## GENERAL DISCUSSION

**Dr. E. R. Buckle** (*Sheffield*) said: As Jackson will be aware, in using Volmer's theory to predict the conditions under which a vapour will condense to the solid rather than the liquid, one comes up against problems in the choice of data on physical constants. The surface tensions of molten Zn and Cd, for example, are reported to increase and then decrease as the temperature is raised from the melting point.<sup>1</sup> If the critical roughening temperature lies below the melting point would it be likely to result in a discontinuous change in the specific free energy of the crystal-melt interface?

**Dr. E. R. Buckle** (*Sheffield*) said: A catalytic effect of water on ethanol condensation is an interesting possibility. What sizes of nuclei are being distinguished as liquid or solid in table 1 of the paper by Wegener and Wu? If the presence of a miscible impurity affects the chance of nucleation when  $x \ge 1/n^*$ , where x is the mol fraction, quite appreciable amounts would be necessary at very fast cooling rates, where  $n^*$ becomes very small at onset. Perhaps this idea could be tested by suitable variation in the mass flowrate. How pure was the water that condensed from the moist air or steam used in the experiments of table 1?

**Prof. P. P. Wegener** (*New Haven*) said: The distinction between solid or liquid nuclei has been made formally by using the tabulated properties for the proper phase in eqn (1). The lowest mole fraction of ethanol in water vapour (see fig. 1) is roughly one order of magnitude larger than the inverse number of water molecules in the critical cluster for either phase. The thought advanced by Buckle could be tested as suggested, and we are grateful for this recommendation. The application of binary nucleation theory to study the observed trends becomes difficult since at such low mole fractions of a second vapour the steady-state assumption inherent in the classical approach breaks down (our ref. (29)). No special efforts to purify water were generally made in the experiments of our ref. (8) to (15). However, the excellent agreement of the results from several laboratories testifies to the absence of appreciable heterogeneous nucleation effects. This is to be expected theoretically as discussed, e.g., on p. 215 of our ref. (16) and sources given therein.

**Dr. F. Abraham** (San Jose) said: Concerning your closing comment that computer calculations may possibly improve our understanding of the empirical factor  $\Gamma$ , we have compared the total Helmholtz free energies predicted by the approximate theories—the Becker-Döring (classical) theory and the Lothe-Pound (revised) theory—with the exact results of the Monte Carlo study for clusters of Lennard-Jones atoms (F. F. Abraham, *Homogeneous Nucleation Theory*, (Academic Press, New York, 1974), Chapter 9, Section 9.5).

We found that the Lothe-Pound theory agrees very favourably with the exact results of the Monte Carlo experiment. This is consistent with the hypothesis that "liquid" clusters of *simple* atoms should be described by the Lothe-Pound theory (F. F. Abraham, J. Chem. Phys., 1969, 50, 3977).

<sup>1</sup> D. W. G. White, Met. Trans., 1972, 3, 1933.

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**Prof. P. P. Wegener** (*New Haven*) said: The experimental difficulty in testing the interesting thought advanced lies in the practical choice of a vapour that fulfills the requirements stated by Abraham. Typically, argon tested by us in nozzles condenses appreciably below the triple point. We would be interested in receiving a suggestion on a substance that is "simple" and condenses as a liquid in the supersaturated state. Such a material could readily be studied in our shock tube, in which work on condensation of several vapours is currently in progress.

In summing up, after hearing the comments made on our paper, in addition to the work cited, we wish to note the excellent agreement of experiment and droplet growth theory in the entire condensation zone. These laws used for onset states only (table 1) work well throughout, as seen, e.g., in fig. 5 of our ref. (6). Moreoever, in results soon to be published we show that once our factor  $\Gamma$  has been determined, predictions with the same factor correctly account for changes of cooling rate at least within a Since many aspects of the classical formalism give such excellent factor of five. results, it is worthwhile to retain these methods in practical applications until nucleation theory is based on first principles. Finally, if we view the time scales of the different experimental techniques ranging from the near-stationary diffusion cloud chamber to the extreme cooling rates of gasdynamic molecular beams, we find the nozzle technique in the middle-to-high range with cooling rates of the order of  $10^6$  C/s. The shock tube can be arranged to cover the entire range between the Wilson cloud chamber and the nozzle. This fact, in conjunction with the need for small, wellprepared vapour samples rather than large amounts of substance, makes this last technique particularly attractive.

Dr. F. Abraham (San Jose) said: In the closing paragraph of his paper, Katz makes the important point that the numerical value of the product of surface tension and surface area is the relevant quantity in nucleation theory. In a model calculation of nucleation of fcc microcrystallites from the vapour, the results for the droplet model using the capillarity approximation are compared with the *exact* properties of "spherical" microcrystallites (F. Abraham, *Homogeneous Nucleation Theory* (Academic Press, New York), Chapter 6, Section 6.10). We find that the capillarity approximation overestimates the surface free energy of a spherical microcrystallite. This is surprising in view of the fact that the surface free energy per surface atom for the microcrystallite is greater than the surface free energy per surface atom for a planar surface. The reason for this surprising feature is that the capillarity assumption grossly overestimates the number of surface atoms for clusters less than 500 atoms.

**Dr. H. A. Davies** (*Sheffield*) said: Katz deserves our congratulations for his elegant experimental work. However, one might seriously question whether molecular clusters, of only about 3 molecules diameter, could possibly have the same surface tension as the corresponding bulk species. Would not such small clusters have a packing density and structure appreciably different from the bulk and hence an appreciably different surface tension also?

**Prof. J. L. Katz** (*Potsdam*) said: The fact that classical nucleation theory agrees well with experiment implies that the *product* of surface area and surface tension is indeed independent of size. This surprising conclusion thus implies that radius dependent effects on surface tension and number of surface atoms cancel. I have no explanation other than to say that this is what we observe.

Dr. M. R. Dunn (Thornton) (communicated): Although the heat pulse cloud cham-

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ber described by Buckle and Pointon has proved useful in the study of collective behaviour of particle aerosols, it might easily be adapted to observe the formation and initial submicroscopic growth of these particles. Such information may be obtained by the application of a laser light scattering method, which has been used at Thornton to study the growth kinetics of very small particles (diameter 1–20 nm) in the coagulation of molten lead aerosols on a millisecond time scale.<sup>1</sup>

In a development of this method, scattering measurements coupled with multiple wave length extinction have been applied to the study of soot formation following the shock tube pyrolysis of aromatic and alicyclic hydrocarbons.<sup>2-5</sup> In certain cases it has been possible to obtain information about the shapes of the submicroscopic soot particles by rotating the polarization of the laser beam.<sup>6</sup> It is hoped that techniques of this kind will come into more general use in studies of condensation and precipitation phenomena.

**Prof. J. M. Thomas** (*Aberystwyth*) said: The electron micrograph of the supercooled nickel certainly did indicate that the material was amorphous. I wonder, however, whether Davies endeavoured to push the high-resolution electron microscopic technique, and associated optical diffractometry, to their limits. Did the authors examine whether, on the ultrastructural scale (e.g., 1000 Å<sup>2</sup> or less), evidence of crystallinity exists?

Dr. H. A. Davies (Sheffield) said: The electron-transparent regions of the splatquenched foils of nickel were, we estimated, at least 100 nm thick in all cases. Hence, in order to perform very high resolution microscopy (for instance, lattice imaging or dark-field techniques) effectively, we would have needed to thin the foils down by about an order of magnitude. However, the splat-quenched foils produced by the "gun" technique are very variable in thickness and difficult to thin down in a controlled way; we have, therefore, not yet attempted high resolution microscopy on the glassy nickel phase though we have attempted this for an amorphous, splat-quenched aluminium-copper phase.<sup>2\*</sup> The results *indicated* the absence of crystallinity but we cannot yet be conclusive about this because of the excessive thickness of the specimen. Recent work that we have done in collaboration with Dr. A. Howie of the Cavendish Laboratory would seem to indicate that lattice imaging techniques can prove useful in some cases for the investigation of small crystallites >2 nm diameter dispersed in a glassy matrix. Particular examples would be in the early stages of crystallization or in partly crystalline, as-quenched alloys.

Returning to the nickel splat-quenched phase, we deduced,<sup>5\*</sup> for a number of reasons, that the structure was amorphous rather than microcrystalline. However, we cannot be absolutely sure from the experiments performed so far that there were no crystallites >2 nm diameter present in the glassy matrix. If there were any present in the areas investigated, the number would probably have been very small. It is of

- <sup>1</sup>S. C. Graham and J. B. Homer, Faraday Symp. Chem. Soc., 1973, 7, 85.
- <sup>2</sup> S. C. Graham and J. B. Homer, in *Recent Developments in Shock Tube Research* (Proc. Ninth Int. Shock Tube Symp.) ed. D. Bershader and W. Griffith, (Stanford University Press, 1973) pp. 712– 719.
- <sup>3</sup> S. C. Graham, J. B. Homer and J. L. J. Rosenfeld, Proc. Roy. Soc. A, 1975, 344, 259.
- <sup>4</sup> S. C. Graham, J. B. Homer and J. L. J. Rosenfeld, in *Modern Developments in Shock Tube Research* (Proc. Tenth Int. Shock Tube Symp.), ed. G. Kamimoto, (Kyoto, 1975) pp. 621-631.
- <sup>5</sup> S. C. Graham, J. B. Homer and J. L. J. Rosenfeld, Second Symp. (European) on Combustion, Orleans, 1975, p. 374.
- <sup>6</sup> S. C. Graham, to be published 16th Int. Symp. Combustion, 1976.
- \* Reference numbers as in our paper.

interest to note that the criterion that we adopted theoretically for glass formation was a fraction of crystal  $<10^6$ . This corresponds to about one crystal  $\sim 5$  nm diameter or about six of diameter  $\sim 2$  nm in a volume 1  $\mu$ m  $\times$  1  $\mu$ m  $\times$ 100 nm thick. Hence we have made a fairly liberal allowance for the existence of crystallites and/or critical nuclei but none were observed experimentally.

We are planning to investigate further the formation and structure of this glassy nickel phase, in particular, to employ the technique mentioned by Thomas.

Dr. J. F. Ogilvie (Newfoundland) said: In regard to the results of Thomas et al. on the light-stimulated precipitation in organic molecular crystals,<sup>1</sup> some of our recent results may be pertinent. In work done in collaboration with D. P. Craig and P. A. Reynolds at the Australian National University, we calculated the effects of vacancies, dislocations and orientational disorder on the possible provision of nucleation sites for facile dimerisation of anthracene in pure single crystals under photochemical conditions. Using the atom-atom potential method, essentially similar to that described by Hoare and McInnes,<sup>2</sup> we estimate that there are at least three crystal structures close in energy (within 10 kJ mol<sup>-1</sup> of lattice energy) above the observed  $P 2_1/c$  phase (notation as described in standard tables).<sup>3</sup> We estimate that the mole fraction of misoriented molecules according to a  $P\bar{I}$  structure may be 0.001–0.01 at 300 K; these misoriented molecules may form strings of molecules of 10-100 units in the *b* direction (in association with vacancies), and further misoriented molecules are undoubtedly associated with dislocations. For such misoriented molecules dimerisation of adjacent pairs appears to be sterically possible. Furthermore, a  $P 2_1/a$  structure of anthracene could be formed by the cleavage of regular bianthracene molecules in their known lattice. In both cases the estimated unit-cell dimensions are such that "precipitation" of regions of a photochemically produced substance within another single-crystal host lattice appears to be possible, according to the usage of the term "precipitation" by Thomas et al. Some experimental evidence supports these theoretical results. A full discussion will be published separately.

<sup>1</sup> J. M. Thomas, J. O. Williams, C. F. Ng and D. O. Donati, paper at this Discussion.

<sup>2</sup> M. R. Hoare and J. McInnes, paper at this Discussion.

<sup>3</sup> International Tables for X-ray Crystallography, Vol. 1 (Kynoch Press, Birmingham, 1969).