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〈Invited Review Article〉
Vapor Bubble Nucleation : A Microscopic Phenomenon

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In this article, vapor bubble nucleation in liquid and the evaporation process of a liquid droplet at its superheat limit were discussed from the viewpoint of molecular clustering (molecular cluster model for bubble nucleation). For the vapor bubble formation, the energy barrier against bubble nucleation was estimated by the molecular interaction due to the London dispersion force. Bubble nucleation by quantum tunneling in liquid helium under negative pressure near the absolute zero temperature and bubble nucleation on cavity free micro heaters were also presented as the homogenous nucleation processes.

Key Words : Evaporation, Molecular Cluster, Quantum Tunneling, Superheat Limit, Tensile Strength, Vapor Bubble

Nomenclature

A_s	: Surface area of heater
d_m	: Average distance between molecules
D_n	: Rate of molecules striking on the surface of n-mer cluster
d_w	: Van der Waals' diameter of liquid molecules
E_I	: Ionization potential
F_n	: Free energy needed to form n-mer cluster
F_r	: Free energy needed to form a bubble with radius of r
$\hbar$	: Plank constant
j	: Nucleation probability, Eq. (19)
J	: Nucleation rate of bubble per unit volume
J_n	: Nucleation rate of n-mer cluster per unit volume
J_s	: Nucleation rate per unit area
k_B	: Boltzman constant
m	: Mass of molecule
M	: Molecular weight
m	: Nmber of molecules in a cluster
N	: Nmber density $(=\rho_m/m)$
P_e	: Pressure inside a bubble
P_v	: Vapor pressure
P_∞	: Ambient pressure
r	: Radius of bubble
R	: Gas constant
R_d	: Radius of evaporated sphere in the droplet
T	: Temperature of liquid
T_c	: Critical temperature
T_f	: Melting temperature of liquid
t_l	: Time lag of nucleation events
T_s	: Superheat limit of liquid
V	: Volume of a droplet
v_l	: Molar volume of liquid
V_m	: Effective molecular volume of liquid
Z	: Coordination number
Z_f	: Zeldovich nonequilibrium factor

Greek letters

α	: Polarizability of a liquid molecule
β	: Accommodation coefficient
ΔH_{vap}	: Enthalpy of evaporation
ΔH_f	: Enthalpy of fusion
ε_0	: Potential parameter of the London dispersion attraction
ε_m	: Energy needed to separate a pair of molecules
ε_{vib}	: Vibrational energy

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μ : Chemical potential
ρ_m : Density of liquid
ρ_c : Critical density of liquid
σ : Interfacial tension
τ : Tensile strength of liquid
ω : Tunneling frequency

Subscript

c : Critical cluster or critical size bubble

1. Introduction

The classical theory of homogeneous bubble nucleation is a mixture of macroscopic and molecular concepts. For the initiation of bubble formation, the classical theory initially assumes the formation of the critical size bubble. Given the macroscopic interfacial tension σ, the condition for the formation of the critical bubble is given by

$$P_e - P_\infty = 2\sigma / r_c \tag{1}$$

The above equation, known as the Laplace equation states that the critical bubble is in mechanical equilibrium with the liquid. Further, the critical bubble is in the thermal and chemical equilibrium (Jarvis et al., 1975) where the equilibrium pressure of the bubble P_e is related to the vapor pressure of P_v corresponding to the liquid temperature T_o at given ambient pressure of P_∞ (van Stralen and Cole, 1979). That is

$$P_e = P_v \exp\left[-\frac{v_l (P_v - P_\infty)}{RT_o}\right] \tag{2}$$

With the condition given in Eq. (1), the free energy needed to form the critical size bubble becomes

$$F_{rc} = \frac{4}{3}\pi r_c^2 \sigma = \frac{16\pi}{3} \frac{\sigma^3}{(P_e - P_\infty)^2} \tag{3}$$

This expression, originally proposed by Gibbs, has been used previously for the variety of purposes (Skripov, 1974). However, it is doubtful whether Eq. (1) is pertinent when r_c approaches molecular dimension (Kwak, 1990). The classical theory of nucleation kinetics, ascribed to Doering (1937, 1938), Volmer (1939), and Zeldovich (1943), supplies a steady states of nucleation for critical bubbles. For the limiting cases in which near critical size bubbles are in mechanical equilibrium with the bulk, the nucleation rate may be estimated with the kinetic argument as (e.g. Blander and Katz, 1975)

$$J = N\left(\frac{\sigma}{\pi m B}\right)^{1/2} \exp\left[-\frac{16\pi\sigma^3}{3k_B T (P_e - P_\infty)^2}\right] \tag{4}$$

where B is an arbitrary constant. Usually it is assumed that experimental observation of bubble nucleation in a liquid is possible when the nucleation rate is between $J=1$ and $J=10^6$ bubbles/cm^{3}s. However the classical bubble nucleation theory discussed above fails to predict the tensile strength of liquids (Briggs, 1950, 1951). In addition, this classical nucleation theory gives no information about the intensity of evaporation at the superheat limit (Avedisian, 1982). The theory, with the work of formation of the critical bubble Eq. (3), was widely accepted because it is quite successful in predicting the superheat limit of liquids with nucleation rate about $J=10^4$-10^6 bubbles/cm^{3}s (Blander and Katz, 1975). The validity of the capillary approximation-the assumption that the value of the surface tension, an equilibrium property of the macroscopic interface, is applicable to the nucleation phenomena-has often been discussed (Buckle, 1968). In fact, from a series of experiments, Hemmingsen (1977) realized that the surface tension at the gas-water boundary of the bubble nucleus must be at least an order of magnitude lower than that obtained from the macroscopic bubble dimensions.

In this article, vaporous bubble nucleation in liquid and the evaporation process of a liquid droplet at its superheat limit were discussed by using a molecular cluster model or an activated complex model because a critical cluster is an intermediate state before the formation of a critical size bubble. The essential element of the cluster model (Kwak and Panton, 1983, 1985) is the application of molecular concept to the surface energy for the formation of the critical cluster as it retains the kinetic formalism of the classical theory of nucleation. Some examples for the bubble nucleation, which have not been understood properly yet, will also be discussed by using the molecular cluster model.

2. Vapor Bubble Formation

As is well known, the vaporous bubble formation can be achieved by heating a liquid at a given ambient pressure or by reducing the pressure of the liquid at a given temperature. In any cases, the difference between the vapor pressure at a given temperature and the pressure at the maximum metastable state may be called the tensile strength of liquid. The thermodynamic view point of tensile strength also shows that it is immaterial whether the pressure at the maximum superheated state is positive or negative. For room temperature this pressure is negative, hence the name tensile strength, but for higher temperatures the maximum superheated state is at a positive pressure. Briggs (1955) recognized this situation and performed an experiment where water was carefully heated at a constant pressure of 1 atm. By avoiding boiling, a surface phenomenon, he could reach a maximum temperature of 270℃ before vapour bubbles formed homogeneously. This same metastable state would also result from an isothermal decompression of the saturated state at 270℃ and 54 atm. Hence, the tensile strength of water at 270℃ may be defined as 53 atm. Formally the tensile strength at a given temperature T_0 can be defined as

$$\tau=P_\infty-P_v \tag{5}$$

We shall adopt this definition in the work which follows. For the vapor bubble formation, the energy required to cut across a cluster to overcome the attraction of nearest neighboring molecules is ascribed to the role of an equivalent cluster surface tension. The cluster total energy is then maximized to find when a cluster becomes stable. From the equations representing these processes it is possible to infer the tensile strength of the liquid.

2.1 Surface energy of cluster in metastable state

An essential element required for the calculation is an estimate of the surface energy of the proposed clusters. It is well known that the various intermolecular interactions such as the metallic bond, the hydrogen bond and the London dispersion force (or van der Waals force) cause the surface tension of liquids (Fowkes 1963). However it is assumed that only the London dispersion force is important for simple liquids in the metastable state. Even for a polar molecule such as water, this assumption may be valid since the electrostatic interactions are broken for water at a high temperature (Walrafen, 1966), a metastable state. The potential corresponding to the London dispersion force at large distances, which is quantum mechanical in origin (e.g. Itzykson and Zuber 1980) varies as the inverse sixth power of the intermolecular distance d_m. The potential for the attractive interaction between molecules in the liquid is given by (Fowkes 1964)

$$\frac{3}{4}\,\frac{E_I\alpha^2}{d_m{}^6} \tag{6}$$

A face centered cubic lattice structure is assumed for the liquid concerned. With this liquid model, the average intermolecular distance between molecules d_m may be found from the density data,

$$\frac{\pi}{6}\,d_m{}^3N=V_mN=0.7405 \tag{7}$$

where 0.7405 is the packing fraction of the Face Centered Cubic (FCC) lattice structure. This liquid model may be considered as a cell model (Hirschfelder et al 1954) with an average field interaction. A fluid at the critical point has zero surface tension and may be considered as being in a gaseous-like state. (At the critical point, saturated liquid and saturated vapor states are identical.) The energy required to separate a pair of molecules from a distance d_m apart to the distance d_c (mean distance between molecules at the critical point), the cut-off distance characteristic of the critical point is

$$\varepsilon_m=4\varepsilon_0\left[1-\left(\frac{\rho_c}{\rho_m}\right)^2\right]\left[\left(\frac{d_w}{d_m}\right)^6-\left(\frac{d_w}{d_m}\right)^{12}\right] \tag{8}$$

Here d_w is the van der Waals diameter (see Streitwieser and Heathcock 1981) which is the effective size of the molecule. In the above equation, the potential including the repulsive force is assumed to be a Lennard-Jones type (Prausnitz, 1969). The potential parameter ε_0 in Eq. (8) is given by

$$\varepsilon_0 = \frac{3}{16}\frac{E_I \alpha^2}{d_m^6} \tag{9}$$

The cut-off distance d_c has a value around 1.6 d_w for the liquid considered in this work. Using this cut-off potential, the interaction between molecules is restricted to the nearest neighboring molecules since the distance to the next-nearest neighboring molecules is 1.73 d_w for a FCC lattice liquid (lattice liquid model). The metastable state under tension is expected to contain clusters formed by activated molecules. When a single molecule is surrounded by Z nearest neighboring molecules ($Z=12$ for a FCC lattice structure), the molecules may be separated from the group by applying the energy $W = Z\varepsilon_m/2$ (Prausniz, 1969). The energy W_n required to cut across a cluster composed of n molecules from the surrounding liquid (Feynman, 1972) is

$$W_n = W \cdot n^{2/3} = \frac{1}{2} Z\varepsilon_m n^{2/3} \tag{10}$$

This energy is considered as the surface energy for the cluster of activated liquid molecules in superheated liquid. It is the energy required to form a vapor bubble by overcoming the attraction between the nearest neighbor molecules in the cluster. Note that this surface energy vanishes at the critical point.

2.2 Thermodynamics of clusters

For vapor bubble formation, the free energy required to from a n-mer cluster with the surface energy as postulated in Eq. (10) is given by

$$F_n = (P_\infty - P_v)\, n V_m + \frac{1}{2} Z\varepsilon_m n^{2/3} \tag{11}$$

The stability condition for a cluster requires that F_n is maximum with respect to n. A straightforward calculation from Eq. (11) shows that the maximum free energy barrier for the bubble formation occurs at $n = n_c$ when

$$-(P_\infty - P_v)\, n_c^{\frac{1}{3}} = \frac{2}{3}\left(\frac{1}{2} Z\varepsilon_m \Big/ V_m\right)$$

$$= \frac{2}{3}\left(\frac{\textit{potential energy of a molecule}}{V_m}\right) \tag{12a}$$

Solving this equation for $P_\infty - P_v$ and using Eq. (5) one obtains the tensile strength as

$$-\tau = \left(\frac{1}{3} Z\varepsilon_m / V_m\right) \Big/ n_c^{\frac{1}{3}} \tag{12b}$$

Thus, identifying the critical state of a cluster with the conditions required for rupture of a homogeneous liquid leads to an expression for the tensile strength. The right-hand side of Eq. (12a) is a function of the molecular properties. On the left-hand side n_c, the number of molecules in a cluster of the critical size, remains to be found. Nucleation rate per unit volume obtained from the kinetic theory argument will supply this number. Note that if clusters do not form, or if one molecule constitutes a cluster, then the right-hand side of Eq. (12a) is an ideal (absolute) tensile strength.

2.3 Nucleation kinetics for clusters

The growth of a cluster depends on kinetic events within the liquid medium. If we assume that the growth is a quasi-stationary phenomenon caused by monomer addition of activated molecules, the nucleation rate J_n (of the n-mer cluster) per unit volume may be written as (e.g. Frenkel, 1946)

$$J_n = N D_n Z_f \exp(-F_n/k_B T) \tag{13}$$

where Z_f is the Zeldovich non-equilibrium factor (e.g. Feder et al, 1966) which is given by

$$Z_f = \left[-\frac{1}{2\pi k_B T}\left(\frac{\partial^2 F_n}{\partial n^2}\right)\right]^{1/2}$$

Estimates for D_n are obtained from the kinetic theory formula relating the flux to the mean velocity $\bar{v}$, the number density $\bar{n}$ of activated molecules, and the cluster area A_n, $D_n = \beta \bar{v}\, \bar{n} A_n / 4$. In this formula β is the accommodation coefficient. To distinguish activated molecules we choose the energy level ΔH_{vap} corresponding to the enthalpy of evaporation. Thus the number of such molecules is $\bar{n} = N \exp(-\Delta H_{vap}/RT)$. Furthermore, the effective mean velocity of molecules in a liquid (Faber, 1972) is

$$\bar{v}=(8k_BT/\pi m)^{1/2}\exp(-\Delta H_f/RT_f) \qquad (14)$$

Combining these results gives

$$D_n=\frac{\beta}{4}N\left(\frac{8k_BT}{\pi m}\right)^{1/2}\exp\left(-\frac{\Delta H_{vap}}{RT}-\frac{\Delta H_f}{RT_f}\right)\cdot A_n \qquad (15)$$

Next, we consider the energy for the critical cluster, F_{nc}. This is obtained by substituting Eq. (12a) into Eq. (11) to arrive at

$$\frac{F_{nc}}{k_BT}=\frac{Z}{6}\left(\frac{\varepsilon_m}{k_BT}\right)n_c^{2/3} \qquad (16)$$

Hence, by inserting Eqs. (15) and (16) into Eq. (13), the nucleation rate of the critical clusters is

$$J_{nc}=J_{CLA}=N\left(\frac{k_BT}{2\pi m}\right)^{1/2}\left[\frac{Z}{18\pi}\left(\frac{\varepsilon_m}{k_BT}\right)\right]^{1/2}$$
$$\cdot 4\pi\beta\left(\frac{3V_m}{4\pi}\right)^{2/3}\cdot\exp\left(-\frac{\Delta H_{vap}}{RT}-\frac{\Delta H_f}{RT_f}\right)N \qquad (17)$$
$$\times\exp\left(-\frac{Z}{6}\frac{\varepsilon_m}{k_BT}n_c^{2/3}\right)$$

This is the final expression for J_{nc}, which is similar to that of Hirth and Pound (1963) for the kinetics of homogeneous nucleation in the process of ebullition.

2.4 Evaluation of tensile strength of liquids

The model to predict the tensile strength of a liquid in terms of its molecular properties is now complete. If the potential parameter ε_0 is known, ε_m can be calculated from Eq. (8). The van der Waals diameter of simple liquid molecules is taken as the hard sphere diameter from the virial coefficient (Hirschfelder et al, 1954). Moreover if we choose a level for the critical nucleation rate, J_{nc}, then Eq. (17) becomes a relation for determining n_c, the number of molecules in a critical cluster. With n_c and the molecular properties known, the tensile strength is readily found from Eq. (12b). The calculated tensile strength of water with both $J_{nc}=1$ and $J_{nc}=10^6$ bubbles/cm^{3}s at 10℃ are 238 atm and 273 atm respectively while the experimental value measured in a rotating capillary tube (Briggs, 1950) is about 277 atm. Using the classical theory, the tensile strength estimated at this temperature is over 1000 atm. However, at temperature less than 10℃, the tensile strength falls rapidly as shown in Fig. 1. Obviously different physical mechanism is important here (Kwak and Panton, 1985).

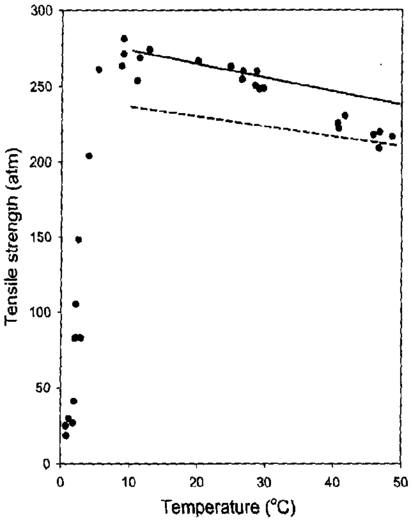


Fig. 1 Tensile strength of water as a function of temperature, including the melting region. (—) $J=10^6$; (---) $J=1$. Experimental points (•) by Briggs (1950)

The results of computation for tensile strength of simple liquids with both $J_{nc}=1$ and $J_{nc}=10^6$ nuclei/cm^{3}s are given in Table 1. The tensile

Table 1 Tensile strength of simple liquids

Liquid	Molecular cluster model		Fisher	Temperley	Experiment
	J=1	J=10^6			
He (2.6K)	0.7	0.8	3.9	9.0	0.16* (1.9K)
H2 (16K)	26	29	41	55	
Ar (85K)	46	52	243	147	12*
N_2 (75K)	24	27	159	147	10*
O_2 (75K)	71	81	380	213	15*
CH_4 (105K)	36	40		149	
H_2O (10℃)	238	273	1778	1111	277**

*Beams (1959)
**Briggs (1950)

strengths computed by Fisher's theory (1948) and by Temperley's theory (1947) are also listed in this Table together with experimental data of Beams (1959) and Briggs (1950). Temperley's theory, using the minimum point of the van der Waals isotherm, usually give values two to five times higher than those obtained from the molecular cluster model. Fisher's theory, based on the growth of holes in the liquid, generally predicts tensile strengths that are even higher.

2.5 Nucleation rate at the superheat limit of liquid

It is important to note that Eq. (17) is valid in the steady state after the transient stage. The time lag t_l, which represents the duration of the transient state after the onset of nucleation may be written as (Feder et al., 1966)

$$t_l = (4\pi D_{nc} Z_f^2)^{-1} \qquad (18)$$

Now the remaining problem is how to determine the nucleation rate of critical clusters, J_{nc}, for the specific case of homogeneous nucleation. To estimate this value, one may use the nondimensional parameter (Feder et al., 1966) j from Eq. (17)

$$j = J_{nc}/ND_{nc}Z_f = \exp(-F_{nc}/k_B T) \qquad (19)$$

Lienhard and Karimi (1981) considered homogeneous nucleation corresponding to the spinodal line of the liquid. They assigned a value F_{nc}, which can be characterized as the potential energy (Tien and Lienhard, 1979), and expressed this value in terms of the critical temperature $F_{nc}/k_B T_c = 11.5$. At the superheat limit, the reduced temperature is around 0. 9 ; hence the above value becomes $F_{nc}/k_B T_c = 13.0$ or $j \cong 10^{-6}$. Now one can estimate the nucleation rate of the critical clusters. With a typical number density of $N = 10^{21}$ molecules/cm^3 and a value $D_{nc}Z_f = 10^7$/s, the nucleation rate at the superheat limit is approximately $j_{nc} = jND_{nc}Z_f = 10^{22}$ nuclei/cm^{3}s. In their work, Oxtoby and Evans (1988) also predicted the nucleation rate enhancement of 10 to 17 orders of magnitude over the classical prediction for bubble formation because the chemical potential difference between metastable state and the saturated state of liquid spinodal is smaller than that at the gas spinodal. The actual correct nucleation rate can be best found by comparing experimental results on the evaporation of a droplet at its superheat limit.

2.6 Calculation of the superheat limit

Since the pre-exponentional factor of Eq. (17) depends only on molecular properties such as ε_m, V_m and N, which are slowly varying functions of temperature, the number of molecules in the critical cluster, J_{nc}, can be determined from Eq. (17) with a specified value of the nucleation rate, Jnc, at given temperature. The van der Waals diameter of liquid molecules (Streitwieser and Heathcock, 1981) may be obtained from the liquid molar volume at a specified temperature (Kwak and Lee, 1991). With the value of n_c and the molecular properties known, the intrinsic tensile strength of liquid at given temperature is readily found from Eq. (12b). Now the superheat limit corresponding to the vapor pressure, P_v, is determined from the intersection between the pressure curve, Eq. (5) and the intrinsic tensile strength curve, Eq. (12b). In other words, the liquid under a tensile stress equal to its intrinsic tensile strength ruptures to evaporate spontaneously.

The nucleation rate, $J_{nc} = 10^{22}$ nuclei/cm^3-s (obtained from the observed evaporation speed of a butane droplet at the superheat limit), was assumed for other fluids for predicting the results from droplet explosion experiments. Our predictions for the superheat limit of hydrocarbons are shown in Table 2. In addition, the superheat limits calculated by the classical nucleation theory with a macroscopic surface tension are listed as well as the experimental results by various authors (Kenrick, Gilbert and Wismer, 1924; Blander, Hengstenberg and Katz, 1971; Eberhart, Kremsner and Blander, 1975, Porteus and Blander, 1975; Patric-Yeboch and Reid, 1981). The calculated superheat limits of various hydrocarbons using the molecular cluster model are shown to be in good agreement with the measurements by the droplet explosion technique, which verified that it is possible to predict the superheat limit of liquid as well as the evaporation phenomenon at this

Table 2 Superheat limits of hydrocarbons

Liquid	Molecular cluster model $K(T_s/T_c)$		Classical theory ($J=10^6$)	Experiment	References (authors' initial)
	$J_{nc}=1$	$J_{nc}=10^{22}$			
Ethane	261.5 (0.8563)	275 (0.9005)	269.5	269.2	PB
Propane	311.0 (0.8410)	329.5 (0.8910)	328.5	326.2	PB
Butane	358.5 (0.8431)	377.5 (0.8878)	378.4	376.9	PB
Pentane	396.0 (0.8433)	421.0 (0.8965)	421.5	421.0	BHK
Hexane	430.0 (0.8475)	456.5 (0.8997)	457.5	457.0	BHK
Heptane	460.0 (0.8515)	485.5 (0.8987)	487.7	486.7	EKB
Octane	485.0 (0.8527)	517.5 (0.9098)	515.9	513.0	EKB
Nonane	507.5 (0.8535)	536.0 (0.9014)	535.0	538.5	EKB
Decane	513.5 (0.8314)	557.5 (0.9027)	556.0	558.5	EKB
Isobutane	343.5 (0.8417)	363.0 (0.8895)	360.8	361.0	PB
2, 3-Dimethyl butane	419.5 (0.8392)	439.0 (0.8782)	449.1	446.4	EKB
Cyclopropane	338.0 (0.8497)	356.5 (0.8962)	-	350.7	PB
Cycropentane	432.5 (0.8454)	453.5 (0.8864)	446.4	456.7	EKB
Cyclohexane	468.0 (0.8457)	491.0 (0.8872)	489.5	492.8	EKB
Benzene	482.5 (0.8584)	507.0 (0.9020)	501.0	504.0	PR
1, 3-Dimethyl benzene	522.5 (0.8468)	550.5 (0.8922)	-	(508.4)	KGW

limit by avoiding the macroscopic capillarity approximation.

2.7 Evaporation phenomena of a droplet at the superheat limit

Shepherd and Sturtevant (1982) observed the evaporation of a butane droplet at its superheat limit. They also measured the evaporation rate, as well as the far field pressure signal emanating from the evaporating droplet. Their photographic study revealed that the evaporation process (nucleation) first started at an asymmetric point in the droplet. Thereafter, the evaporation continued step by step to spread, eventually covering the whole droplet. This is a remarkable conformation of the idea of L. Szilard (Farkas, 1927); the formation of a viable embryo is required to start the chain of evaporation. Indeed, such a chain reaction mechanism is in the context of the classical kinetic theory.

With a rather simple model we can predict the evaporation of a droplet at the superheat limit. Even though the nucleation center at first is found to be at an asymmetric position in the droplet, this problem may be treated symmetrically by assuming that the nucleation point at first coincides with the center of the droplet. Let R_d be the radius of the evaporated sphere in the droplet at time t. If the increment of the radius of the evaporated sphere is dR_d (assume $dR_d \ll R_d$) during , the total number of evaporated molecules in the volume $4\pi R_d^2 dR_d$ is $4\pi R_d^2 dR_d N$. Since the evaporation rate, that is, the number of molecules evaporated per unit time and unit volume (Frenkel, 1946), is $J_{nc} n_c$, then the total number of molecules evaporated during in a volume $4\pi R_d^2 \cdot 1\text{cm}$ becomes $(J_{nc} \cdot 1\text{cm})\, n_c\, 4\pi R_d^2\, dt = J_s n_c \cdot 4\pi R_d^2 dt$ where $J_s (= J_{nc} \cdot 1\text{cm})$ is the nucleation rate with unit depth. In the above equation, it is assumed that the surface area is covered with the critical nuclei. From this argument, one may obtain the velocity of the vapor sphere in the droplet for the one-dimensional evaporation case:

$$dR_d/dt = J_s n_c/N \tag{20}$$

With Eq. (7), the above equation can be written as

$$dR_d/dt = 1.3504\, V_m J_s n_c = v_l J_s n_c \tag{21}$$

Since J_{nc} is a constant during the steady-state nucleation process, the speed growth of the vapor sphere remains constant. This finding is consistent with Shepherd and Sturtevant's observation: "the growth rate of the vapor sphere appears to be linear with a mean velocity of approximately $1.43 \cdot 10^3$cm/s." Also McCann et al. (1989) obtained a similar value for a bubble growth in a droplet at the superheat limit. With this observed value of the dR_d/dt, Eq. (20) may be used to determine the nucleation rate of clusters at the superheat limit. Also, the superheat limit of the liquid can be predicted with the nucleation rate evaluated from Eq. (20). The nucleation rate that meets these conditions is about 10^{22} nuclei/cm^3-s for butane. The bubble growth in the initial stages may be restricted by the condensation and evaporation process (Skripov, 1974). The above equation is valid until the droplet is fully evaporated (about 40μs). After complete evaporation, the molecules become a vapor bubble. The subsequent nonlinear growth and collapse mechanism of the gas bubble are governed by the well-known Rayleigh equation (Rayleigh, 1917; Kwak et al., 1995). In Fig. 2, a fully evaporated cyclohexane droplet at its superheat limit and subsequent evolution of a bubble from the droplet (Park et al., 2003) are shown. The bubble oscillation can be visualized by the far field pressure signal from the evolving bubble as shown in Fig. 3. The pressure signal was measured by a pressure transducer at a 4mm distance from the bubble center.

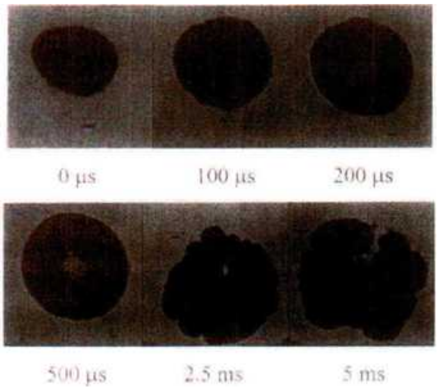


Fig. 2 Fully evaporated cyclohexane droplet at its superheat limit and snap shots of the evolving bubble from the droplet

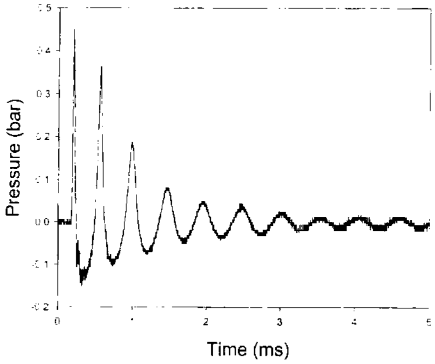


Fig. 3 Far field pressure signal from the evolving bubble

The absolute rate of evaporation, $\rho_m\sqrt{k_BT/2\pi m}$ (Schrage, 1953 ; liquid density rather than vapor density in this case), may be achieved for the case in which a cluster is constituted by one molecule. This absolute limit corresponds to molecular evaporation (Schrage, 1953). Certainly the rate of evaporation at the superheat limit is much less than the absolute rate of evaporation because of the exponential term in Eq. (17), which distinguishes activated molecules (ΔH_{vap}) and reduces the mean velocity of molecules in liquid (ΔH_f ; Faber, 1972). To estimate the life time of the droplet at the limit, Sinitsyn and Skripov (1968) defined the time scale of the event, t_s, as

$$t_s = (JV)^{-1} \tag{22}$$

For a 1-mm-dia droplet with nucleation rate value $J=10^6$ bubbles/cm^3-s, this time is on the order of microseconds (see Fig. 3), which is the time scale of the bubble oscillation after the complete evaporation (Shepherd and Sturtevant, 1982). Note that the nucleation theory itself, does not allow any arbitrary value for nucleation rate ; that is, if the nucleation rate is known the superheat limit can be determined and vice versa (Kwak and Lee, 1991). Simultaneous prediction of theses two quantities such as the superheat limit and the complete evaporation time of a droplet with a given nucleation rate is plausible. For pure liquids such as butane and pentane (Porteous and Blander, 1975), the deviation from the mean value of the measured superheat limit obtained by droplet explosion technique is less than 0.5℃. With such a narrow range of the superheat limit the complete evaporation time of a droplet can be reasonably defined.

The evaporated state where the molecular volume of what in the saturated liquid state is retained, is characterized by its very high pressure;

$$P_n = -(P_\infty - P_v)\, n_c^{1/3} = \frac{Z\varepsilon_m}{3} \Big/ V_m \tag{23}$$

For example, the value of P_n is about 138 bar for butane at its superheat limit. The equilibrium vapor pressure P_v may be achieved with the equilibrium vapor volume of v_g. Pressure discontinuity rather than the volume discontinuity occurs in the nonequilibrium transition from liquid to vapor. Therefore the classical nucleation theory which assumes that the formation of the critical size bubble whose pressure inside is the equilibrium vapor pressure cannot explain the transition of liquid to vapor in the nonequilibrium condition.

3. Example of Vapor Bubble Nucleation Phenomena

In the preceding sections, the evaporation process at the superheat limit and the vapor bubble formation under tension were formulated based on the interaction between molecules. In this section, typical examples for the bubble nucleation, which have not been understood properly yet, will be discussed by using the molecular cluster model.

3.1 Bubble formation on micro heaters

Device miniaturization evolved from IC-based micro-fabrication technology has brought forth rapidly importance of understanding fluid flow in micro channel and phase change in micro geometry. Especially bubble nucleation on micro heaters, which has been successfully utilized for bubble jet printers (Nielson, 1985), has many potential applications in bubble powered micro thermal machines (Lin and Pisano, 1994), which motivated the study on bubble nucleation on the micro heaters. Lin et al. (1998) have observed that a bubble forms on a micro line heater made of polysilicon as soon as the highest temperature in the heater reaches the critical temperature of fluorocarbons. Recently Avedisian et al. (1999) precisely measured the temperature of bubble nucleation on a metallic microheater when the voltage pulse was applied to the heater. The highest nucleation temperature measured was 560K for the metallic heater immersed in water. This finding is drastically different from our previous knowledge ; the wall superheat needed for boiling nucleation on a metal surface is only 30℃ or so, even for subcooled boiling (Judd and Hwang, 1976). The temperature for bubble nucleation on the cavity free micro heater may be obtained by utilizing the molecular cluster model.

If the liquid is in contact with a solid surface, the nucleation temperature with considering the effect of contact angle may be obtained by the following equation (Avedisian, 1998).

$$T=\frac{F_{nc}\Phi}{k_B}\bigg/\left[\ln\frac{CN^{-1/3}(\zeta/\Phi^{1/2})}{J_{sm}}\right] \qquad (24)$$

where C is the pre-exponential factor in Eq. (17), and surface area truncation, respectively of the bubble due to the contact angle (Van Stralen and Cole, 1979; and Avedisian, 1998).

$$\zeta=\frac{1}{2}(1+\cos\theta) \qquad (25)$$

$$\Phi=\frac{1}{4}(1+\cos\theta)^2(2-\cos\theta) \qquad (26)$$

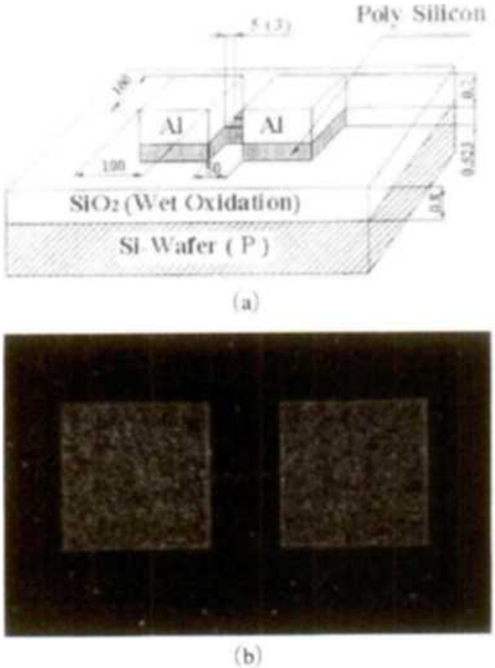
The surface nucleation rate may be obtained by using the following equation (Avedisian et al, 1999).

$$J_{sm}=\frac{1}{A_s}\left|\frac{d(F_n/k_BT)}{dT}\right|\dot{T} \qquad (27)$$

where $\dot{T}$ is the measured heating rate, which is about 5×10^7℃/s so that the nucleation rate for the micro line heater shown in Fig. 4 is about 10^{13}/cm^2-s.

The polysilicon heaters fabricated on the 0.8μm silicon dioxide layer with P-type prime wafer, have same length of 50±0.1μm and thickness of 0.523±0.004μm and two different widths of 3±0.1μm and 5±0.1μm. Two driving pads, which connect with the line heater electrically, have dimension of 100×100μm^2. The pads which were made by deposition of aluminium film with thickness of 0.7μm on the polysilicon as shown in Fig. 4. The heater works when a current is applied through the two driving pads that have much larger volume than that of the heater. The silicon substrate beneath the silicon dioxide layer acts as heat sinks. Applying energy conservation to the differential element in the heater one can obtain a heat diffusion equation for the heater (Lin et al., 1998). Solving the heat diffusion equation with appropriate initial and boundary conditions, one may obtain a theoretical current-resistance (I-R) characteristic for the heater.

Measured I-R characteristics curve up to the bubble nucleation point for the 3μm-width heater in FC-72 is shown in Fig. 5. The corresponding theoretical I-R curve, which is fitted closely to the measured one by adjusting the variables such as polysilicon resistivity ($\rho_0=2.9\times10^{-4}\,\Omega$-cm) and its temperature coefficient ($\zeta=0.75\times10^{-3}$/℃) is



(a)

(b)

Fig. 4 Schematic (a) and enlarged (b) view of micro line heater (unit; μm)

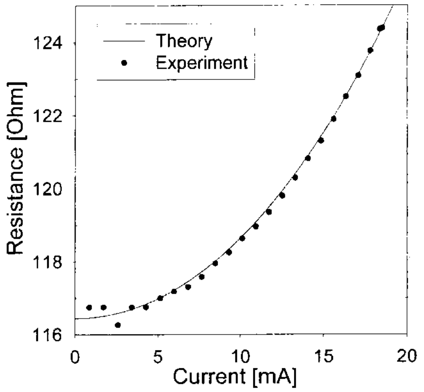


Fig. 5 Calculated (—) and experimental (•) I-R characteristics for the polysilicon heater of 50×3×0.523μm^3 in FC-72. The theoretical characteristics was obtained with $\rho_o=5.90\times10^{-4}\,\Omega$-cm and $\xi=0.75\times10^{-3}$/℃

also shown in Fig. 5. Hardly one can obtain such closely fitted curves by adjusting the variables related to the heat transfer mechanism. With these adjusted values of ρ_0 and ξ, one can obtain the accurate nucleation temperature (Lee et al., 2003), which is shown in Fig. 6. DC voltage to the heater was increased in 0.01V~0.1V increment to obtain the I-R (current-resistance) characteristic curves for the heaters, from which the temperature for bubble nucleation can be deduced. The measured nucleation temperature along with the superheat limit calculated by the molecular cluster model (Kwak and Panton, 1985) and the thermodynamic limit estimated by the Berthelot equation of state (Eberhart and Schnyders, 1973) are given in Table 3. Quite different nucleation temperatures for the different width heaters were obtained. Apparently heterogeneous nucleation takes place on the 5μm-width heater. With the temperature dependent nucleation rate of $10^{11}-10^{13}$/cm^2-s, the nucleation temperatures as function of the contact angle, are obtained by Eq. (24) and shown in Fig. 7. With a contact angle of 110°, which was supposed to be reasonable for such well wetted liquids, the nucleation temperature turns out to be good agreement with the measured values with 5μm-width heater as shown in Table 3.

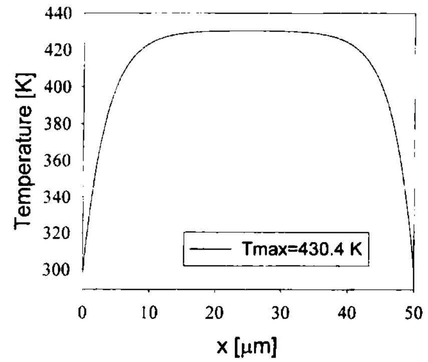


Fig. 6 Steady state temperature distribution along the 3μm-width line heater at the current of 13.45mA at which bubble nucleation occurs

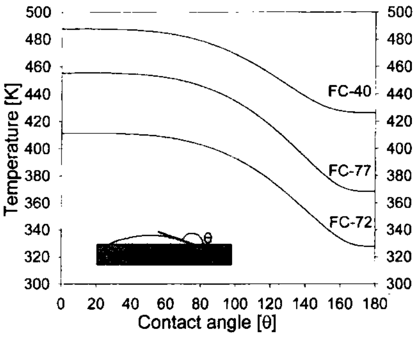


Fig. 7 Predicted nucleation temperature with contact angle for FC-72, FC-77 and FC-40 with the nucleation rate values of 10^{13}, 10^{12} and 10^{11}/cm^{2}s respectively

Table 3 Measured nucleation temperature depending on heater width in various fluorinerts and the liquid superheat limits estimated by theoretically (The superheat limit for FC-40 was calculated with a nucleation rate of 10^{21}/cm^{3}s).

Liquids	Heater width (μm)	Measured Nucleation Temperature (K)	Superheat Limit (K)	Adjusted resistivity** ρ_o(Ω-cm)/ and temperature coefficient, ξ(/℃)
FC-72	3	430.4	421.0 (414.6*)	$5.90\times10^{-4}/0.75\times10^{-3}$
	5	389.7		$6.90\times10^{-4}/0.80\times10^{-3}$
FC-77	3	467.8	473.2 (458.7*)	$5.90\times10^{-4}/0.78\times10^{-3}$
	5	424.5		$6.11\times10^{-4}/0.79\times10^{-3}$
FC-40	3	515.7	515.8 (499.2*)	$5.91\times10^{-4}/0.80\times10^{-3}$
	5	464.2		$6.09\times10^{-4}/0.84\times10^{-3}$

* Calculated from the Berthelot equation of state.

* * Listed values of resistivity and temperature coefficient for polysilicon are 7.5-$10^{-4}\Omega$-cm and 1.2×10^{-3}/℃ respectively (Lin and Pisano, 1991).

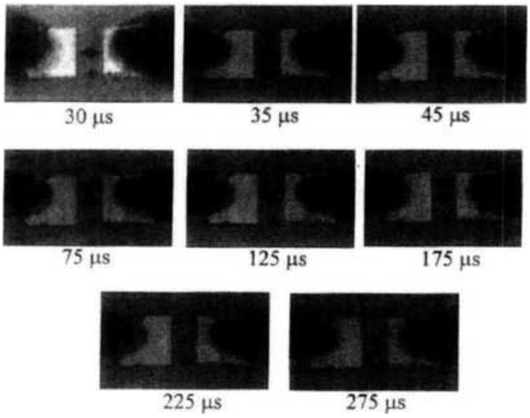


Fig. 8 Bubble growth on a micro line heater when a voltage of 3V with 100μs is applied

As has been observed in the previous study by Lin et al (1998), the liquid around the heater turns out to be white before the bubble nucleation occurs. This may be due to the evaporation of liquid adjacent to the heater. A series of bubble nucleation, growth and subsequent collapse on a 5μm-width heater in FC-72 are shown in Fig. 8. The duration of voltage (3V) applied to the heater was about 100μs. Clearly the first frame shows the evaporation layer of liquid above the heater. When a spherical bubble formed from the spheoridal shape of the superheated liquid layer, the dimension shrinks as shown in the second frame of Fig. 8. These pictures were taken by microscope-CCD camera with a μs flash unit (Jung et al., 2003).

3.2 Vapor bubble formation via quantum tunneling

As the temperature approaches absolute zero, the value of the exponential term in Eq. (17) becomes infinite, indicating that the formation of nuclei due to the thermal fluctuations is impossible. Close to the absolute zero temperature, the phase transition from liquid to vapor may be realized only as result of quantum fluctuations (Lifshitz and Kagan, 1972). Instead of the nucleation kinetics which involves the growth of cluster by monomer addition, one may consider the kinetics associated with the quantum tunneling (Chudnovsky, 1992) of the virtual nuclei near the absolute zero. Now assume that a cluster of an aggregate of activated molecules has kinetic (vibrational) energy state under the potential barrier with tension of $\tau = P_\infty - P_v$. Then the total energy of the metastable may be written as

$$E_n = \frac{1}{2} m r_m^2 \dot{x}^2 n^{5/3} - F_n \tag{28}$$

where $\dot{x}$ has unit of 1/s. In the above equation, the second term represents, as is assumed, the vibrational energy analogous to the phonon energy in the semiclassical oscillator system under the reversed potential of F_n given in Eq. (11). Figure 9 shows the energy barrier for several cases of different negative pressures at given temperature in helium-4. Certainly, as shown in Fig. 9, the energy barrier is higher at lower negative pressure so that bubble nucleation hardly occurs at the lower negative pressure condition, which can be achived by a focusing ultrasonic wave (Marston, 1976; Xiong and Maris, 1991).

Assuming that the vibrational energy of the cluster can have smaller value than the potential barrier, the tunneling frequency through the barrier may be obtained from the following equation with $E_n = (\alpha_r - 1) F_n$ where α_r is less than unity (Kwak et al., 2001).

$$\begin{aligned}\omega &= \sqrt{\alpha_r} \cdot 2\pi \left(\frac{Z\varepsilon_m}{m r_m^2} \right)^{1/2} \Big/ \int_0^{x_1} x^{3/2} dx \Big/ \sqrt{1 - \frac{2|\Delta\mu|}{Z\varepsilon_m} x} \\ &= \sqrt{\alpha_r} \frac{2^{7/2}}{3^2} \frac{\sqrt{F_{n_c}}}{\sqrt{m r_m^2 / 2}} \Big/ n_c^{5/6}\end{aligned} \tag{29}$$

where F_{n_c} is the maximum potential barrier for

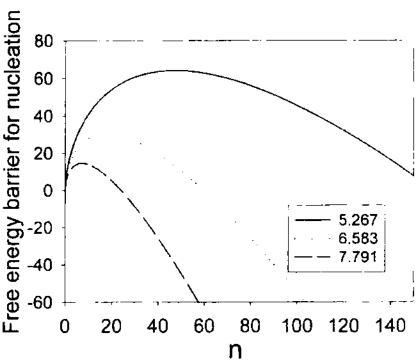


Fig. 9 Energy barrier depending on negative pressure for helium-4 at 0.5K

nucleation, which is given by $F_{n_c}=Z\varepsilon_m n_c^{2/3}/6$. Equation (29) gives the magnitude of the vibrational energy of the activated molecules in the cluster. That is

$$\varepsilon_{vib}=\frac{1}{2}\,m{r_m}^2\omega^2=\alpha_r\cdot\frac{2^7F_{n_c}}{3^4}\Big/n_c^{\frac{5}{3}} \qquad (30)$$

The intervals for the integral given in Eq. (29) are $x=0$ and $x=x_1=Z\varepsilon_m/2\,|\Delta\mu|$. If the vibration energy satisfies the quantization condition or $\varepsilon_{vib}=l\hbar\omega$ where l is integer, the frequency turns out to be just multiples of the single particle quantum vibration, or $\omega=l\hbar(m{r_m}^2/2)$. The estimated tunneling frequency which is about 10^{11}/s at the ideal tensile strength for helium-4 is quite larger than the number of particles striking the surface of the cluster in the nucleation kinetics given in Eq. (17). With help of the vibrational energy given in Eq. (30), the total energy of the molecules in a critical cluster is given by

$$E_{n_c}=\left[-1+\alpha_r\cdot\frac{2^7}{3^4}\Big/n_c^{5/3}\right]F_{n_c} \qquad (31)$$

With the value of $\alpha_r=0.1$, the vibrational energy is about 5% of the total energy of the cluster. If the kinetic and potential energy are always equal (Maris, 1995), the value of α_r is just $3^4\cdot n_c^{5/3}/2^7$. However the WKB approximation is no longer good with this assumption. For a particle with kinetic energy of $m{r_m}^2\dot{x}^2/2$, encountering a potential barrier F_n, the tunneling probability in the WKB approximation is proportional to the factor exp(-B) provided that the kinetic energy of the particle is much smaller than that of the potential energy where

$$B\cong\frac{2}{\hbar}\int_0^{x_1}\sqrt{2mF_n}\,dx \qquad (32)$$

With the tunneling frequency given in Eq. (29), the formation rate of the nuclei in a unit volume per unit time is given by the expression

$$J_{QUM}=N\omega(F_{n_c})\exp[-B] \qquad (33)$$

where

$$\begin{aligned}B&=\frac{3^4\cdot5\sqrt{2}\,\pi}{2^9}\,\frac{\sqrt{\varepsilon_{Vib}F_{n_c}}}{\hbar\omega}\,n_c^{5/6}\\&=\frac{{\alpha_r}^{1/2}\cdot3^2\cdot5\sqrt{2}\,\pi}{2^{11/2}}\,\frac{F_{n_c}}{\hbar\omega}\end{aligned} \qquad (34)$$

One may obtain the equivalent quantum "temperature" defining the scale of the quantum fluctuations, by comparing the terms in the exponentials in Eqs. (17) and (33). This is given by approximately

$$T_{QUM}=\frac{2^{11/2}}{\sqrt{\alpha_r}\cdot3^2\cdot5\sqrt{2}\,\pi}\,\frac{\hbar\omega}{k_B} \qquad (35)$$

More exact value of T_{QUM} can be obtained with $J_{nc}=J_{QUM}$. As can be seen in Eq. (34) or Eq. (35), the thermal fluctuation represented by k_BT can be replaced by or k_BT_{QUM}, the quantum fluctuation temperature for the nucleation of bubbles in liquid helium. The estimated quantum temperature with $\alpha_r=0.1$ is about 0.25 K for helium-4 and 0.175 K for helium-3 so that the nucleation of bubble below this temperature occurs only by the quantum tunneling. The density data at the negative pressure, which is required to estimate the molecular volume of liquid and the chemical potential difference in

$$\Delta\mu=\int V_m dP=0.7405m\int\frac{dP}{\rho_m} \qquad (36)$$

may be obtained from the sound velocity data at a positive pressure. In fact one can obtain the equation of states for helium under negative pressure by extrapolating the sound velocity data at positive pressure into negative region (Maris and Xiong, 1989). Relations between density and pressure were obtained from the sound velocity data measured by Abraham et al. (1970) for helium-4. Estimated nucleation rates depending on the tensile strengths at temperatures of 0.25K, 0.30K, 0.6K and 1.0K are shown in Fig. 10 for helium-4. Therefore one can conclude that the liquid-vapor transition occurs through the thermal motion decisively above 1.0K in helium-4. On the other hand, the nucleation barrier is rarely overcome by thermal fluctuations near the absolute zero temperature so that quantum nucleation prevails. Calculation results suggest that the liquid-vapor transition occurs only due to quantum fluctuation below 0.25K in liquid helium-4. Above 0.25K, thermal fluctuation may lead the bubble nucleation process at the negative pressure concerned so that one can consider the cross-over temperature for liquid helium-4 as 0.25K. Bubble

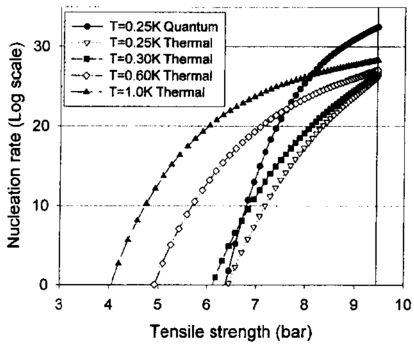


Fig. 10 Tensile strength of helium-4 depending on temperature

nucleation in liquid helium near the absolute zero temperature is a typical example of a macroscopic phenomenon due to quantum tunneling.

4. Conclusions

The molecular cluster model of bubble nucleation, which can predict the tensile strength, and the superheat limit of liquids may be applied to the bubble formation on a cavity free surface (Oh et al, 1999) and the bubble nucleation by quantum tunneling of activated molecules in liquid helium-4. Calculated temperature of bubble nucleation on micro heaters as well as the tensile strength for bubble nucleation in liquid helium near the absolute zero is in good agreement with observed results. The molecular cluster model presented for the vapor bubble can be applied to the laser-induced cavitation (Byun and Kwak, 2004) which has become particularly important in the field of laser-mediated surgery (Vogel et al., 1990). Molecular dynamic simulation (Rao et al., 1978 ; Park et al., 2000) and Monte-Carlo simulation (Punnathanman and Corti, 2002) which tracks the growth and decay process of a nucleus have not yet been applied to predict the tensile strength or the superheat limits of liquids for bubble nucleation. Classical theory of bubble nucleation with capillary approximation may not be applicable to a nanometer size cluster whose interface is not well defined. In conclusion, the bubble nucleation is an inherently microscopic process so that the macroscopic argument is improper.

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