potential, yet not sufficiently strong for Compton scattering to be significant. In that regime, the dipole approximation should be valid as long as the atomic structure has no effect. It is not our intention to dismiss unconditionally the validity of the dipole approximation in multiphoton processes. Clearly it will be valid under a wide range of circumstances. We do however wish to point out that its validity is not as general as has been assumed on the basis of the usual argument that for optical wavelengths the dipole approximation is valid. Although this is correct for weak fields, in the presence of strong fields and multiphoton processes the argument loses its generality.

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Observation of Anomalously Large Supercooling in Carbon Dioxide*

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We have observed supercooling in liquid CO_2 near the critical temperature greatly exceeding that allowed by existing theories of homogeneous nucleation.

We report here a calorimetric study of nucleation in *liquid* carbon dioxide (CO_2). We have clearly observed that in the vicinity of the critical point, CO_2 may be "supercooled" at constant density to temperatures well below those at which homogeneous nucleation of vapor bubbles is predicted to occur by current theories.[1-5] Some hint of this anomalously large supercooling in the critical region of CO_2 is apparent in earlier calorimetric experiments by Straub[6] and in experiments where nucleation was observed visually.[7] Anomalously large supercooling has also been found near the critical point of the binary liquid mixture C_7H_{14}-C_7F_{14} by Sundquist and Oriani[8] and by Heady and Cahn.[9] These earlier experiments, reinforced by the present one, indicate that there is a serious gap in our understanding of nucleation in fluids near their critical points.

We have made three other significant observations: (1) Supercooling could be achieved only in samples filled to a density greater than the critical density, ρ_c. (2) Repeated runs with a given density, ρ, yielded identical nucleation temperatures when ρ was near ρ_c but a wide distribution of nucleation temperatures for samples with ρ far from ρ_c. In contrast, homogeneous nucleation theory predicts an extremely narrow distribution of nucleation temperatures at all densities. (3) A neutron source placed near the calorimeter would not trigger nucleation in a sample closest to ρ_c but would trigger nucleation in the samples further from ρ_c.

We will explicitly compare our measurements with a Becker-Döring–like theory as developed by Zeldovich and discussed by Frenkel[2] and applied to the critical region of Langer and Turski.[5] This type of theory has been widely and successfully used to describe nucleation in fluids away from critical points.[3,10] Becker and Döring considered the metastable phase to contain "embryos" of the nucleating phase (in the case of nucleation of droplets in a vapor these would be dimers, trimers, etc.). An embryo may grow by accretion or it may divide. Once an embryo exceeds a critical size, it is identified as a nucleus of the new phase which then grows rapidly. The critical size is determined by the condition that the increase in the thermodynamic potential from the formation of the interface between the nucleus and the metastable phase is equal to the decrease of the thermodynamic potential from the formation of the volume of stable phase (i.e., the nucleus). The Becker-Döring theory predicts[11] a rate of condensation (i.e., the number of monomers, Q, that become incorporated into embryos reaching the critical size each second):

$$Q = N\frac{v_B}{v_A}g\left(\frac{2\sigma}{\pi m}\right)^{1/2}\exp\left\{-\frac{16\pi\sigma^3 v_B{}^2}{3(\varphi_A-\varphi_B)^2 kT}\right\}. \quad (1)$$

(Here, N is the total number of molecules, g is the number of monomers compromising a critical nucleus, σ is the interfacial tension between the metastable phase A and the nucleating phase B. φ_A, φ_B, and v_A, v_B are the chemical potentials and the volume per molecule in phase A and B, T is the absolute temperature, and m is the mass of the molecule.) Near the critical temperature, T_c, it is convenient to introduce the scaled supersaturation, $\delta T/\epsilon$, where $\delta T = (T_{\rm coex} - T_{\rm nucl})/T_c$ and $\epsilon = (T_c - T_{\rm coex})/T_c$. $T_{\rm nucl}$ is the temperature at which the nucleation rate is being observed and $T_{\rm coex}$ is the coexistence temperature at the density of the sample. Then following page 3239 of Ref. 5, we express the temperature dependence of σ using the critical exponent[12] ν'; we express $(\varphi_A - \varphi_B)/v_V$ in terms of σ and $\delta T/\epsilon$, and we divide Eq. (1) by g and by the sample volume to obtain J, the number of nuclei per cubic centimeter which are formed each second. Thus the Langer-Turski result[5] [their Eq. (7.25)—referred to by them as the Becker-Döring theory] is

$$J = J_{\rm BD}\epsilon^{\nu'}\exp\{-(\tau_0/T_c)^2(\epsilon/\delta T)^2\}. \quad (2)$$

The prefactor $J_{\rm BD} = n_c(2\sigma_0/\pi m)^{1/2}$, where n_c is the critical density, σ_0 is the amplitude of the surface tension, i.e., $\sigma = \sigma_0\epsilon^{2\nu'}$. The parameter τ_0, a complicated function of scaled equation-of-state parameters, is defined in Eq. (7.14) of Ref. 5.

For CO_2, one of the most thoroughly studied simple fluids, $J_{\rm BD}$ and τ_0 may be evaluated from existing data.[13] Taking the recently remeasured exponent $\nu' = 0.63$, we find $J_{\rm BD} = 5.25\times10^{33}$ cm^{-3} sec^{-1} and $\tau_0 = 248$ K. With these parameters, the nucleation rate J in Eq. (2) is a very sensitive function of δT but insensitive to $J_{\rm BD}$. For example, over the range of densities spanned by these experiments, a 7% increase in δT increases J from 1 to 10^5 cm^{-3} sec^{-1}. Thus the value of δT for which $J = 1$ cm^{-3} sec^{-1} is, in fact, a prediction for the practical limit of supercooling obtainable in a macroscopic sample of a fluid. We will call this predicted limit the Becker-Döring limit.

In the present work we have studied CO_2 samples in permanently sealed glass ampules (a detailed description of the preparation of these ampules is published elsewhere[14]). Each ampule was placed in a commercially made "isothermal" (or "heat flow") calorimeter.[15] This calorimeter uses a thermopile to measure the temperature difference between its inner wall which is in good contact with the ampule and its massive outer wall which is near the temperature of a circulating air bath. When a supercooled sample separates into two phases after nucleation has occurred, a pulse of heat, H, is liberated. The size of this pulse is approximately

$$H = N(T_{\rm coex} - T_{\rm nucl})T_{\rm nucl}\left(\frac{\partial P}{\partial\rho}\right)_T\left(\frac{d\rho}{dT}\right)_{\rm coex}^{2}\rho^{-2}. \quad (3)$$

Here $(d\rho/dT)_{\rm coex}$ is the derivative of the coexistence curve and P is the pressure. The heat pulse is less than 10 min long (the response time of the calorimeter) when $\rho = 1.529\rho_c$ and more than 30 min long when $\rho = 1.172\rho_c$. When the pulse is short, its size could be measured with an accuracy of ± 5%. This measurement together with Eq. (3) and the known equation-of-state parameters for CO_2 can be used to estimate $T_{\rm coex} - T_{\rm nucl}$ independently for comparison with the directly measured value. The temperature at which nucleation actually occurred was measured with both a quartz crystal thermometer and a thermistor located within the calorimeter adjacent to the ampule. The coexistence temperature of each sample was found by noting the temperature at which the meniscus disappeared at the top of the ampule as it was warmed in a water bath. We estimate that the transfer of the thermometers from the water bath to the calorimeter introduces an error in the measurement of $T_{\text{coex}} - T_{\text{nucl}}$ of ± 4 mK. This is the greatest source of error in the measurement of δT for the samples with densities near ρ_c.

In order to establish unambiguously the conflict between our observations and nucleation theory, we repeatedly conducted the following experiment: The sample with density $1.247\rho_c$ was cooled in the calorimeter to a temperature well below the Becker-Döring limit. The sample temperature was then held approximately constant for at least 3 times the characteristic time (20 min) which describes the sample's approach to thermal equilibrium by conduction of heat.[7] This wait guarantees that the sample was at a uniform temperature equal to that of the interior of the calorimeter. We then verified that the sample was indeed in a metastable state for this length of time by inducing nucleation with a neutron source. In one run, this sample was held at a constant temperature (± 1mK) for 245 min (12 times the equilibrium time) while supercooled 1.84 times the Becker-Döring limit before inducing nucleation with the neutron source. The size of the heat pulse which followed nucleation was within 6% of that calculated from Eq. (3) for these conditions, thus verifying the excess supercooling indicated by our thermometer. This single stringent run indicates that the Becker-Döring theory (and other theories which give similar predictions) fails to describe nucleation in CO_2 near the critical point.

All our results and those of Straub are presented in Fig. 1. In this figure the rectangles indicate the range of scaled supersaturation at which nucleation occurred spontaneously; the integers indicate the number of runs used to establish this range. The crosses in Fig. 1 correspond to measurements in which nucleation was induced with the neutron source. The circled cross denotes the run discussed in the previous paragraph.

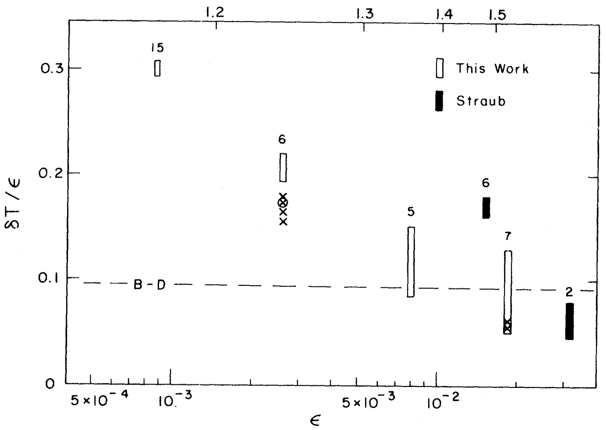

FIG. 1. Supercooling in CO_2. The horizontal scales indicate (bottom) the samples' reduced coexistence temperatures $\epsilon \equiv (T_c - T_{\text{coex}})/T_c$, and (top) the samples' densities in units of ρ_c. Plotted on the vertical axis is the scaled supersaturation at which nucleation occurs: $(\delta T/\epsilon) \equiv (T_{\text{coex}} - T_{\text{nucl}})/(T_c - T_{\text{coex}})$. The dashed line (B-D) corresponds to the predictions of the Becker-Döring theory. Spontaneous nucleation was observed within the rectangles. The integers denote the number of such observations by us (open rectangle) and by Straub (Ref. 6) (solid rectangle). The crosses denote additional runs in which we triggered nucleation with a neutron source. The circled cross denotes a particular run discussed in the text.

The two most notable features of Fig. 1 are (1) increased spread of nucleation temperatures with increasing sample density, and (2) the anomalously larger supercooling which can be achieved at densities near the critical density. The increased spread can be explained, we suggest, by assuming that far from the critical point cosmic rays trigger nucleation. It was for the purpose of testing this hypothesis that the 1-Ci Be-Pu neutron source was introduced. (The two most important effects of the neutron flux are the production of short-ranged α particles from the n-α reaction in the boron in the borosilicate glass ampule and the production of charged ions in CO_2 via a knock-on reaction.) We crudely estimate that the source produced 10 knock-on events per second in the sample, while the approximately 1-MeV γ rays from the source produced 10^2 electrons/sec by the Compton and photoelectric effect. By comparison, cosmic-ray background corresponds to roughly 10^{-1} muons/sec and 10^{-3} protons/sec passing through the sample. As noted above, the source had no effect on the sample of density $\rho/\rho_c = 1.172$ but did trigger nucleation when brought within 0.5 m of two supercooled samples of higher density.

It seems intuitively reasonable that as the critical point is approached, the size of the smallest possible bubble must grow as the correlation length grows. Thus it is not surprising that at a given scaled supersaturation charged particles which induce nucleation of vapor bubbles far from T_c are not effective close to T_c. Indeed, such an effect has been predicted by a droplet model of nucleation.[16] This droplet model also predicts an increase in $\delta T/\epsilon$ for homogeneous nucleation (with, say, $J = 1\ \mathrm{cm}^{-3}$); however, the increase (about 20% in the density range covered by this experiment) is too small to explain the anomalously large supercooling we have observed close to the critical point of CO_2 as has been observed in binary liquid mixtures.

To summarize, the results reported here are inconsistent with presently existing theories of nucleation in two respects: Far from the critical density, nucleation occurs over a wide range of temperatures, while near the critical density, the supercooling is anomalously large. The former effect may be accounted for by invoking inhomogeneous nucleation by cosmic rays. An explanation of the anomalously large supercooling may require a more fundamental theoretical attack on the nucleation problem.

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