

## Droplet Model and Nucleation of Supersaturated Vapors Near the Critical Point

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Fisher's droplet model is applied to the calculation of the nucleation rate in a metastable supersaturated vapor near  $T_c$ . At a constant scaled supersaturation  $A \propto (\mu - \mu_c)/(T_c - T)^{\beta\delta}$  we find a strong critical slowing down for the nucleation rate. Experiments to check this theory are proposed.

The condensation of a nonideal gas into the liquid state has been described by a droplet model.<sup>1-5</sup> The classical theory of homogeneous nucleation of a supersaturated vapor was developed by Volmer and Weber, Becker and Doering, Zeldovich, Frenkel, and Kuhrt.<sup>1</sup> Two assumptions were used: It is an equilibrium rate theory (detailed balance and stationary state), and the equilibrium concentration of the droplets is obtained from the Helmholtz free energy of the embryos (condensation nuclei).

The equilibrium concentration of droplets containing  $l$  molecules is calculated from the free energy  $f_l$  of these droplets. This  $f_l$  consists of a bulk term ( $\propto l$ ), a surface term ( $\propto l^\sigma$ ;  $\sigma \approx \frac{2}{3}$ ) vanishing at  $T = T_c$ , and a logarithmic term  $\tau kT \ln l$ , arising from internal vibrations<sup>6,7</sup> and other contributions.<sup>2,3</sup> Thus

$$f_l = l\mu_c - l^\sigma kT \ln x + \tau kT \ln l, \quad (1a)$$

where  $\ln x = \text{const}(T - T_c)/T_c$  ( $\text{const} \approx 4$  in  $\text{CO}_2$ ) and  $\mu_c$  is the chemical potential on the coexistence curve. The concentration  $n_l$  of  $l$ -droplets is

$$n_l = q_0 \exp[-(f_l - \mu l)/kT] \quad (1b)$$

with<sup>4</sup>  $q_0 \approx \rho_c/5$ . The more microscopic theories<sup>2</sup> estimate  $1 \geq \tau \geq -4$ . In Fisher's droplet picture the numbers  $\sigma$  and  $\tau$  are fitted from experiments as is the microscopic surface tension entering into  $f_l$  through  $\ln x$ . This surface tension is not identical with the macroscopic surface tension (cf. Ref. 5) but can be determined<sup>4</sup> from the shape of the coexistence curve. In  $\text{CO}_2$  it agrees with the macroscopic one at  $T = 0.999T_c$ . The parameter  $\tau$  can be determined<sup>3</sup> from the critical isotherm:  $\rho_c - \rho \propto (\mu_c - \mu)^{\tau-2}$  at  $T = T_c$ ;  $\tau = 2.2$  from experiment. Thus the "translation-rotation paradox" of how to determine  $\tau$  does not hinder our calculation near  $T_c$ . This was already noticed by Stillinger<sup>6</sup>; but the critical indices in

his publications<sup>6</sup> disagree with scaling assumptions. The comparison of Fisher's droplet model with experiment shows<sup>4</sup> that the resulting numerical factors for static properties are correct within <30% below and at  $T_c$ . The critical exponents agree exactly with the scaling laws.<sup>3</sup> We calculate the nucleation rate from the usual assumptions<sup>1,2</sup> combined with Fisher's droplet model. (For a different approach in a van der Waals gas see Strickfaden and de Sobrino.<sup>8</sup>) This nucleation rate is the first transport property to be calculated from Fisher's droplet picture.

As we will rederive later [before Eq. (6)], the principle of detailed balance leads to a nucleation rate

$$J_s = P_1 (2\pi m_1 kT)^{-1/2} / \sum_l (S_l n_l)^{-1}, \quad (2)$$

where  $S_l = S_1 l^\sigma$  is the surface area of an  $l$ -droplet and  $P_1 \approx P_c$  and  $m_1$  are partial pressure and mass of single molecules. Here the droplets are assumed to grow and shrink by incorporation and evaporation of single molecules only. In the integral replacing the sum (2) the term  $1/S_l n_l$  has a minimum at  $l = l^*$  if the vapor is supersaturated ( $\mu > \mu_c$  and  $T < T_c$ ). Thus the integral is reduced to one of the type  $\int \exp[-\text{const}(l - l^*)^2] dl$ . The  $l^*$  is found from the maximum of  $f_l - \mu l$ ; for a small "scaled supersaturation"  $A$  the variation of  $\tau \ln l$  and of the surface area  $S_l$  can be neglected.  $A$  is defined by

$$A = (\mu - \mu_c)/kT |\ln x|^{1/\sigma} \propto (\mu - \mu_c)/(T_c - T)^{1/\sigma} \quad (3a)$$

and indicates how far the state is in the interior of the metastable region;  $A = 0$  on the coexistence curve  $\mu = \mu_c$ .  $A$  can be measured by lowering the temperature at constant density:

$$A = 1.55(T_{\text{coex}} - T)/(T_c - T_{\text{coex}}) \quad (3b)$$

or by enlarging the density at constant  $T$ :

$$A = 4.5(\rho - \rho_{coex}) / (\rho_c - \rho_{coex}). \quad (3c)$$

Here  $T_{coex}$  is the temperature at which the coexistence curve is reached at the given density, and  $\rho_{coex}$  is the density at which it is reached at the given temperature. Because of  $\partial P / \partial \mu = \rho$  we

can easily relate<sup>7</sup>  $\ln(P/P_{coex})$  to  $A$ . [We assumed in deriving (3b) and (3c) that  $A \ll 1$ ,  $\mu - \mu_c = (\partial \mu / \partial T)_\rho (T - T_{coex})$ ,  $\beta = 0.35$ ,  $\delta = 4.5$  from experiment; then  $\tau = 2.22$ ,  $\sigma = 0.635$  because generally<sup>3</sup>  $\tau = 2 + 1/\delta$ ,  $\sigma = 1/\beta\delta$  with the usual notation<sup>3</sup> for the critical indices.] Using these assumptions we find from (2)

$$J_s = P_1 S_1 q_0 (2\pi m_1 kT)^{-1/2} [2\pi(1-\sigma)]^{-1/2} \sigma^{(\sigma-\tau-1/2)/(1-\sigma)} |\ln x|^{(\tau+1-\sigma)/\sigma} A^{(\tau+1-3\sigma/2)/(1-\sigma)} \times \exp[(\sigma-1)\sigma^{\sigma/(1-\sigma)} A^{-\sigma/(1-\sigma)}] = 3.4 P_1 S_1 q_0 (2\pi m_1 kT)^{-1/2} |\ln x|^{4.08} A^{6.22} \exp(-0.166A^{-1.74}). \quad (4)$$

This result means a critical slowing down of the nucleation rate  $J_s \propto (T_c - T)^{4.1}$  at a constant  $A$ , whereas for a constant  $\mu$  the nucleation rate depends exponentially on temperature. The critical slowing down should be observable as a slight increase for  $T \rightarrow T_c$  in the  $A$  necessary for the decay of the metastable state.

To derive (4) we approximated the integral (2) by a Gaussian  $[e^{-x^2} dx]$  [cf. Eq. (9) in Feder *et al.*<sup>1</sup>] and assumed  $A \ll 1$ . Both approximations can be avoided by using a Taylor expansion in powers of  $A^{-\sigma}$  for  $1/J_s$ :

$$J_s = P_1 S_1 q_0 (2\pi m_1 kT)^{-1/2} |\ln x|^{(\tau+1-\sigma)/\sigma} A^{\tau+1-\sigma} \left[ \sum_{n=0}^{\infty} A^{-n\sigma} \frac{\Gamma(n\sigma + \tau + 1 - \sigma)}{n!} \right]. \quad (5)$$

Even if  $A$  is not very small, (5) remains valid; but then  $A$  should be determined directly by (3a) and not by the approximations (3b) and (3c). For the small value of  $A$  near  $T_c$  given later, the difference between (4) and (5) is nearly negligible.

The nucleation rate is made smaller by a factor  $\propto [(T_c - T)/T]^{(\tau-1/2)/\sigma} (T_c - T)^{2.7}$  if we made the speculative assumption that the droplets grow and shrink only by incorporation and evaporation of droplets with volume  $= \xi^3$  where  $\xi$  is the coherence length, containing  $l = l_\xi$  molecules instead of 1.<sup>7</sup> (We define the coherence size  $l_\xi$  by requiring  $|\ln x|_{l_\xi} = 1$  on the coexistence curve.<sup>5</sup>) If we set in our derivation of that result simply  $l_\xi = 1$  we recover (2).<sup>9</sup> The derivation is as follows: In a stable state the number  $n_l$  of  $l$ -droplets remains constant; thus  $n_l \alpha_l S_l = n_{l-l_\xi} b_\xi S_{l-l_\xi}$ . Here  $\alpha_l$  is the rate at which droplets of size  $l_\xi$  evaporate from an  $l$ -droplet;  $b_\xi = P_\xi (2\pi m_\xi kT)^{-1/2}$  is the rate at which they impinge on it per unit time and area.  $P_\xi = P_1 l_\xi^{-\tau}/e$  is the partial pressure and  $m_\xi$  the mass of the  $l_\xi$ -droplets. If in a metastable state all droplets of size  $\geq L$  (say,  $L = 2l^*$ ) are removed from the system and the corresponding number of molecules is inserted into the system as single molecules or  $l_\xi$ -droplets then the distribution  $n_l$  changes into a modified one,  $n'_l$ , with  $n'_L = 0$ ,  $n'_1 = n_1$ . In a stationary state the quantity  $J_\xi = n_{l-l_\xi} b_\xi \times S_{l-l_\xi} - n'_l \alpha_l S_l$  gives the rate at which  $(l-l_\xi)$ -droplets become  $l$ -droplets;  $J_\xi$  is independent of  $l$  and equal to the nucleation rate. Eliminating  $\alpha_l$  we find

$$J_\xi = n_{l-l_\xi} b_\xi S_{l-l_\xi} (n_{l-l_\xi} / n_{l-l_\xi} - n'_l / n_l).$$

Summing up in steps of  $l_\xi$  (indicated by  $\sum_{(l_\xi)}$ ; upper and lower bounds are unimportant if sufficiently greater and smaller than  $l^*$ ), one gets

$$\sum_{(l_\xi)} \frac{J_\xi}{n_{l-l_\xi} b_\xi S_{l-l_\xi}} = J_\xi \sum_{(l_\xi)} (n_l b_\xi S_l)^{-1} = \frac{n'_1}{n_1} - \frac{n'_L}{n_L} = 1 - 0 = 1, \quad J_\xi^{-1} = \sum_{(l_\xi)} (n_l b_\xi S_l)^{-1} = l_\xi^{-1} \sum_{l=1,2,\dots} (n_l b_\xi S_l)^{-1}. \quad (6)$$

This is the result (2) multiplied by  $l_\xi^{-\tau+1/2} \propto [(T_c - T)/T_c]^{(\tau-1/2)/\sigma}$ .

If we assume<sup>1</sup> the metastable state to decay as soon as  $J_s$  reaches  $10^5$  nuclei/cm<sup>3</sup> sec then  $A = 0.045$  in CO<sub>2</sub> at this decay point ( $\ln x = 0.1$ ,  $T = T_c - 8$  K is assumed). With<sup>10</sup>  $J_s = 10^{15}$  nuclei/cm<sup>3</sup> sec our  $A$  is about twice as large. Preliminary experiments<sup>11</sup> made on the *liquid* side of the coexistence curve indicate  $0.27 \geq A \geq 0.07$  at the decay point ( $T_c - 6$  K  $\geq T \geq T_c - 12$  K). More experiments are necessary and partly in progress<sup>11</sup> in order to get a clearer picture: (1) determination of  $A$  at the decay point with different cooling rates to detect possible time lag effects, (2) optical methods to determine when macroscopic droplets occur first and what concentration they have at the decay point, (3) accurate measurements at different temperatures to indicate a critical slowing down of  $J_s \propto (T_c - T)^{6.8}$  or  $(T_c - T)^{4.1}$ .

Even if the pre-exponential factors of the present theory are wrong the "dynamical scaling" result<sup>12</sup> (4) and the critical slowing down can be checked.

The methods used in our theory near  $T_c$  will be applied<sup>7</sup> also to the discussion of (homogeneous) nucleation far below  $T_c$ .

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## New Observations of Dielectric Breakdown in Air Induced by a Focused Nd<sup>3+</sup>-Glass Laser with Various Pulse Widths

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Dielectric breakdown in air induced by a train of subnanosecond laser pulses was found to occur as a sequence of strong point explosions, with each pulse producing breakdown at a different spot. The angular dependence of the scattered laser light was found to be due to the reflection and diffraction from the breakdown spots which were approximately spherical with diameters of about 9  $\mu\text{m}$ . For atmospheric breakdown, analysis of results indicates that a plasma density as high as  $7 \times 10^{20}$  electrons/cm<sup>3</sup> was created in the breakdown region.

This Letter reports some new observations of dielectric breakdown in air induced by a focused Nd<sup>3+</sup>-glass laser with various pulse widths. While it has been eight years since the first observation of optical dielectric breakdown in air,<sup>1</sup> many important aspects of the phenomenon remain to be understood. Most notable among them are the angular dependence of the scattered light at the laser frequency<sup>2</sup> and the dependence of the threshold power on the pulse width.<sup>3</sup> Using laser pulses with a width of 1 nsec or shorter, we have found that the scattering pattern can be explained quantitatively in terms of the reflection and diffraction from plasma "bubbles" created in the breakdown region. At atmospheric pressure, these bubbles are about 9  $\mu\text{m}$  in diameter and have a

plasma density as high as  $7 \times 10^{20}$  electrons/cm<sup>3</sup>. Of particular interest is the observation that with a train of such pulses each individual pulse induced breakdown at a different spot in air. The evolution of these breakdown spots was found to be characteristically similar to that of the shock wave generated by a strong point explosion.

The experiments were performed with a Nd<sup>3+</sup>-glass laser with intracavity acoustic modulation (Fig. 1). Q switching was achieved with a saturable-dye cell (or a rotating prism), resulting in a train of pulses about 20 psec (or 1 nsec) in duration and separated by 12.5 nsec, the round-trip transit time of the cavity. With the saturable-dye cell (rotating prism), the half-width of the train is about 200 nsec (100 nsec). In both cases,