few bubbles appeared to stick to the silica walls and did not move.

A few experiments were also performed with molten glass contained in 0.5 mm ID silica capillary turbes on the platinum strips. However, it was more difficult to view the bubbles in this case, and molten glass had to be placed outside the capillary to bring about reasonable thermal contact with the platinum strips.

Table 1 Behavior of bubbles in organic melts contained in horizontal tubes heated at the ends

Compound	Bubble behavior
CBr_4 (all grades)	Generally immobile, with occasional slight erratic movement
Commercial (very impure) camphene	Moved to *cold* end at $\beta \approx 0.1$ K/mm: Indicative of preferential evaporation of one component (probably camphene, which is quite volatile)
Zone refined camphene (still rather impure)	Moved to hot end at $\beta \approx 0.3$ K/mm
Commercial succinonitrile	Generally immobile
Distilled and zone refined succinonitrile (very pure)	Very mobile to hot end at all β. Maximum $V_b \approx 1.3$ mm/s

Table 2 Behavior of bubbles in organic melts contained in horizontal tubes and heated with a soldering iron

Compound	Bubble behavior
Zone refined biphenyl	Followed soldering iron at first but stopped after a few minutes (indicates thermal degradation or oxidation to produce surfactant)
Commercial succinonitrile	Immobile
Commercial camphene	Followed iron readily
Commercial borneol	No apparent movement, but results uncertain because of rapid evaporation of melt
CBr_4	A few bubbles moved slowly toward iron, but most immobile
Dow Corning No. 200 silicone oil	Moved readily toward iron
Commercial Salol (phenyl salicylate)	Slight tendency to move toward iron
Commercial naphthalene	Immobile

Organic Melts in Horizontal Tubes

Pyrex tubes 10 mm i.d. × 10 mm long were partially filled with organic compounds and sealed under a moderate vacuum, insufficient to remove all gas. Each tube was placed in a slot in an aluminum block. The block was horizontal and had heaters at both ends. The organic compound was melted with both heaters at the same temperature. A 5-10 mm long × 2-4 mm deep bubble formed and was centered by mechanical leveling of the tube (as with a carpenter's level). The temperature of one heater was then increased and bubble behavior observed. In these experiments the tube diameter was really too large and some bulk convection undoubtedly occurred. Nevertheless, the experiments were useful for screening, with the results summarized in Table 1. Note the substantial effects of sample purity on bubble migration behavior.

In a still simpler test, originally suggested by Young et al.,[7] air bubbles at about 1 atm were introduced into organic melts in horizontal tubes. A temperature gradient was applied by means of a hot soldering iron touched to the top of the tube. If the bubbles moved toward the iron, the iron was moved slowly down the tube. The results summarized in Table 2 were obtained.

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References

[1] Papazian, J. M. and Wilcox, W. R., "Interaction of Bubbles with Solidification Interfaces," *AIAA Journal*, Vol. 16, May 1978, pp. 447-451.

[2] Yee, J. F., Lin, M. C., Sarma, K., and Wilcox, W. R., "The Influence of Gravity on Crystal Defect Formation in InSb-GaSb Alloys," *Journal of Crystal Growth*, Vol. 30, 1975, pp. 185-192.

[3] Larson, D. J., "Skylab M553 Sphere Forming Experiment," *Proceedings of the Third Space Processing Symposium*, NASA M-74-5, Huntsville, Ala., June 1974, pp. 101-113.

[4] Deruytere, A., Aernoudt, E., Gueminne, M., Smeesters, F., Arkens, O., and Verhaeghen, M., "M565 Silver Grids Melted in Space," *Proceedsings of the Third Space Processing Symposium*, NASA M-74-5, Huntsville, Ala., June 1974, pp. 159-201.

[5] Kawada, T., Takahaski, S., Yoshida, S., Ozaga, E., and Yoda, R., "Preparation of a Silicon Carbide Whisker Reinforced Silver Composite Material in a Weightless Environment," *Proceedings of the Third Space Processing Symposium*, NASA M-74-5, Huntsville, Ala., June 1974, pp. 203-233.

[6] Raymond, L. and Ang, C. Y., "Casting Dispersion Strengthened Composites at Zero Gravity," *Space Processing Applications Rocket Project. SPAR I Final Report,* NASA TM X-3458, Dec. 1976, Chap. VI.

[7] Young, N. O., Goldstein, J. S., and Block, M. J., "The Motion of Bubbles in a Vertical Temperature Gradient," *Journal of Fluid Mechanics*, Vol. 6, Oct. 1959, pp. 350-356.

[8] McGrew, J. L., Rehm, T. L., and Griskey, R. G., "The Effect of Temperature Induced Surface Tension Gradients on Bubble Mechanics," *Applied Scientific Research*, Vol. 29, June 1974, pp. 195-210.

[9] Papazian, J. M. and Wilcox, W. R., "Thermal Migration of Bubbles and Their Interaction with Solidification Interfaces," *Space Processing Applications Rocket Project. SPAR III Final Report*, NASA TM 78137, Jan. 1978, Chap. IV.

[10] Wilcox, W. R., "Anomalous Gas-Liquid Inclusion Movement," *Industrial and Engineering Chemistry*, Vol. 61, March 1969, pp. 76-77.

[11] Anthony, T. R. and Cline, H. E., "The Thermomigration of Biphase Vapor-Liquid Droplets in Solids," *Acta Metallurgica*, Vol., 20, Feb. 1972, pp. 247-255.

[12] Wilcox, W. R., "Fractional Solidification Phenomena," *Separation Science*, Vol. 4, April 1969, pp. 95-109.

[13] Cormack, D. E., Stone, G. P., and Leal, L. G., "The Effects of Upper Surface Conditions on Convection in a Shallow Cavity with Differentially Heated End-Walls," *International Journal of Heat and Mass Transfer*, Vol. 18, May 1975, pp. 635-648.

[14] Hart, J. E., "Stability of Thin Non-Rotating Hadley Circulations," *Journal of Atmospheric Sciences*, Vol. 29, May 1972, pp. 687-697.

[15] Cormack, D. E., Leal, L. G., and Imberger, J., "Natural Convection in a Shallow Cavity with Differentially Heated End Walls. Part 1. Asymptotic Theory," *Journal of Fluid Mechanics*, Vol. 65, Aug. 1974, pp. 209-229.

[16] Cormack, D. E., Leal, L. G., and Seinfeld, J. G., "Natural Convection in a Shallow Cavity with Differentially Heated End Walls. Part 2. Numerical Solutions," *Journal of Fluid Mechanics*, Vol. 65, Aug. 1974, pp. 231-246.

[17] Imberger, J., "Natural Convection in a Shallow Cavity with Differentially Heated End Walls. Part 3. Experimental Results," *Journal of Fluid Mechanics*, Vol. 65, Aug. 1974, pp. 247-260.

[18] Arpaci, V. S., *Conduction Heat Transfer,* Addison-Wesley Publishing Co., Reading, Mass, 1966, pp. 111-112.

[19] Smith, H. D., Mattox, D. M., Wilcox, W. R., and Subramanian, R. S., "Glass Fining Experiments in Zero Gravity," Westinghouse R&D Document No. 77-9D6-FINES-R5 to Marshall Space Flight Center, June 1977.

[20] Shartsis, L., Spinner, S., and Smock, A. W., "Surface Tension of Compositions in the Systems $PbO\text{-}B_2O_3$ and $PbO\text{-}SiO_2$," *Journal of Research of the National Bureau of Standards*, Vol. 40, Jan. 1948, pp. 61-66.