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Probability of Trapping Solid Particles during Zone Melting

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Abstract

The probability P of trapping of glass beads was measured for tilt rotating zone melting of camphor. P increased with increasing zone travel rate, increasing tilt angle, decreasing tube rotation, and increasing mass of beads. P also decreased dramatically with distance down the tube. This is attributed to increasing impurity content as the zone moves down the tube and by the changing shape of the freezing interface due to the diminished content of glass beads. Trapping was predominantly by periodic bands, indicating one or more catastrophic trapping mechanisms.

In the absence of stirring, suspended foreign particles are engulfed by a solidifying material only if the freezing rate exceeds a critical value V_c (*1–8*). A series of experiments with rotating zone melting has shown that V_c is substantially increased by stirring (*9–12*). With a horizontal tube containing a gas bubble contacting the freezing interface, an increased rotation rate increased V_c for trapping at the center of the tube and decreased V_c at the tube wall for copper and carbon particles in naphthalene (*9*). No increase with rotation rate was observed for glass beads in naphthalene (*12*). In the absence of a gas bubble contacting the freezing interface, virtually no trapping was observed with a rotating horizontal tube (*10*). As the tilt angle was decreased and as rotation rate was increased, V_c increased for coal fly ash particles in camphor (*11*).

While V_c decreases for increasing particle size in the absence of stirring

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(*1–8*), the reverse is true for rotating zone melting (*12*). V_c was also found to decrease as the number of particles is increased.

Impurity additions to naphthalene were found to increase slightly V_c for glass beads (*13*), even though theory predicts the reverse (*14*).

While the concept of a critical freezing rate has been useful, it does not convey sufficient information for design of separation processes such as particle chromatography (*9–11*). At least with stirring, it has been found that a very small amount of trapping does occur below V_c, while trapping is not immediate above V_c (*9–12*, *15*). Thus a trapping probability may be more appropriate. We may define a trapping probability P as a fraction of the particles trapped per unit length x of solidification, or mathematically

$$P \equiv -\frac{dW_l}{W_l\,dx} = -\frac{dN_l}{N_l\,dx} \tag{1}$$

where W_l is the mass of particles present in the melt and N_l is the number of particles. Thus P is the negative slope of a plot of ln W_l vs x.

The purpose of the research described here was to determine the dependence of trapping probability P on the operating parameters for tilt rotating zone melting.

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EXPERIMENTAL METHODS

The experiments are described in detail elsewhere (*16*). Class VI-A microbeads from the Ferro Corp. (Jackson, Mississippi 39205) were used

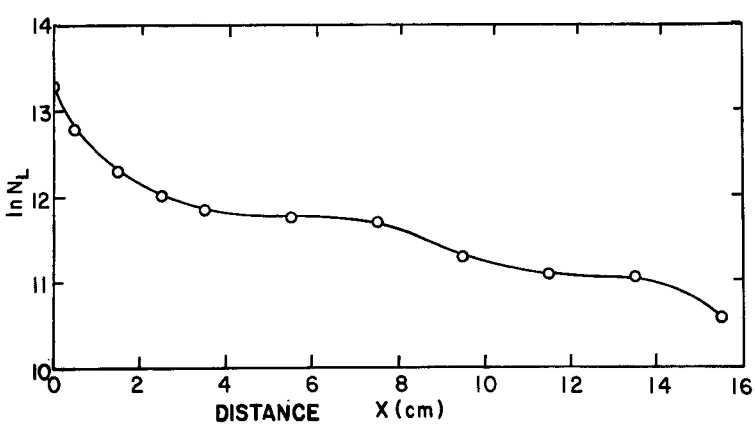

FIG. 1. Number of beads N_l in liquid zone vs position. 37 μm beads, 45° tilt, 1.03 cm/hr zone travel rate, 10 rpm rotation, 0.05 g initial mass of beads.

with camphor as a host. These beads were guaranteed to all be within 4% of the indicated sizes and to be 95% spheres. The camphor was first given 12 upward vertical zone passes in argon at 1 cm/hr using zones about 2.5 cm long in a sealed 1 cm i.d. Pyrex tube. After zoning, most (but not all) of the zoned material was colorless, transparent, and reasonably free of cracks. The top 7.6 cm containing a yellow impurity was melted and poured off. An additional length was melted, the beads added and allowed to sink, and then the tube again sealed in argon.

Each tilt rotating zone melting run was made with constant heater power, tilt, rotation, and zone travel rate. During zoning the zone was observed through an optical microscope at 10 to 70×. Neither cellular nor dendritic growth was observed, and the solid was clear except for trapped particles. After zoning the glass tube was fractured and removed. The camphor was cut into sections and placed on weighing paper. It was evaporated off in a vacuum oven and the beads weighed. Typical results are shown in Figs. 1 and 2.

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RESULTS

If P is constant, then Eq. (1) may be integrated to yield

$$\frac{W_L}{W_0} = \frac{N_L}{N_0} = e^{-Px} \tag{2}$$

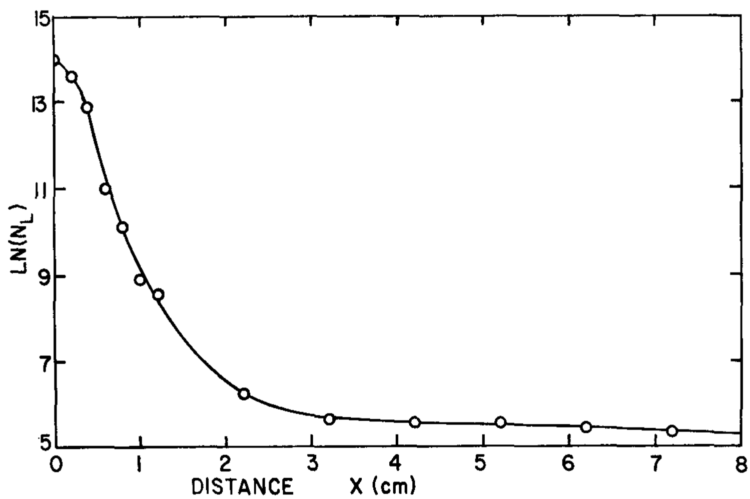

FIG. 2. Number of beads vs position. 0.1 g of 37 μm beads, 60° tilt, 0.1 cm/hr zone travel rate, 5 rpm.

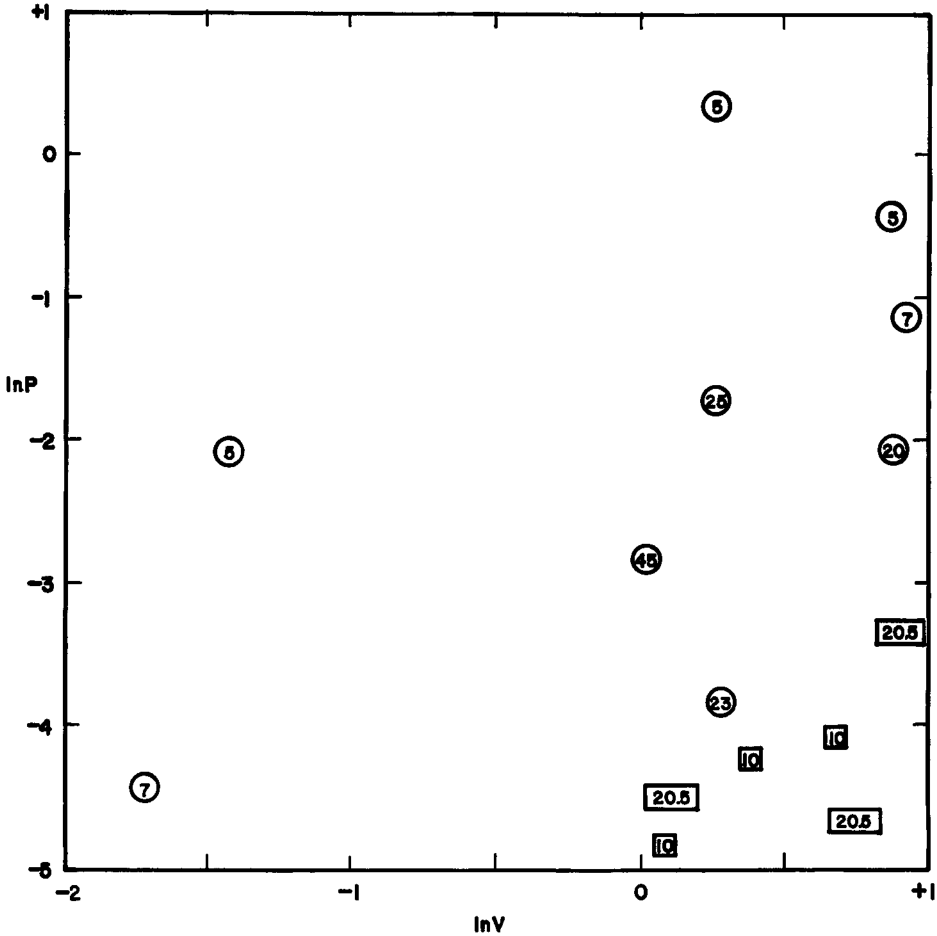

FIG. 3. Trapping probability P in cm^{-1} vs zone travel rate V in cm/hr for 37 μm beads, 30° tilt angle (from horizontal). Numbers are rotation rates in rpm. Circles are for 0.1 g starting weight of beads, rectangles for 0.05 g.

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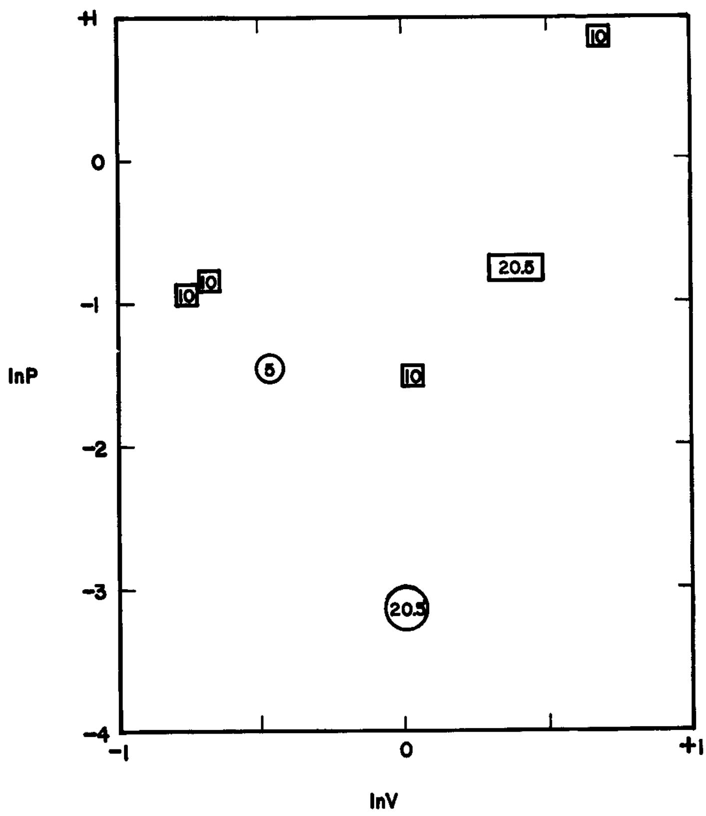

FIG. 4. P in cm^{-1} vs V in cm/hr for 37 μm beads, 45° tilt. Numbers are rpm. Circles for 0.1 g, rectangles for 0.05 g.

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where W_0 is the initial mass of beads and N_0 is the initial number. This yields a straight line on semilog paper. As exemplified by Figs. 1 and 2, our data rarely gave a straight line semilog plot. The slope diminished rapidly with distance. Possible explanations for this are discussed later.

Using those initial data points (3 to 10) which fell reasonably well on a straight semilog plot, a least squares fit was made to Eq. (2) to determine values of trapping probability P. The square of the correlation coefficient, r^2, ranged from 0.6 to 0.9993, with half being 0.9 or above.

These initial values of P for 37 μm beads are plotted in Figs. 3–7. There is a good deal of scatter in the data, but nevertheless it is possible to see certain trends:

(1) P increases with increasing V. Multiple regression analysis shows rough proportionality.

(2) From Figs. 3 and 5, P appears to increase with increasing mass of beads, in agreement with Ref. *12* for V_c with horizontal operation. Figure 4 appears to show the reverse behavior.

(3) From Figs. 3 and 4, P decreased with increasing rotation rate,

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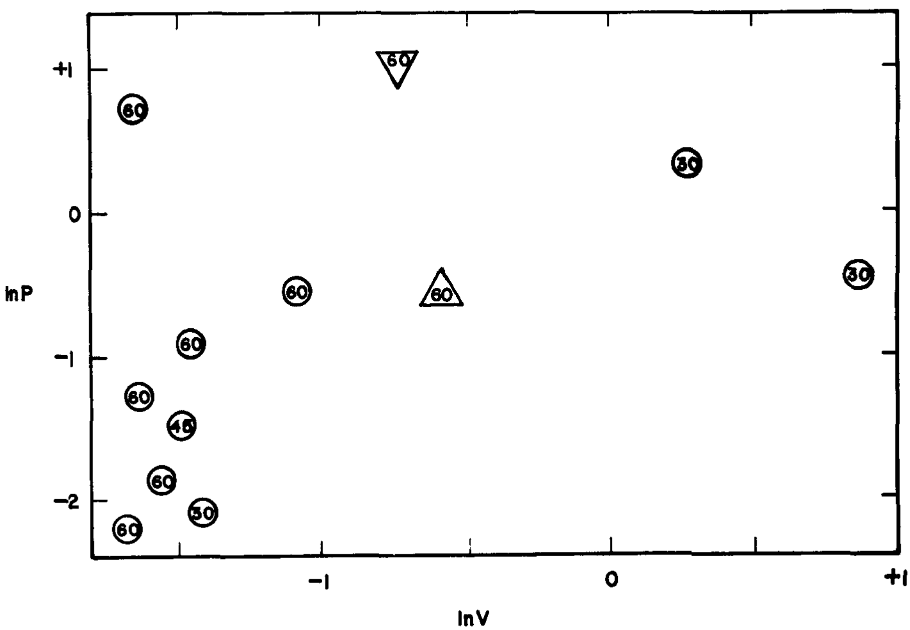

FIG. 5. P in cm^{-1} vs V in cm/hr for 37 μm beads, 5 rpm rotation rate. Numbers are tilt angle degrees. Circles for 0.1 g, triangle for 0.2 g, inverted triangle for 0.3 g.

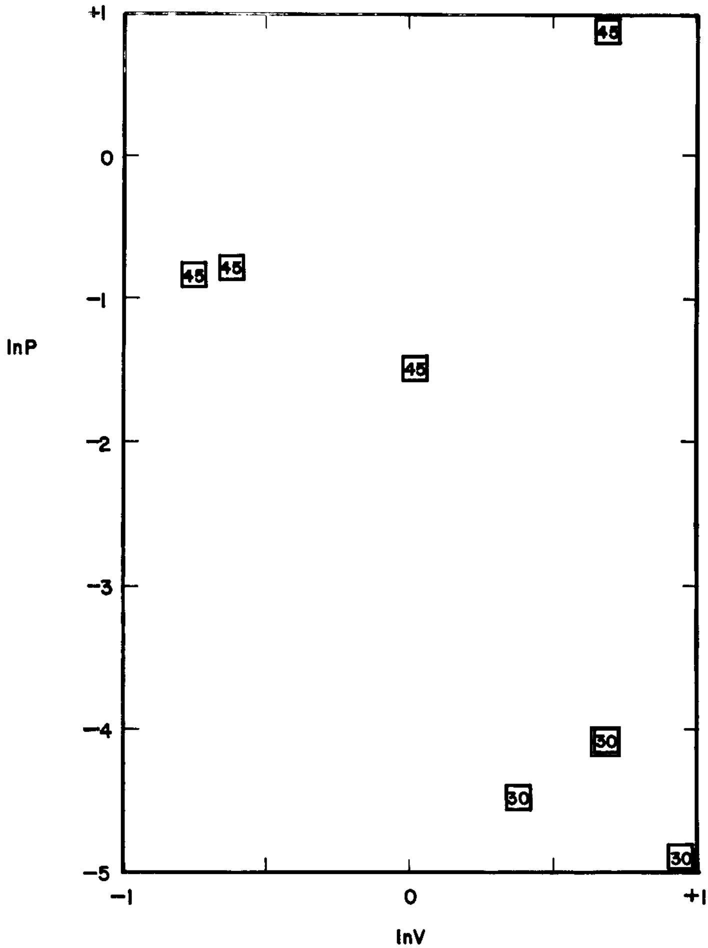

FIG. 6. P vs V for 37 μm beads, 10 rpm rotation. Numbers are tilt angle. Squares for 0.05 g.

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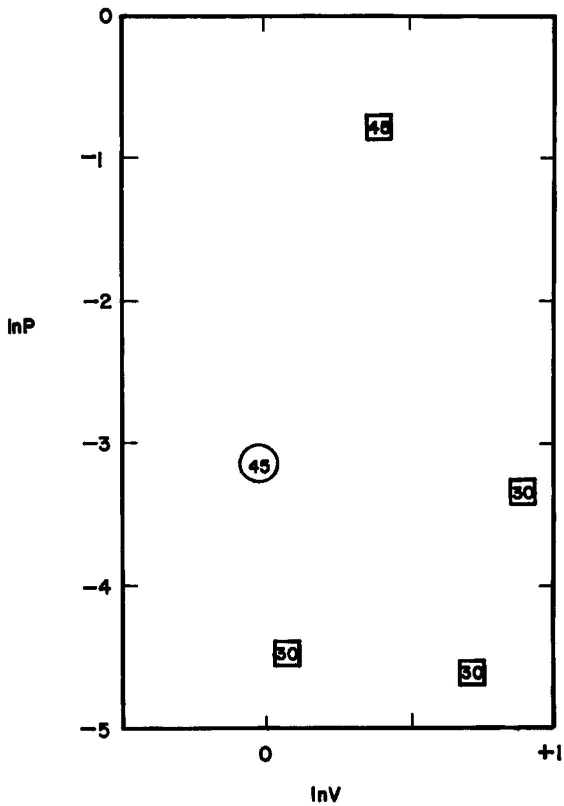

FIG. 7. P vs V for 37 μm beads, 20.5 rpm. Numbers are tilt angle. Circle for 0.1 g, squares for 0.05 g.

especially for small rpm. This is in agreement* with V_c results of Refs. *11* and *12*.

(4) From Figs. 5–7, P increases with increasing tilt angle, in agreement with the V_c results of Ref. *11*.*

Several runs were also performed with 105 and 250 μm beads, although complete analyses were not made. Trapping was significantly less than with the 37-μm beads used for all of the previous experiments. For example, no visible trapping was observed for 0.05 g of 250 μm beads at 10 rpm with

(1) 45° tilt, 1.03 cm/hr zone travel rate

*By agreement with previous V_c results, it is meant that one would expect P to decrease under the same conditions causing V_c to increase, as observed.

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(2) 30° tilt, 4.22 cm/hr zone travel rate

Once again this agrees with previous results for V_c, i.e., V_c increases and P decreases as particle size increases for tilt rotating zone melting.

OBSERVATIONS AND DISCUSSION

We noted earlier that P almost invariably dropped dramatically during every run. Since P decreases with decreasing W_l, and W_l decreases during each run, part of the drop is due to this. However, the decrease in P is much larger than one would expect from the decrease in W_l. Data were correlated much more poorly by including P vs W_l data throughout all runs, rather than by the method described of calculating only one P value for W_0. We believe the primary reason for P decreasing during a run is the increase in impurity content in the zone that normally occurs during zoning. Recent work here has shown that both V_c for a free glass bead and the force exerted on a fixed glass bead increase with increasing impurity content in naphthalene (*13*). In succinonitrile the force decreases with impurity additions, however (*17*).

Similarly, part of the scatter in the P values from one run to the next may have been due to uncontrolled variations in impurity content. Much greater care must be taken with purity in future research on particle pushing/trapping.

Many other important observations were made during and after the runs that bear both on the decrease of P with distance and the scatter of the P data from one run to another. The most important is that trapping almost always occurred in discrete bands, as in previous particle chromatography experiments (*10*, *11*). These bands were very periodic, usually 100 to 300 μm thick with a period of 500 to 1000 μm. At first, we feared that these bands were due to temperature fluctuations or to stiction in the zone drive mechanism. Extensive lubrication and additional constant voltage transformers had absolutely no effect on the banding. The band spacing was not proportional to freezing rate as would be expected for periodic heater power fluctuations. We are convinced that banding or catastrophic trapping is a fundamental phenomenon. One may speculate that the higher thermal conductivity of the beads is somehow responsible. Trapping of a few beads would lower the effective thermal conductivity of the melt and raise the effective thermal conductivity of the solid, causing the interface to shift toward the heater by momentarily moving at a higher velocity. This would cause more bead trapping, etc. This mechanism might occur over the entire interface or only over localized spots.

Another important observation is that addition of beads to the zone

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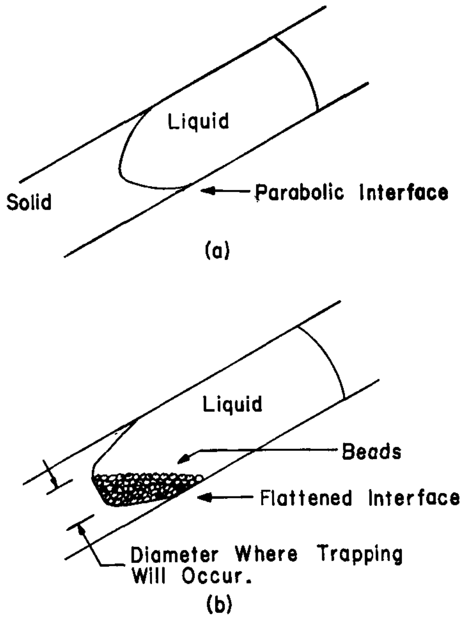

FIG. 8. Change in shape of freezing interface with addition of beads to moving zone.

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during zoning caused an immediate change in the shape of the interface, with the magnitude of the change increasing as the amount of beads increased. As shown in Fig. 8, the bottom of the zone flattened out. Trapping of beads was greatly enhanced in the flattened portion of the interface. As beads were trapped, the flattened portion decreased, the zone returned to its original shape, and the trapping gradually diminished. This accounts for part of the decrease in P with distance.

Fours types of bead motion were observed during this research. These were:

(a) No motion relative to interface. Beads always trapped unless something started them moving, since the zone travel rates used were about an order of magnitude higher than V_c for stationary beads.
(b) Beads slid along interface in large group. Not trapped unless something caused sliding to stop.
(c) Rolling along interface. Occurred only with high zone travel rates and very few particles. Seldom trapped. Visible tracks (furrows) left on interface, presumably due to retardation of growth under bead and higher thermal conductivity of bead.

(d) Suspended in melt. Only for 37 μm beads. No trapping unless bead contacts interface.

Bead motion (b) often led to catastrophic trapping and band formation by the following mechanism observed under the microscope. Any bead that stopped momentarily on the interface, which would normally have led to trapping, was pushed by the mass behind. However, beads at the back of the pack could stop without being pushed by others. By the time the tube rotated, these beads were firmly impacted, so that when they met the group of beads tumbling along the interface they were not dislodged but instead caused other beads to stop and also be trapped.

It is worth reporting in detail one run in which the beads were present initially as three bands of 0.1, 0.2, and 0.3 g of 250 μm beads, 45° tilt, 20.5 rpm, 2.47 cm/hr zone travel rate. Before the first group of beads (0.1 g) dropped into the zone, the solidifying interface was parabolic, as shown in Fig. 8(a). Afterwards it had a "U" shape with a flat bottom, as in Fig. 8(b). Trapping took place on the flat part of the interface as monolayer bands with about 1 mm periodicity. Little change was noticed until the second set of beads (0.2 g) dropped. The flat portion of the interface increased and the diameter of the bands increased accordingly. The period decreased to about 0.75 mm. As beads were trapped and removed from the melt, the flat portion of the interface diminished in diameter, resulting in the cone-shaped trapping region shown in Fig. 9.

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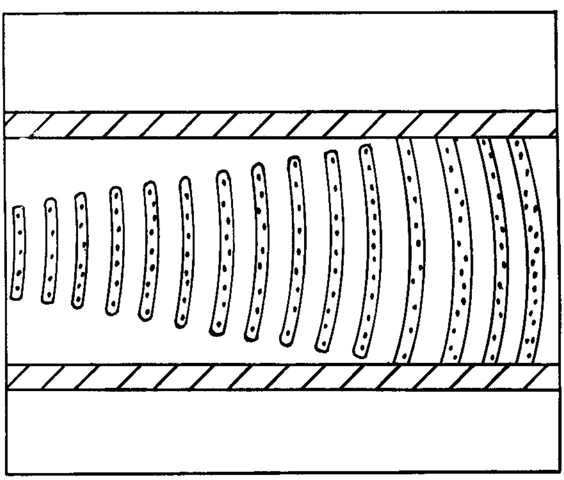

FIG. 9. Cone-shaped trapping region caused by effect of changing mass of beads on interface shape and on trapping.

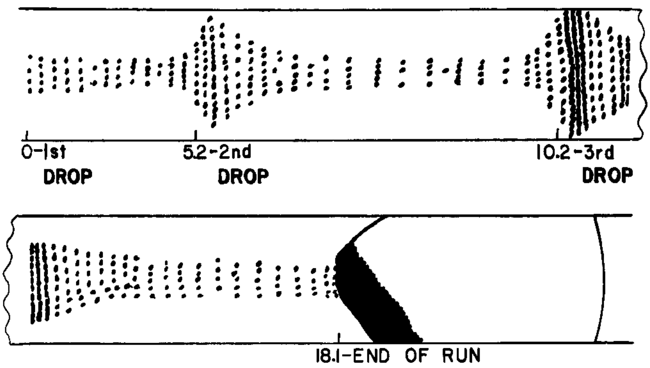

FIG. 10. Result of run with three separate drops of beads into zone.

The same sort of behavior occurred when the third bead drop took place, leading to the final behavior shown in Fig. 10.

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REFERENCES

1. A. E. Corte, *J. Geophys. Res.*, *67*, 1085 (1962).
2. D. R. Uhlmann, B. Chalmers, and K. A. Jackson, *J. Appl. Phys.*, *35*, 2986 (1964).
3. P. Hoekstra and R. D. Miller, *J. Colloid Interface Sci.*, *25*, 166 (1967).
4. J. Cissé and G. F. Bolling, *J. Cryst. Growth*, *11*, 25 (1971).
5. J. Cissé and G. F. Bolling, *Ibid.*, *10*, 67 (1971).
6. A. W. Neumann, J. Szekely, and E. J. Rabenda Jr., *J. Colloid Interface Sci.*, *43*, 727 (1973).
7. S. N. Omenyi and A. W. Neumann, *J. Appl. Phys.*, *47*, 3956 (1976).
8. S. N. Omenyi, Ph.D. Thesis, University of Toronto, 1978.
9. V. H. S. Kuo and W. R. Wilcox, *Ind. Eng. Chem., Process Des. Dev.*, *12*, 376 (1973).
10. K. H. Chen and W. R. Wilcox, *Sep. Sci. Technol.*, *13*, 387 (1978).
11. R. P. Kane and W. R. Wilcox, *Ibid.*, *13*, 565 (1978).
12. R. B. Fedich and W. R. Wilcox, *Ibid.*, *15*, 31 (1980).
13. G. Gupta, "Solidification Force," M.S. Thesis, Clarkson College of Technology, 1978.
14. D. E. Temkin, A. A. Chernov, and A. M. Mel'nikova, *Sov. Phys.–Crystallogr.*, *22*, 13 (1977).
15. T. T. Shih and L. F. Donaghey, "Application of Velocity-Selective Freeze-Pushing to the Separation and Characterization of Air-Borne Solid Particulate Matter in Air Pollution Samples," University of California, Berkeley, 1973.
16. J. E. Coon, "Investigation of Particle Trapping Probability during Solidification," M.S. Thesis, Clarkson College of Technology, 1978.
17. R. Rice, M.S. Thesis, Clarkson College of Technology, 1980.

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