

Cluster nucleation during first-order phase transitions in liquid solutions

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A time ordering has been observed in the process by which a cw laser beam initiates the boiling of binary liquid solutions. The effect is interpreted on the basis of a new cluster mechanism for the nucleation of a new phase in a superheated associated liquid.

Two basic mechanisms for the formation of nucleating regions of the new phase in first-order phase transitions (cavitation) in liquids are recognized:

- 1) homogeneous nucleation, which is observed in pure liquids and which is described by fluctuation nucleation mechanisms,
- 2) heterogeneous nucleation, which results from inhomogeneities on a surface being heated, the presence of impurities, etc.^{1,2}

In this letter we are reporting experiments on thermocavitation processes during laser-induced phase transitions in binary solutions. These experiments were begun in Ref. 3. We have observed an ordering of the onset of boiling caused by a cw laser beam upon a switch from a pure liquid to a binary solution. We will show that the effect can be explained on the basis of a cluster mechanism for nucleation in binary solutions. According to this mechanism, the nucleation centers are clusters rich in the volatile component of the solution, and the phase transition begins when the size of a critical nucleus, determined in a homogeneous solution with a concentration corresponding to the mole fraction of the components in the cluster, becomes smaller than the size of a cluster.

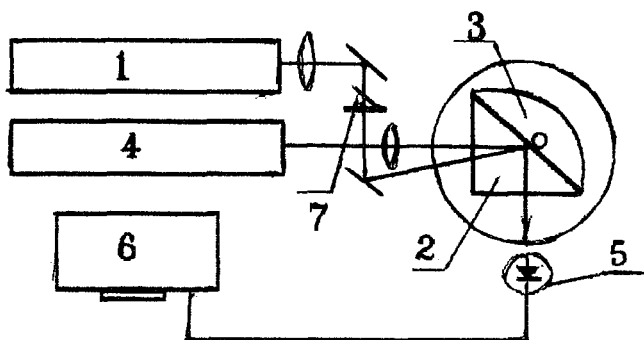


FIG. 1. Block diagram of the experimental apparatus.

The cavitation was initiated by the beam from a cw 1-W argon laser (1 in Fig. 1), which was focused by a lens ($f = 15$ cm) onto the large face of a prism (2), which was the wall of a cell holding the test solution (3). The temperature rise and the time at which a nucleus appeared were determined from the intensity of the beam from a He-Ne laser (4) reflected near the angle of total internal reflection.⁴ The latter beam was focused ($f = 4$ cm) into the heating region. The signal from a photodiode (5) was sent to an S8-9 storage oscilloscope (6). An optical shutter (7) was used to arrange a single laser shot; a single shot was necessary for measuring the instability in the time over which a critical nucleus appeared and for measuring the superheating temperature at this time. We studied water-ethanol solutions, adding the dye rhodamine G to serve as a thermal sensitizer. The amount of dye added was that required to reach an absorption coefficient on the order to 200 cm^{-1} . The dye had little influence on the observed effect, as we verified in some control experiments on the excitation of thermocavitation in pure solutions by means of a CO_2 laser.

The oscilloscope traces in Fig. 2 illustrate the observed ordering of the thermocavitation in this binary solution. The intensity of the reflected light rises because of the increase in the temperature, while the steep decay on the trace is the point of the phase transition. It can clearly be seen that the addition of only 5% ethanol causes the thermocavitation to go from a stochastic regime into a regular, periodic regime. The beginning of the phase transition in the volume of the liquid corresponds to the presence of at least one nucleation center with a size above the critical in the heated volume. The statistics of the onset of boiling are thus determined by the size distribution of the nucleation centers of the new phase.

To prevent the lingering effects of one onset of boiling from influencing the statistics of the appearance of the first critical nucleation center in the heated volume during the next onset of boiling, we carried out measurements in a regime of single laser shots, using a shutter (7). Figure 3 shows the measured temperature dependence of the probability for the appearance of the first critical nucleating center for water and for a 5% solution of ethanol in water. This plot was constructed on the basis of the time interval (t_f) between the operation of the optical shutter and the beginning of the phase transition. We carried out a series of 50 measurements at 1-min intervals, averaged the results, and normalized them. The phase transition temperature T was deter-

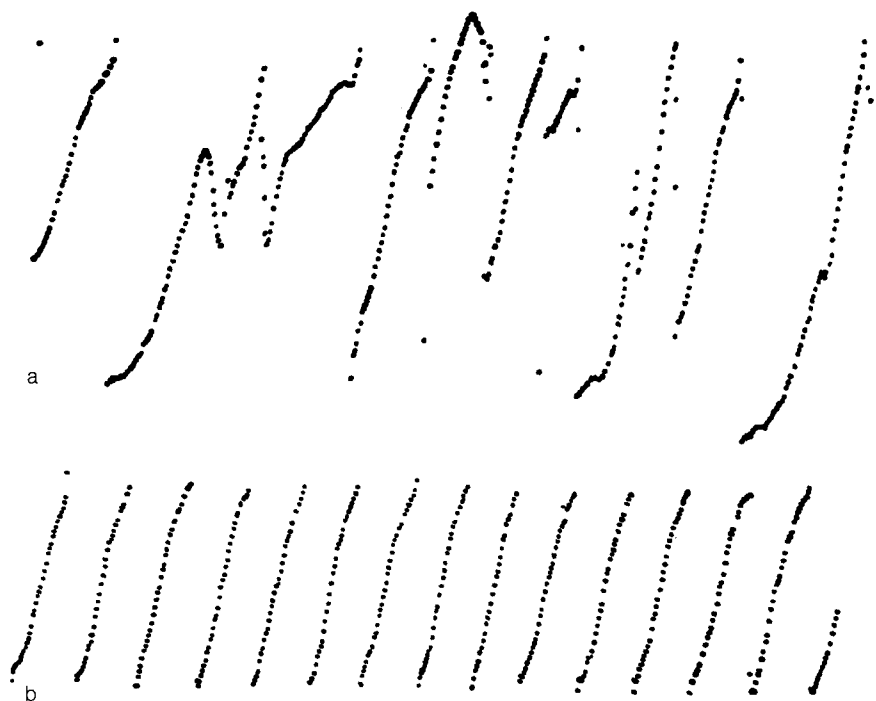


FIG. 2. Intensity of a probe beam reflected from the interface in the phase transition region during the excitation of thermocavitation during continuous heating. *a*—For pure water; *b*—for a 5% ethanol solution. The solid line at the bottom shows the intensity of the reflected beam for a liquid at room temperature.

mined from the heating time t and from the function $T(t)$, found from independent refractometric measurements.

The ordering effect observed during the continuous heating (Fig. 2b) occurs because the rise in the nucleation probability during the continuous temperature rise is steeper in the case of the binary solution than in the case of a pure liquid (Fig. 3a). In comparing Figs. 2b and 3a, we should bear in mind that the time ordering is more obvious in the periodic regime. This result is explained on the basis that the stabilization of the boiling onset temperature in the binary solution leads to a stabilization of the size of the vapor pocket that forms. The latter stabilization leads in turn to a stabilization of that temperature of the liquid by the beginning of the next heating cycle. The initial temperature is not stabilized during thermocavitation in a pure liquid, as is clear from Fig. 2a.

In an effort to explain the features of this effect, we have proposed a new mechanism for the appearance of the critical nucleation center of the new vapor phase in a volume of a binary liquid. This mechanism is a cluster mechanism. The interpretation is based on the circumstance that monatomic alcohols and their aqueous solutions fall in the category of so-called associated liquids, which have a tendency toward cluster formation.⁵

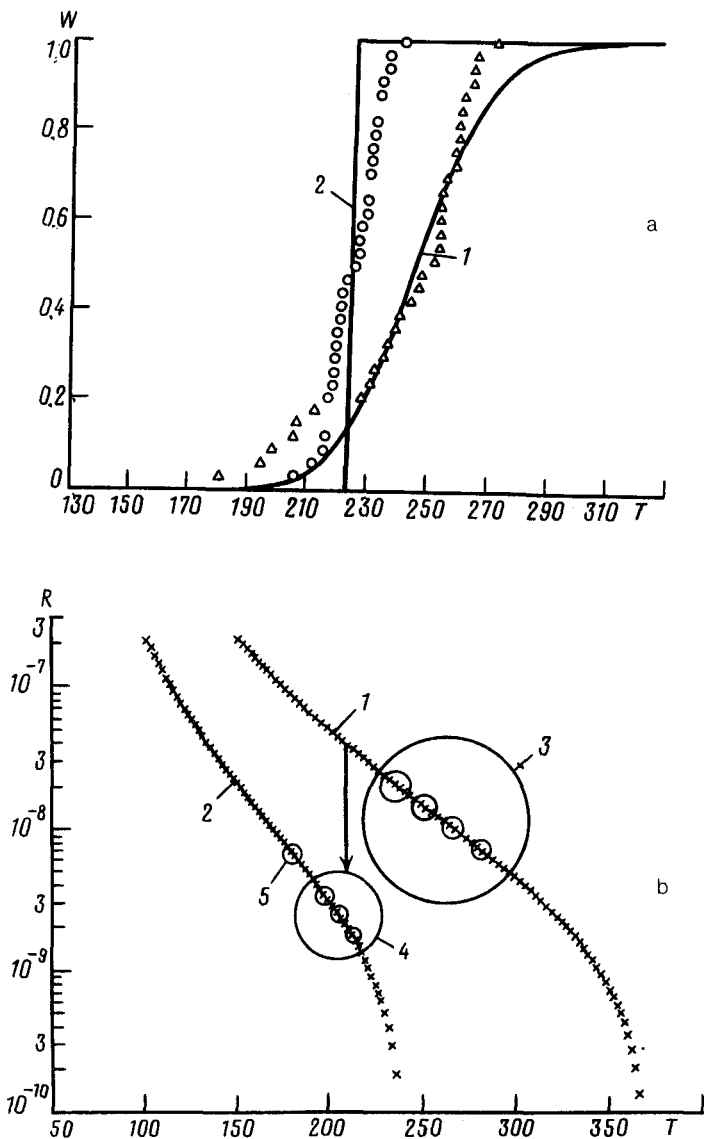


FIG. 3. a: Probability for the appearance of the first critical nucleation center in the heated volume, calculated from expression (3). 1—For water; 2—for a 5% solution of ethanol; Δ , \circ —corresponding probabilities found experimentally in the region of a single laser shot. b: Size of the critical nucleation center versus the temperature for pure ethanol and pure water.

We consider a binary solution with a concentration by volume $C = v_1/(v_1 + v_2)$ of the volatile component; here v_1 and v_2 are the volumes of the volatile and involatile components. The volatile component is associated in N clusters whose composition differs from the average composition over the volume. The concentration of the vola-

tile component in a cluster satisfies $C_c > C$. The mechanism proposed here for the formation of a nucleating center is based on the fact that if the entire solution were homogeneous and had a concentration C_c then a critical nucleation center of a definite volume $v_c(T)$, which contains an amount of substance $m_c(T) = \rho_c v_c(T)$, would correspond to this homogeneous solution. Accordingly, if the mass of cluster i , m_i , in the associated solution is smaller than this value, then the mass of a cluster rich in the volatile component will be insufficient for the formation of a critical nucleation center. In this case the condition for the beginning of a phase transition is $m_i > m_c(T)$. We can show that experiments at low concentrations of the volatile component can be interpreted by assuming that there are clusters which result from a fluctuation in the solution concentration and that the size distribution of these clusters can be found from the Smoluchowski formula.⁶ It is not difficult to show that in this case, in a vessel of volume V , the number (N) of clusters with a volume $v_i = (4/3)\pi R_c^3(T_i)$, in which the alcohol content is 100%, obeys the distribution

$$N(v_i) = \frac{V}{v} \bar{n}^n \exp(-\bar{n}), \quad (1)$$

where $n = v_i/v_s$ is the number of ethanol molecules with volume v_s in a cluster with a critical volume v_c , $\bar{n} = Cv_i/v_s$ is the average number of ethanol molecules in this volume, averaged over the entire volume of the vessel, and $R_c(T_i)$ is the radius of a critical nucleation center calculated for pure ethanol. Here and below, the index $i = 1, 2, 3, \dots, L$ is the index of the discrete step along the temperature scale under considerations, which has been divided into L intervals. The probability (P_i) that there will be at least one particle of mass m_i in the laser-heating region, of volume v_0 , is described by an expression which follows from a Poisson distribution⁷:

$$P(v_i) = 1 - \exp(-\alpha(v_i)), \quad (2)$$

where $\alpha = N(v_i)v_0/V$. If the temperature T_i increases linearly over time, the probability (W_i) that at least one critical nucleating region will appear over the time interval t_i , during which the temperature in the heated volume v_0 reaches T_i , is determined by the probability for the appearance in v_0 of at least one cluster of mass $m_i > m_c(T)$. Consequently, in summing the probabilities P_i from (2) over all clusters v_i which have a mass greater than the critical mass by the time t_i , we obtain the distribution function $W(T_i)$ described by the recurrence relation

$$W(T_{i+1}) = W(T_i) + P(T_{i+1})(1 - W(T_i)). \quad (3)$$

The solid lines in Fig. 3a are distribution functions of (line 1) W found from (3) with the help of (2) and (1) for clusters in a 5% ethanol solution and (line 2) the probability for the appearance of at least one critical nucleating center in pure water to which a dispersion of heterogeneous nucleation centers.

$$N(v_i^w) = c_i \exp(-c_2 R_c^w(T_i)), \quad (5)$$

has been added. Here v_i^w and R_c^w are the volume and radius of a critical nucleation center for water. The constants c_1 and c_2 (with values 1×10^7 and 1×10^8) were found by fitting the theoretical expressions to the experimental data. In comparing the theo-

retical probability for the appearance of a critical region with the experimental probability for cluster nucleation (line 2 in Fig. 3a), we should point out that the experimental behavior is more gently sloping. The reason for this result is evidently the role played by hydrodynamic fluctuations of the convection near the wall, which leads to fluctuations in the $T(t)$ dependence.

The mechanism of cluster nucleation can be explained on the basis of the curves in Fig. 3b of the radii of the critical nucleation centers versus the temperature and the radius of a critical nucleation center for pure water and pure ethanol. These curves were calculated from Ref. 2, with allowance for the temperature dependence of the surface tension,⁸ $\sigma(T)$, and of the saturation vapor pressure. For the pure water, an increase in the temperature corresponds to a motion of the critical nucleation centers along curve 1 in dimension space⁹ (Fig. 3b). A phase transition occurs when a nucleating center with a size equal to the critical size appears in the heated volume (region 3). In a binary solution containing clusters, cavitation sets in earlier, as indicated by the transition along the downward arrow. This transition corresponds to the measured superheating temperature of 220 °C (Fig. 3a). It arises because the temperature sets in when the cluster size exceeds the critical size (region 4). The superheating temperature which is reached in a low-concentration ethanol solution becomes essentially equal to the critical temperature for a cluster with an ethanol concentration of 100%. Point 5 in Fig. 3b corresponds to the phase transition temperature for homogeneous nucleation calculated from the Döring-Folmer theory¹⁰ for pure ethanol. It can be seen from Fig. 3b that the region of cluster nucleation (4) does not coincide with the region of homogeneous nucleation (5) or that of heterogeneous nucleation (3).

The ordering effect was observed over the ethanol concentration range 5–95%. To describe the features of cluster nucleation over this entire concentration range, however, one would have to take into account both the cluster size and the mole fraction of the components in a cluster. This study could be carried out by measuring the probability distribution for the appearance of a critical nucleation center at a given temperature over the entire concentration range. From the shape of the measured function and its deviation from a Gaussian shape, one can then find experimental results on the size and composition of a cluster. The effect observed here and this study thus raise the hope that this effect may find use, along with other diagnostic methods,¹¹ for studying groupings and complexes in liquid solutions.

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Translated by Dave Parsons