Droplet Nucleation by Gas-Phase Positive Ions, Observed through Mobility

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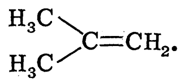
Contrary to expectation, droplets did not nucleate in the critical fluid of isobutene. Droplets formed only at $T/T_c \leq 0.96$, where $n/n_c \leq 0.38$. In low-density vapor, droplet formation began at a temperature greater than the coexistence temperature at that density. The magnitude of the gap ($T_{\text{onset}} - T_{\text{coexist}}$) correlated with the surface tension of the liquid at T_{onset}. Average droplets in the coexistence vapor contained 730 000 molecules at 297 K and 2000 molecules at 397 K.

During the measurement of positive-ion mobilities in the gas phase as a function of temperature and density, it has been found that under certain conditions the mobility plunges by one or two orders of magnitude. The decrease in mobility is attributed to droplet formation around the positive ion. Contrary to expectation, the critical temperature for droplet nucleation is *lower* than the normal liquid/vapor critical temperature. The behavior is different from that recently reported for positrons and positive ions in helium, neon, and argon.[1,2] However, the calculations reported for clustering around positive ions were only for $T > T_c$.[2]

The vapor was isobutene, which has a molecular structure represented by



The electron dipole moment of the molecule[3] is 0.50 D and the average polarizability[4] is 8.3×10^{-24} cm^3. A 1.0-μs pulse of x rays generated about 2×10^9 ions/g in the highly purified gas. The glass-walled conductance cell (Fig. 1) could contain a pressure of 60 bar.

The mobilities were measured by a time-of-flight method.[5] The electron mobility was several orders of magnitude greater than that of the positive ions, and so the gas was swept clear of electrons at the beginning of the ion drift period. Ion mobilities were measured as a function of temperature at six different constant densities, and in the vapor along the vapor/liquid coexistence curve.

Arrhenius plots of the mobilities μ are shown in Fig. 2. As the temperature and density were reduced from the critical point ($T_c = 418$ K, $n_c = 2.51 \times 10^{21}$ molecules/cm^3, $\mu = 3.2 \times 10^{-3}$ cm^2/V·s)

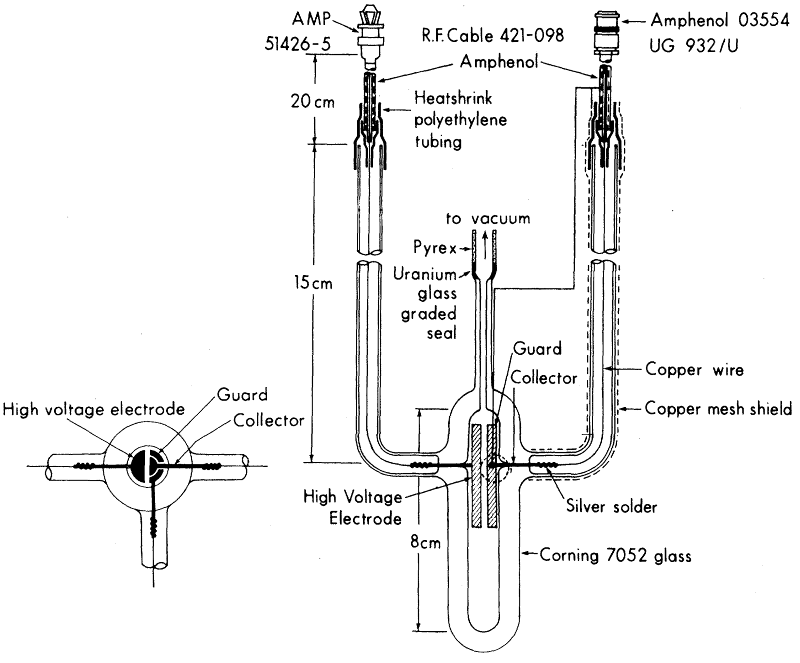


FIG. 1. Conductance cell. The electrodes were stainless steel and the pins Kovar. The distance between the collector and high-voltage electrodes was 3.2 mm and the cell constant 0.125 cm^{-1}.

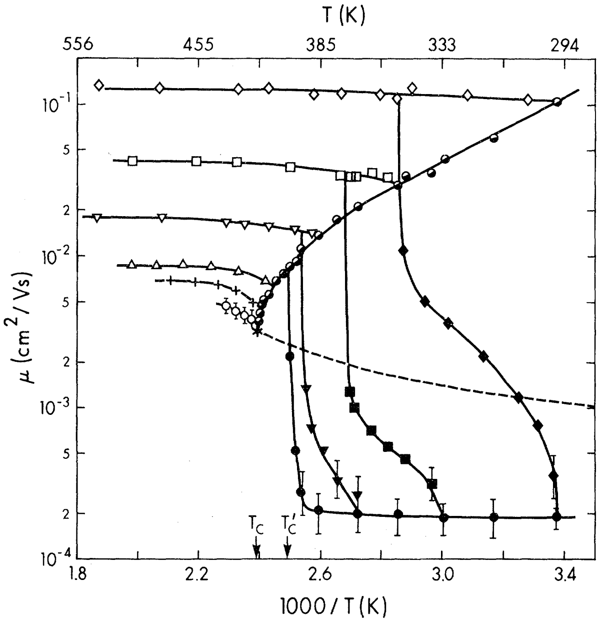


FIG. 2. Arrhenius plots of positive-ion mobilities in isobutene vapor at different densities. The densities n, in units of 10^{20} molecule/cm^3, were as follows: open and solid diamond, 0.69; open and solid squares, 2.6; open and solid inverted triangles, 5.8; triangle, 12.4; plus, 17.7; circle, $n_c = 25.1$; star, critical fluid; half-filled and filled circles, coexistence vapor at that temperature. The full points represent the slow ions. The dashed line represents positive ion mobilities in the coexistence liquid. $T_c = 418$ K; $T_c' = 401$ K, $n_c' = 9.5 \times 10^{20}$ molecule/cm^3. The relative uncertainties of the droplet mobilities, ±34%, are double those of the smaller tons, ±17%.

along the coexistence curve, the mobility increased. The mobility was inversely proportional to the density. At 400 K a new component with a lower mobility appeared in the coexistence gas. The mobility of the slow component rapidly decreased by a factor of 30 within a 7-K decrease of temperature. Below 390 K the mobility of the slow component was nearly constant, being 2.1×10^{-4} cm^2/V·s at 388 K and 1.9×10^{-4} cm/V·s at 296 K. Over this same temperature region the normal ion mobility continued to increase, reaching 0.11 cm^2/V·s at 296 K (Fig. 2).

The upper limits of temperature and density at which the slower ions form in the coexistence vapor are designated $T_c' = 401$ K and $n_c' = 9.5 \times 10^{20}$ molecules/cm^3, or $T_c'/T_c = 0.96$ and $n_c'/n_c = 0.38$.

When mobilities were measured as a function of temperature in a constant-density gas the behavior was more spectacular. At $n = 6.9 \times 10^{19}$ molecules/cm^3 the ion mobility was 0.13 cm^2/V·s, independent of temperature from 535 to 350 K. At 348 K there was a component with a mobility an order of magnitude lower (Fig. 2). The mobility of the slow component descended in an S curve with decreasing temperature, reaching the coexistence curve as the lower boundary. The temperature gap between the onset of the slow component and the normal coexistence curve at this density was 54 K. The temperature gap decreased with increasing density and reached zero at n_c' (Fig. 2).

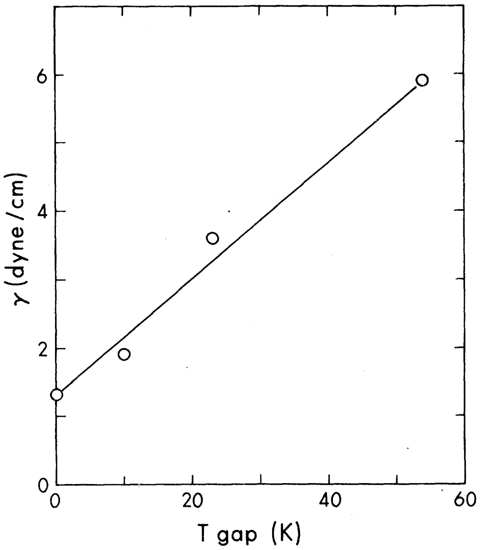


FIG. 3. Temperature gap between the onset of the slow component and the coexistence curve at a given gas density, plotted against the plain surface tension of the liquid at the onset temperature.

The magnitude of the temperature gap correlates with the surface tension γ of the liquid[6] at the temperature of onset of the slow component (Fig. 3). The surface tension is a measure of the intermolecular attractive forces, and hence of the tendency for a droplet to form. Figure 3 indicates that droplets do not nucleate under the present conditions when the plain surface tension is < 1.3 dyn/cm.

A plot of the logarithm of the gas density against T_{onset}^{-1} indicates that the enthalpy of vaporization of the droplets formed just below T_{onset} is 60 kJ per mole of isobutene, compared to 31 kJ/mol for the bulk liquid over the same temperature range. The extra energy is due to the charge dipole interaction between the central ion and the molecules in the droplet.

The droplets in the saturated gas phase have mobilities an order of magnitude *lower* than the ions in the coexistent liquid (Fig. 2). This surprising result draws attention to the large size of the droplets.

The size of the droplets was estimated from the average scattering cross section σ_{av}:

$$\sigma_{\mathrm{av}} = \frac{3e}{16\mu n}\left(\frac{1}{m}+\frac{1}{M}\right)^{1/2}\left(\frac{2\pi}{kT}\right)^{1/2} = \frac{4.96\times10^{7}}{\mu n T^{1/2}}\left(\frac{1}{m}+\frac{1}{M}\right)^{1/2}, \tag{1}$$

where e is the charge on the ion, m and M are, respectively, the mass of the ion and molecule (g/mol), k is Boltzmann's constant, and μn is in units of molecules/cm V·s.[7] The average scattering radius r was taken from

$$\sigma_{\mathrm{av}} = \pi r^{2} \tag{2}$$

and the volume of the droplet from

$$V = (4\pi/3)(r-0.2)^{3}, \tag{3}$$

where $r - 0.2$ is the radius of the droplet in nanometers and 0.2 nm is the van der Waals radius of an isobutene molecule. Under the assumption that the density d of the droplet is similar to that of the liquid at the same temperature, the average numbers N of molecules in the droplets in the coexistence vapor were extimated and are listed in Table I. The value of N is 2000 at 397 K and increases with decreasing temperature, reaching 730 000 at 297 K.

The vapor pressure p of a droplet of radius $r - 0.2$ nm can be compared with that, p_0, of a plain surface of the liquid of the same d, γ, and T through[8]

$$\ln(p/p_0) = 13.5\gamma/dT(r-0.2), \tag{4}$$

where the droplet radius $r - 0.2$ nm is obtained from Eq. (2). The estimated value of p/p_0 for neutral droplets was 1.03 at all temperatures <400 K (Table I); the polarization interaction of the nucleating ion would make the ratio closer to unity. The droplets whose mobilities were measured in the coexistence vapors were therefore close to their equilibrium sizes.

Analysis of the variation of the mobilities at fixed densities (S curves in Fig. 2) may reveal the profile of droplet growth. The present sparse results indicate that the minimum stable radius of a droplet of isobutene nucleated on a positive ion is 4 nm. The lower ends of the droplet mobility curves for 2.6×10^{20} and 5.8×10^{20} molecules/cm^3 seem to reach the lower saturation curve at temperatures below the coexistence temperatures for vapors of those densities (Fig. 2). A degree of vapor supersaturation might be required for the maximum droplet size to be attained in the time available. An extended field-dependence study would assist in sorting out this problem.

Some of the effects described above have been

TABLE I. Properties of the droplets in the coexistence vapor.

T (K)	n^{a} (10^{20} molecules/cm^3)	σ_{av} (nm^2)	N^{b} (molecules)	d^{c} (g/cm^3)	γ^{c} (dyn/cm)	$p/p_0{}^{\mathrm{d}}$
296	0.70	2880	730 000	0.589	12.2	1.03
316	1.14	1710	320 000	0.565	10.0	1.03
333	1.74	1120	160 000	0.545	8.3	1.03
350	2.6	650	66 000	0.513	5.9	1.03
385	5.8	270	15 000	0.445	2.5	1.02
394	7.6	159	6 200	0.420	1.9	1.02
397	8.3	77	2 000	0.410	1.6	1.03
400	9.1	19	190	0.399	1.3	1.05
403	10.0	4.3^{e}	$\sim 1^{\mathrm{e}}$	0.386	1.1	···
403	0.69	4^{e}	$\sim 1^{\mathrm{e}}$	···	···	···

[a] Coexistence gas. For comparison, $n_c = 2.51\times10^{21}$.

[b] Droplet.

[c] Coexistence liquid.

[d] Estimated ratio of the vapor pressures of the droplet p and a plain surface p_0, neglecting the effect of the ion in the droplet.

[e] The normal ion is scattered by the induced and permanent dipoles of the isobutene molecules.

observed for helium positive ions in helium vapor,[9] but on a much smaller scale. Changes in the extent of clustering caused a maximum change in mobility by only a factor of three. However, examination of the results in Figs. 3 and 4 of Ref. 9 indicate that the larger clusters about the ions tend to break up at $n/n_c > 0.60$ and $T/T_c > 0.95$.

Mobility measurement is a powerful tool for the study of droplet nucleation by ions.

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Commensurability in One Dimension at $T \neq 0$

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The finite-temperature commensurability problem is formulated and reduced to the solution of a transfer-integral problem. Numerical solutions for the free energy, equation of state, one- and two-particle densities, ..., provide a detailed description of the behavior of epitaxial systems at $T \neq 0$.

In many contexts in physics we encounter model problems which consist of an interacting system, characterized by a natural length (e.g., an interaction length), which is embedded in an external field, characterized by a second natural length. The question then arises as to the nature of the equilibrium configuration of the interacting system in the external field when there is competition between forces that attempt to establish different "natural" lengths. For example, in a $T = 0$ K model of physisorption Ying[1] distinguished between commensurate and incommensurate structures according to whether the ratio of the natural lengths was or was not a rational number.[2] A commensurate structure is one in which an infinitesimal displacement of the atoms costs a finite extensive amount of energy. On the other hand, an incommensurate structure can be displaced with negligible cost in energy per atom. Recently a great deal of attention has been paid to compounds like $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ and TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane).[3,4] A basic mechanism for conductivity in these compounds is thought to be the phase evolution of a charge-density wave (CDW).[5,6] In this context, questions about the commensurability of the CDW and the underlying lattice are of interest and importance; e.g., an incommensurate CDW can move easily and contribute to the current.[7-9] In this paper we examine the question of commensurability at $T \neq 0$ K for a one-dimensional model system: the sine-Gordon chain with displacement springs. The equilibrium statistical mechanics of this model can be found exactly using transfer integral (TI) techniques.[10,11] As a consequence, we are able to obtain a complete picture of the behavior of this system at $T \neq 0$ K.

As a particular physical manifestation of the model we consider a chain of $M+1$ coupled torsion pendula in a gravitational field and subject to an external torque[6,11] [the torque, τ, works to establish a phase difference between the first