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How high can the temperature of a liquid be raised without boiling?

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How high the temperature of a liquid can be raised beyond its boiling point without vaporizing (known as the limit of superheat) is an interesting subject of investigation. A different method of finding the limit of superheat of liquids is presented here. The superheated liquids are taken in the form of drops suspended in a dust free gel. The temperature of the superheated liquid is increased very slowly from room temperature to the temperature at which the liquid nucleates to boiling. The nucleation is detected acoustically by a sensitive piezoelectric transducer, coupled to a multichannel scaler, and the nucleation rate is observed as a function of time. The limit of superheat measured by the present method supersedes other measurements and theoretical predictions in reaching the temperature closest to the critical temperature of the liquids.

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Any fluid that exists in the liquid form above its boiling temperature is said to be superheated. These liquids are in a metastable state in the thermodynamic sense and can be nucleated to form vapor by homogeneous nucleation or by the presence of heterogeneous nucleation sites such as gas pockets, vapor bubbles, solid impurities, etc. or by the radiation interactions caused by charged particles, neutrons, etc. Vapor embryos of different sizes, which are responsible for homogeneous nucleation, are produced at thermal equilibrium in the superheated liquid. The superheated state owes its existence to an energy barrier that causes the vapor embryo to collapse, rather than lead to nucleation, if it is less than a critical size.

A liquid cannot be superheated up to the critical temperature, there is a limit to the maximum attainable temperature for any given liquid without boiling. This limit is called the ''limit of superheat of the liquid'' (T_{sl}), where the height of the energy barrier, which maintains the superheated state, is of the order of kT, and this temperature is a characteristic of any liquid. In addition to its importance in basic science, the knowledge of T_{sl} is important in a number of industrial operations where a hot, nonvolatile liquid comes into contact with a cold volatile liquid. If the temperature of the hot liquid reaches the limit of superheat of the cold liquid, explosive boiling would result. This explosive boiling is a potential hazard that could damage equipment and injure personnel in the vicinity of the blast [1]. The study of T_{sl} has another importance since the discovery of the bubble chamber by Glaser [2] and the discovery of the superheated drop detector [3]. The operation of this detector depends on the degree of superheat of the liquid—more the liquid is superheated, more sensitive the detector is to lower energy radiations [4]. The minimum energy detectable by such a detector is therefore limited by the limit of superheat of the detecting liquid. The limit of superheat of liquids can be estimated from the theory and can be measured experimentally. Theoretical calculations are performed either from the pure thermodynamic considerations or using the statistical mechanics. Very good and comprehensive reviews on homogeneous nucleation of liquid and on the limit of superheat are available in the literature [5–7]. One has to note that theoretical calculations are performed for ''pure'' homogeneous nucleation where the chance of heterogeneous nucleation arising out of various interfaces with different surface energies, e.g., gas with liquid, liquid with liquid, solid with gas, etc. is completely excluded.

Experimental results reported so far are far below the critical temperature of the liquids. One of the reasons is that observing ''pure'' homogeneous nucleation experimentally, without any chance of heterogeneous nucleation, is difficult to achieve. Hence the goal is to reduce the chance of heterogeneous nucleation as far as possible and to use an improved method of quantitative detection of nucleation to see how close one can reach experimentally to the predicted limit of superheat. The present experiment is designed to achieve this goal. The superheated sample used in this investigation is a homogeneous suspension of superheated drops of three refringent liquids (R-12: CCl_2F_2, R-114: $C_2Cl_2F_4$ and R-22 : $CHClF_2$) in a dust free, viscoelastic, degassed gel medium. Suspending the superheated liquid in another liquid (gel) reduces the chance of heterogeneous nucleation. Nucleation is detected acoustically by a piezoelectric transducer [8], and the pulses thus received are digitized and recorded as a function of time by a multichannel scaler. This improved method of determining T_{sl} supersedes all other measured values in reaching closest to the critical temperatures. Reviews on previous experimental techniques of measuring the limit of superheat of liquid have been described in detail by Avedisian [6]. As has been found from this literature, all previous experiments except one rely on the qualitative observation of the nucleation visually, and therefore the present measurement constitutes a special quantitative measurement of T_{sl} using digital electronics.

The limit of superheat can be estimated from either the thermodynamic stability theory or from the analysis of the dynamics of formation of the critical-sized vapor embryos (statistical mechanical theory). The superheated state of a liquid is a metastable state and the limit of this metastable state is represented on the pressure-volume diagram by the

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spinodal curves. For a pure liquid, the spinodal curve or the thermodynamic limit of superheat is defined by states for which

$$\left(\frac{dP}{dV}\right)_T = 0. \tag{1}$$

Temperley [9] calculated the value of maximum superheat temperature using van der Waals' equation of state. The maximum limit of superheat of a given liquid can be expressed as

$$t_m = \frac{27T_c}{32}, \tag{2}$$

where t_m is the limit of superheat of the liquid. For mathematical simplicity this has been calculated by considering the ambient pressure to be zero. At atmospheric pressure, i.e., at $P=1$, t_m will be slightly greater than the corresponding value at $P=0$. Other equations of state, such as the modified Bertholet equation and the Redlich-Kwong equation have also been used to calculate the limit of superheat [5]. As has been observed by Blander and Katz [5], experimental values of the thermodynamic limit clearly exceeded the van der Waals limit at least for five liquids.

For most of the organic liquids, the thermodynamic limit of superheat can be represented empirically [1] by

$$T_{sl} = T_c[0.11(P/P_c) + 0.89], \tag{3}$$

where T_c is the critical temperature, P_c is the critical pressure, and P is the ambient pressure.

Another method of estimating T_{sl} using statistical mechanics involves considerations of the rate processes of nucleation to form vapor embryos in a superheated liquid. This method does not yield an absolute value of T_{sl}, but it allows one to estimate the probable rate of formation of critical-sized vapor embryos in a superheated liquid at a given temperature. If the rate is very low within the time scale of the experiment, one considers that no nucleation would occur, while if the rate is very high, then one assumes that T_{sl} has been reached. The rate of homogeneous nucleation (J), as given approximately by the Volumer-Doring formula, is given by [1]

$$J = Nf \exp\left(-\frac{B}{kT}\right), \tag{4}$$

where J is the expected rate of formation of critical-sized vapor embryos per unit volume, f is a frequency factor that in general is of the order of 10^{11} sec^{-1}, N is the number density of molecules in the superheated liquid, and B, the minimum amount of energy needed to form a vapor bubble of critical size as given by Gibbs [10] from reversible thermodynamics, is

$$B = 16\pi\gamma^3(T)/3(p_v - p_o)^2, \tag{5}$$

where $\gamma(T)$ is the liquid-vapor interfacial tension, P_v is the vapor pressure of the superheated liquid, and P_o is the ambient pressure. It is to be noted in this connection that which value of J is proper to calculate T_{sl} is not defined and therefore one has to make a ''judicious choice'' about a rate that would correspond to T_{sl}. A J value of 10^6 nucleation/cm^3 sec is often used to define the limit of superheat temperature.

It is to be noted that all of the above discussions are related by the classical theory of nucleation. The effects of other factors like diffusion, viscosity, and other hydrodynamical constraints are discussed by Blander and Katz [5]. As has been pointed out by them, contributions arising out of these effects in calculating the T_{sl} of pure liquids are not very significant.

The experiment is carried out with superheated liquids of R12 (boiling point of $-29.79\,^{\circ}\mathrm{C}$), R114 (boiling point $3.6\,^{\circ}\mathrm{C}$) and R22 (boiling point of $-40.5\,^{\circ}\mathrm{C}$). The superheated drops are suspended in dust free, degassed viscoelastic gel. The gel is a mixture of ''aquasonic'' gel available commercially and glycerine. A glass vial containing the superheated drops homogeneously suspended in gel is placed on the top of a thin layer of degassed gel taken in a beaker. The gel in the beaker improves the acoustic coupling between the superheated drops in the vial and the transducer. The beaker is placed on a piezoelectric transducer with a coupling gel. Some pure gel is placed on the top of the sample and a thermometer was inserted in the pure gel so as to avoid any contact with the superheated liquid sample, thus reducing the chance of heterogeneous nucleation from the liquid-glass interface. The nucleation in superheated drops is detected by the transducer and the output of the transducer is digitized and recorded by a multichannel scaler. The vial was wrapped with a heating coil covering the gel and sample. The temperature of the sample is increased slowly from room temperature and the count rate (dN/dt) is recorded by a multichannel scalar MCS. As nucleation proceeds, the number of superheated drops are depleted and hence the nucleation rate is normalized with respect to the number of drops present. What we expect ideally,

$$\left(\frac{1}{N}\right)\frac{dN}{dt}$$

is zero till the temperature reaches the limit of superheat where there will be a sudden increase in

$$\left(\frac{1}{N}\right)\frac{dN}{dt}$$

(the entire liquid nucleates) and there will be no nucleation beyond this temperature. Considering the experimental uncertainty, one may observe the similar behavior as presented in Fig. 1. The comparison of the observed limit of the superheat with other experimental results is presented in Table I. The reduced limit of superheat defined as T_{sl}/T_c (taken in K) for these liquids is also presented in Table I along with theoretically predicted values and other experimental results.

As could be seen from Table I, the measured limit of superheat exceeded the predicted limit of superheat and other experimental values. It is to be noted in this connection that all theoretical predictions are approximate, as discussed before. Therefore the present experimental measurements indicate the need for an improved calculation of the limit of superheat. That the van der Waals' limit is exceeded was reported before by Blander and Katz [5]. Table I also gives a

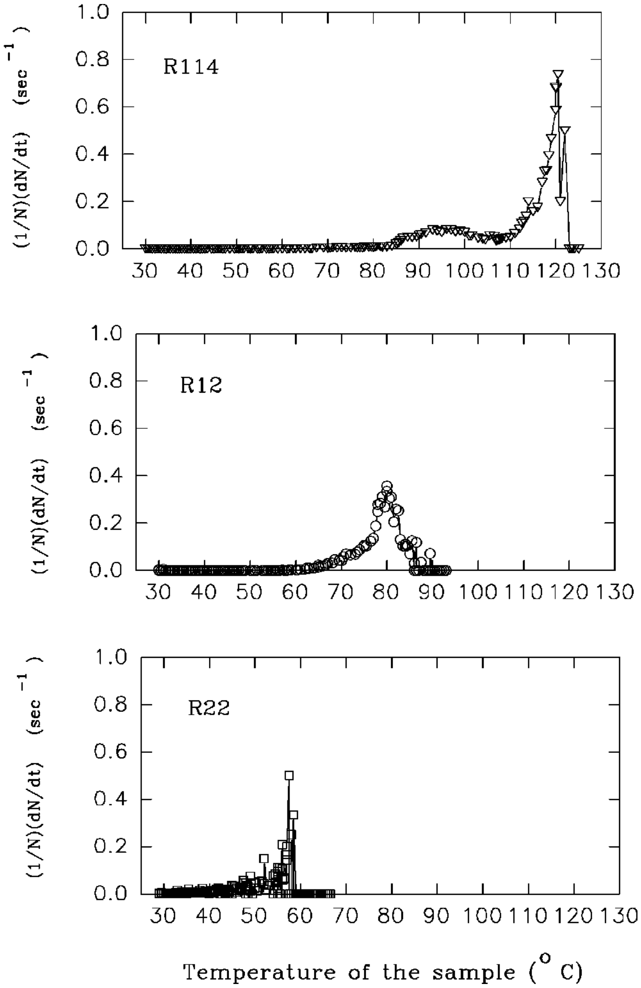

FIG. 1. Variation of nucleation rate with the temperature of the sample.

useful insight about the nucleation process. As can be seen from Table I, for liquids with lower boiling points, it is harder to come close to the critical temperature. This is quite expected, as the chances of heterogeneous nucleation increases in the case of liquids with lower boiling points. Whether complete elimination of heterogeneous nucleation in experimental measurement is possible or not is an open question. No other measurements have been able to come so close to reaching the critical temperature. It is to be noted in this connection that the limit of superheat of only 14 liquids out of 56 liquids studied by Blander and Katz [5] hardly exceeded 90% of the critical temperature.

Therefore by reducing the chances of heterogeneous nucleation by suspending the superheated sample in another ''pure'' liquid and using precise electronic measurement, we have been able to come closer to reaching to the critical temperature that has hitherto been unattainable. In spite of the fact that theoretical calculations are performed for ''pure'' homogeneous nucleation, they fall below the experimental values, which indicates the inadequacy of the present method of calculation discussed here and warrants improved calculations.

TABLE I.

Liquid	T_c	Observed T_{sl} °C		Reduced limit of superheat $[T_{sl}(\mathrm{K})/T_c(\mathrm{K})]$				
				Predicted values from			Experiment	
	K	Present	Others	Eq. (2)	Eq. (3)	(Eq. (4)	Present	Others
CCl_2F_2	384.5	80.0	72.0 [1]	0.84	0.89	0.90	0.92	0.90 [1]
$C_2Cl_2F_4$	418.7	120.5	102.0 [1]	0.84	0.89	0.91	0.94	0.90 [1]
$CHClF_2$	369.0	57.5	54.0 [1]	0.84	0.89	0.89	0.89	0.89 [1] 0.89 [6]

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