

The absolute metastable limit of liquids under tension-A review[†]

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Abstract

A quest for obtaining the absolute metastable limit of liquids has been attempted by many researchers using various methods. The absolute limit obtained was the case having the maximum nucleation rate with one molecule critical cluster from a nucleation theory based on molecular interactions. In this study, the tensile strengths measured by various techniques were compared to the theoretical absolute metastable limit. The tensile strength of water, measured in microscopic inclusions, is close to the absolute metastable limit of 160 MPa while the tensile strength values measured by the centrifugal and acoustic methods is only about 15% of the absolute metastable limit. It has been found that the tensile strength values depend on the experimental conditions which determine the nucleation rate values. Problems related to predicting the absolute metastable limit by the classical bubble nucleation theory were also discussed.

Keywords: Absolute metastable limit; Bubble nucleation; Superheat limit of liquids; Tensile strength of liquids

1. Introduction

Liquids can be stretched under tension. The maximum metastable limit of negative pressure at which the breakdown occurs due to bubble formation or evaporation is called the tensile strength of liquid. A quest to obtain the absolute metastable limit of liquids has been attempted by many researchers using various techniques. An ingenious experiment to measure the tensile strength of liquid by the centrifugal method in a rotating capillary tube was done by Briggs [1]. The maximum tensile strength value obtained by Briggs for water at 7°C is about 28.0 MPa. A maximum tensile strength value of water at 8.3°C, which was obtained by an improved Berthlot tube technique [2], is about 2.03 MPa [3]. The tensile strength values measured recently by an acoustical method [4], whose values vary from 26.40 MPa at 0.1°C to 16.50 MPa at 80°C, are close to the values obtained by Briggs [1]. However, the measured stability limit of liquid water in a vapor-coupled void formed in a hydrogel membrane [5] at 21.4°C is about 22.09 MPa, which is quite lower than the value measured by Briggs [1] and Herbert et al. [4]. A maximum tension of 140.03 MPa for water at 42°C was obtained in microscopic inclusions [6], in which very high tension can be generated [7] by the Berthlot tube principle [2]. On the other hand, an anomalously low value of the tensile strength of water was ob-

tained through dynamic stressing experiments [8]. For example, Couzens and Trevena [9] obtained a value of 1.50 MPa for degassed and deionized water by the bullet-piston technique.

The thermodynamic viewpoint of tensile strength shows that it is immaterial whether the pressure at the maximum metastable state is positive or negative. By avoiding boiling, Briggs [10] was able to reach a maximum temperature of 270°C before a vapor bubble formed homogeneously in water at 1 atm. The same metastable state could also result from an isothermal decompression from the saturate state of water at 270°C and at 5.50 MPa to 0.1 MPa. Hence, the tensile strength of water at 270°C may be defined as 5.40 MPa. Consequently, the tensile strength at a given temperature may be defined as

$$-\tau = P_{\infty}(T) - P_f, \quad (1)$$

where P_f is the final ambient pressure, and P_{∞} is the vapor pressure for a given temperature.

In this study, the absolute metastable limits of liquid were obtained from a nucleation theory based on molecular interactions [11] for vapor bubble formation. The measured values of the tensile strength of liquid found in rotating capillary tubes [1], by the acoustic method [4] and in microscopic inclusions [6] were compared to the theoretical absolute metastable limit.

2. Classical theory of bubble nucleation

The classical theory of bubble nucleation is a mixture of

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macroscopic and molecular concepts. For the bubble formation, the classical theory initially assumes the formation of the critical size bubble in the mechanical equilibrium condition. Given the macroscopic interfacial tension, the condition for the formation of the critical size bubble is given by

$$P^* - P_f = 2\sigma/R_c. \quad (2)$$

The equilibrium pressure of the bubble P^* is related to the vapor pressure P_∞ corresponding to the liquid temperature T at a given ambient pressure P_f [12]. That is,

$$P^* = P_\infty \exp\left[-\frac{v_1(P_\infty - P_f)}{k_B T}\right]. \quad (3)$$

The maximum energy needed to form the critical size bubble, which can be obtained from a thermodynamic argument [13], is given by

$$F_{R_c} = \frac{4}{3}\pi R_c^2 \sigma = \frac{16\pi}{3} \frac{\sigma^3}{(P^* - P_f)^2}. \quad (4)$$

The above expression, Eq. (4), originally proposed by Gibbs, has been used previously for a variety of purposes [14]. However, it is doubtful whether Eq. (2) is pertinent when R_c approaches a molecular dimension [15]. The classical theory of nucleation kinetics, ascribed to Doering [16], Volmer and Weber [17], and Zeldovich [18], supplies unimolecular steady state processes of nucleation for the critical bubble. For the limiting cases in which near-critical-sized bubbles are in mechanical equilibrium with the bulk, the nucleation rate can be calculated from the kinetic theory argument with an ideal behavior assumption for the gas inside the critical bubble. A detailed derivation is given in Debendetti [19], which is given by

$$J = N \left(\frac{\sigma}{\pi m B}\right)^{1/2} \exp\left[-\frac{16\pi\sigma^3}{3k_B T (P^* - P_f)^2}\right] \quad (5)$$

where B is a constant whose value is $2/3$ for the bubble formation.

3. Vapor bubble nucleation theory based on molecular interactions

In the metastable state under tension, one can imagine the formation of clusters or aggregates of activated liquid molecules. When a single molecule is surrounded by Z nearest neighboring molecules ($Z=12$ for the FCC structure), the molecule may be separated from the group by applying energy [20], $W=Z\varepsilon_m$. Then, the energy required to cut across a composition of n molecules from the surrounding liquid is given by

$$W_n = \frac{1}{2} Z \varepsilon_m n^{2/3}. \quad (6)$$

With this surface energy and the chemical potential difference between saturated and metastable liquid molecules acting as the driving force for the clustering of activated molecules, Kwak and Panton [11] obtained the stability condition for the critical cluster and the corresponding free energy for bubble nucleation. These are

$$(P_\infty - P_f)n_c^{1/3} = \frac{Z}{3} \varepsilon_m / v_m \quad (7)$$

$$F_{n_c} = \frac{Z \varepsilon_m}{6} n_c^{2/3}. \quad (8)$$

In Eq. (7), n_c is the number of vapor molecules inside the critical cluster, and ε_m is the energy required to separate a pair of liquid molecules from the given liquid state to the critical state. This is approximately given by [11]

$$\varepsilon_m = 4\varepsilon_o \left[1 - \left(\frac{\rho_c}{\rho_m}\right)^2\right] \left[\left(\frac{d_w}{d_m}\right)^6 - \left(\frac{d_w}{d_m}\right)^{12}\right]. \quad (9)$$

The average distance between molecules d_m in Eq. (9) and the effective molecular volume v_1 can be found from the number density of the liquid, N . The relation is

$$\pi d_m^3 N / 6 = v_m N = 0.7405 \quad (10)$$

where 0.7405 is the packing fraction of the FCC lattice structure. The parameter ε_o in Eq. (9) is the potential corresponding to the London dispersion interaction. This term is given by [21]

$$\varepsilon_o = \frac{3 E_1 \alpha^2}{16 d_w^6}. \quad (11)$$

The growth of a cluster depends on the kinetic events within the liquid medium. The kinetic theory for the cluster formation may be explained by Frenkel's pre-transition theory [22]: a cluster of different sizes may be treated as a molecule of a different kind. If we assume that the growth is a quasi-stationary phenomenon caused by the monomer addition of activated molecules, then the nucleation rate J_{nc} of the critical cluster per unit volume may be written as [22]

$$J_{nc} = Z_f D_n N \exp\left[-\frac{Z \varepsilon_m}{6 k_B T} n_c^{2/3}\right]. \quad (12)$$

Here, N is the number density of dissolved molecules in the solution, and Z_f is the Zeldovich non-equilibrium factor [23], which is given by

$$Z_f = \left[-\frac{1}{2\pi k_B T} \left(\frac{\partial^2 F_n}{\partial n^2}\right)\right]_{n=n_c}^{1/2}. \quad (13)$$

Estimates for D_n are obtained from the kinetic theory formulae relating the flux to the mean velocity \bar{v} , the number

Table 1. Absolute instability limits calculated and the measured values of the tensile strength for various organic liquids at 20°C.

Liquid	Density (g/cm ³)	Absolute tensile strength (MPa)	Corresponding nucleation rate value (/m ³ s)	Measured tensile strength (MPa)
CCl ₄	1.5205	48.09	8.9x10 ³¹	29.00 (60.3%)
Chloroform	1.4100	50.88	3.5x10 ³⁰	27.22 (53.5%)
Acetic acid	0.9960	53.33	3.0x10 ²⁸	28.80 (54.0%)
Benzene	0.8398	48.34	3.9x10 ³⁰	15.00 (31.0%)
Aniline	0.9969	54.22	6.4x10 ²⁶	28.00 (51.6%)

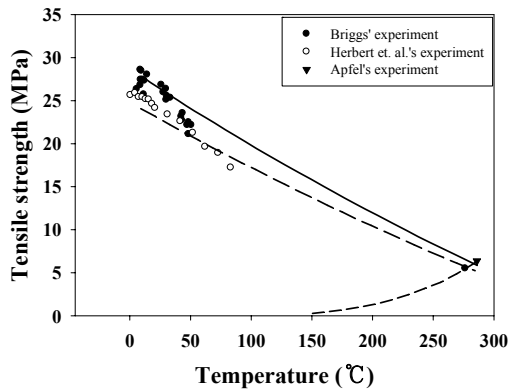


Fig. 1. Tensile strength of water as a function of temperature up to the superheat limit with nucleation rate values of $J_{nc}=1 / \text{cm}^3\text{s}$ (dashed line), $J_{nc}=10^6 / \text{cm}^3\text{s}$ (solid line) and vapor pressure line (dot-dash line). Briggs' experiment at 270°C is a result of decompression experiment.

density \bar{n} of activated molecules, and the cluster area of A_n ; $D_n = \beta v n A_n / 4$. In these formulae, β is the accommodation coefficient. To distinguish the activated molecules, we choose the energy level ΔH_{vap} corresponding to the enthalpy of evaporation. Thus, the number of activated molecules is

$$\bar{n} = N \exp(-\Delta H_{vap} / RT). \tag{14}$$

Furthermore, the effective mean velocity of molecules in a liquid [24] is

$$\bar{v} = (8k_B T / \pi m)^{1/2} \exp(-\Delta H_f / RT_f). \tag{15}$$

Hence, ΔH_f is the enthalpy of fusion, and T_f is the melting temperature. Combining these results gives

$$Z_f D_n = \frac{N}{\sqrt{6\pi}} \left(\frac{k_B T}{2\pi m} \right)^{1/2} 4\pi \left(\frac{3v_m}{4\pi} \right)^{2/3} \beta \exp \left[-\frac{\Delta H_{vap}}{RT} - \frac{\Delta H_f}{RT_f} \right]. \tag{16}$$

The nucleation theory presented in this section predicts the superheat limit of liquids [25], as well as the evaporation process at the superheat [25, 26] at which bubble formation does not occur as predicted by the classical nucleation theory. Furthermore, the theory correctly predicts the temperature at

which bubble nucleation occurs on the micro-heater used in an ink-jet printer and the normal boiling point of liquid at the flat interface [27].

4. Calculation results and discussion

In Table 1, the absolute instability conditions for the vapor nucleus, calculated from Eq. (7) with $n_c=1$, along with the experimental values by Briggs [28] are given. Except for benzene, the observed tensile strengths by Briggs are about 50–60% of the maximum metastable limits. In this calculation, the density decrease in the negative pressure was taken into account. The isothermal compressibility data by ultracentrifugation [29] were used to estimate the density in the negative pressure region for organic solutions.

Fig. 1 shows the theoretical tensile strength curve of water as a function of temperature with a nucleation rate value of $J_{nc}=1$ and $J_{nc}=10^6 / \text{cm}^3\text{s}$ along with the observed values by Briggs [1,10], Herbert et al., [4] and Apfel [30]. Among these, there is very good agreement with the experiment, including the prediction of the superheat limit at 279.5°C [30]. The measured values of the tensile strength of water in rotating capillary tubes are in the range of the calculated theoretical values of $J_{nc}=1$ and $J_{nc}=10^6$ up to 45°C. Also, the experimental results executed remarkably by the acoustic technique [4] fall in the same range of the theoretical values up to 50°C. However, a rapid drop in the tensile strength near 0°C that appeared in the rotating capillary tube experiment [1] was not observed in the acoustic method. Such good agreement between theory and observation for the tensile strength of water indicates that homogenous bubble nucleation in a pool of liquid occurs at the nucleation rate values considerably less than at the absolute metastable limit. This observation indicates that homogeneous bubble nucleation is possible even at 10–17% of the maximum metastable limit in a pool of water. On the other hand, the predicted tensile strength of water by the classical nucleation theory is over 150.0 MPa at 20°C, which is much higher than the observed value by either the centrifugal method [1] or the acoustical method. [4]. The superheat limit in Fig. 1 is determined from the intersection between the vapor pressure curve, $P_\infty - P_f$, and the tensile strength curve obtained from Eqs. (1) and (7).

$$-\tau = P_\infty - P_f = \left(\frac{Z \epsilon_m}{3v_m} \right) / n_c^{1/3} \tag{17}$$

In Table 2, the estimated superheat limit for various organic solutions by the nucleation theory [11] with a nucleation rate value of $J_{nc}=10^{22}$ nuclei/cm³s, and the absolute metastable limit and the measured tensile strength, estimated by $P_\infty(T_s) - P_f$, where T_s is the superheat limit, are also given. The values of the measured tensile strengths are approximately 17% of the absolute metastable limit.

One of the parameters that characterize the nucleation events is time lag, which is defined as the time required to

Table 2. Absolute instability limits and the measured tensile strength at the superheat limit for various organic liquids.

Liquid	Calculated superheat limit, T_s (K) with $J_{nc}=10^{22}/\text{cm}^3\text{s}$	Density (g/cm^3) at the superheat limit	Absolute metastable limit (MPa) by Eq. (7) with $n_c=1$	Measured tensile strength (MPa) $P_{\infty}-P_f$
Propane	329.0	0.4379	10.63	1.84 (17.3%)
Butane	378.0	0.4613	9.00	1.61 (17.9%)
Pentane	421.0	0.4625	6.81	1.45 (21.3%)
Hexane	457.0	0.4693	5.78	1.30 (22.5%)
Heptane	487.0	0.4719	4.77	0.81 (17.0%)
Benzene	504.5	0.6050	10.45	2.23 (21.3%)
Cyclohexane	493.0	0.5454	9.85	1.73 (17.6%)

reach the steady state nucleation rate. The time lag may be given by [23]

$$t_l = \left(\frac{1}{4\pi D_n Z_f^2} \right). \quad (18)$$

The time lag for the bubble nucleation in a pool of water for the cases shown in Fig. 1 is about a fraction of a second. On the other hand, the calculated time lag with a nucleation rate value of $J_{nc}=10^{22}$ clusters/ cm^3s for the butane droplet evaporated at its superheat limit is about 16 μs , and the calculated evaporation time of a 1-mm-diameter butane droplet is about 40 μs [25], which are close to the observed values [26]. Certainly, the classical theory, which assumes the formation of the critical size bubble, cannot explain the evaporation process at the superheat limit of liquid.

In Table 3, the absolute metastable limits of water with a stretched density in the temperature range between 0°C and 100°C are shown. The density of stretched water under negative pressure was estimated using the following equation [31], which is formulated from the equation of state for water by Chen, Fine, and Millero [32] in the ranges 0–100°C and 0–100 Mpa:

$$\rho = \rho_s \left[1 + \sqrt{(1-P/P_s)/B_s} \right]. \quad (19)$$

In the above equation, the fitted parameters, ρ_s , P_s and B_s for the stretched water are taken from Speedy [31]. As can be seen from Table 3, the absolute metastable limit found by Eq. (3) with $n_c=1$ is lower than the pressure at the spinodal point by Speedy and by the HGK equation of water [33]. As can be seen in Table 3, the maximum metastable limits estimated with the density data of a stretched liquid under negative pressure are certainly less than those obtained with the density data of a static liquid. As shown in Fig. 2, the calculated maximum metastable limits at various temperatures for water are close to the spinodal points calculated by the HGK equation of state for water. On the other hand, the calculated

Table 3. Calculated absolute metastable limits and the corresponding nucleation rate values for water at various temperatures.

Temperature (°C)	Density (g/cm^3)	Absolute tensile strength (MPa)		Nucleation rate J_{nc} ($/\text{cm}^3\text{s}$)
		With density data under negative pressure	With density data of static water	
0	0.8779	158.69	226.60	3.7×10^{23}
10	0.8884	164.16	226.60	9.9×10^{23}
20	0.8927	166.44	225.42	2.4×10^{24}
30	0.8977	166.97	224.25	5.7×10^{24}
40	0.8923	166.22	221.93	1.2×10^{25}
50	0.8890	164.50	219.64	2.6×10^{25}
60	0.8844	162.09	216.82	5.3×10^{25}
70	0.8786	159.04	213.46	1.0×10^{26}
80	0.8713	155.32	210.18	1.9×10^{26}
90	0.8630	151.06	206.41	3.5×10^{26}
100	0.8535	146.31	202.18	6.2×10^{26}

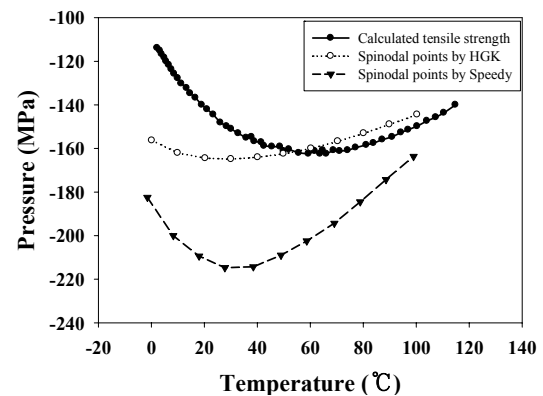


Fig. 2. Calculated absolute metastable limit for water with stretched density (full circle) depending on the temperature, the spinodal by the HGK equation of state for water (empty circle) and the spinodal by Speedy (triangle).

maximum metastable limits with a static density show the lowest tensile strength values, as shown in Fig. 2.

The nucleation rate at this particular process may be estimated by the following equation:

$$N_{\text{nucl}} = J_{nc} n_{cv} V_{\text{nucl}} t_{\text{nucl}} \quad (20)$$

where V_{nucl} is the volume of nucleation, and t_{nucl} is the duration of the nucleation process. The number of molecules involved in the nucleation process, N_{nucl} , can be estimated by the ideal gas law or $PV_{\text{nucl}} = N_{\text{nucl}} k_B T$. For the vapor bubble nucleation of water in the micro-inclusions under tension, the radius of the nucleated volume [6] was found to be about 0.4 μm so that $V_{\text{nucl}} = 0.033 \mu\text{m}^3$. Since the number of molecules involved in the nucleation process is about 10^6 and the nucleation duration is ms so that the nucleation rate is about $10^{24}/\text{cm}^3\text{s}$, which is close to the nucleation rate at the maximum metastable limit of $10^{25}/\text{cm}^3\text{s}$ for water at 40°C, as shown in Table 2. With a tensile strength of 140.03 MPa

rather than the absolute metastable limit of 166.22 MPa for water at 40°C, the nucleation rate reduces to $10^{24}/\text{cm}^3\text{s}$. The absolute rate of evaporation, $\rho\sqrt{k_B T/2\pi m}$ [34], may be achieved for the case in which a cluster is constituted by one molecule, the absolute metastable limit.

The nucleation rate value estimated by Eq. (5) at the tensile strength limit of 140.03 MPa is about 10^6 bubbles/ cm^3s . At this condition, the radius of the critical bubble estimated from Eq. (2) is about 1nm. It is also noted that the number of molecules inside the critical size bubble having a volume of 4.2 nm^3 is about 50, so that such a nano bubble is hardly defined. Certainly, the concept of interface cannot be defined in this dimension. Furthermore, with this nucleation rate value, the waiting time calculated by a relation, $J_{nc} V_{nuc} t_{nuc} = 1$ [35], is about $3 \times 10^7 \text{ s}$ ($\cong 1 \text{ yr}$) for the nucleated of $0.4 \mu\text{m}$ diameter in a micro-inclusion. This calculated result for the waiting time for nucleation is too long.

Except for the vapor nucleation in micro-inclusions, the absolute metastable limit can hardly be achieved. In fact, the tensile strength achieved at the superheat limit of liquid by the droplet explosion technique [13, 35] is about 17% of the absolute metastable limit. The tensile strength experiment in micro-inclusions and the test of the superheat limit by the droplet explosion technique suggest that the observed tensile strength for bubble formation may depend on the experimental condition, which determines the nucleation rate. It should be noted that the nucleation theory itself should predict the condition at which nucleation occurs, as well as the nucleation rate, which is related to the intensity of the process. In fact, the nucleation theory itself does not allow an arbitrary value for the nucleation rate. Of course, the nucleate rate is determined by the nucleation process itself. Various gaseous and vaporous bubble nucleation occurred at different conditions are discussed in detail by Kwak [36].

5. Negative pressure obtained from radial distribution function

The absolute metastable limit of liquid may be obtained from the solution of the integral equation for the radial distribution function. Kirkwood et al. [37] obtained the equation of state and thermodynamic functions over a wide range of temperature and density by solving numerically the integral equation for the radial distribution of spherical molecules interacting with the Lennard-Jones potential. The reduced critical properties determined from their study are given as

$$v_c^* = (v_c/N_A)/a^3 = 2.585 \quad (21)$$

$$p_c^* = p_c(a^3/\varepsilon) = 0.199 \quad (22)$$

$$T_c^* = T_c/(\varepsilon/k_B) = 1.433 \quad (23)$$

With the critical temperature and pressure values of water, one may obtain the force constant (ε/k_B) and the characteristic volume a^3 for water, which are 451.7 K and $56.2 \times 10^{-24} \text{ cm}^3$, respectively. With these values and the value of p^*v^*/T^* at $T^* = 0.833$, one may obtain the absolute limit of negative pressure, 214.0 MPa at $T = 103.2 \text{ }^\circ\text{C}$, which is close to the value of the maximum metastable limit at 100°C for water with the normal density data as shown in Table 3. It is noted that the absolute metastable limit, which can be obtained from Eq. (7) with $n_c = 1$, was also obtained using a thermodynamic stability analysis [38].

6. Conclusion

The tensile strength values obtained by various technique were compared to the classical theory of bubble nucleation and a nucleation theory based on molecular interactions. It has been found that the nucleation rate value at which bubble nucleation occurs depends crucially on the experimental methods in which different nucleation rate values should be applied. Dynamic stretching method yielded the lowest value of the tensile strength of water. Homogeneous bubble nucleation in a rotating capillary tube and in liquid under negative pressure generated by an acoustic pulse can be predicted with the nucleation rate of $1 \sim 10^6$ bubbles/ cm^3s . The superheat limit of liquids and the evaporation process at this limit can also be predicted with a nucleation rate value of 10^{22} clusters/ cm^3s by the nucleation theory, based on the molecular interaction. On the other hand, for bubble nucleation in the micro-inclusion under tension, the nucleation rate value is estimated to be about 10^{24} clusters/ cm^3s . Nucleation in a micro-system with a static environment yields a tensile strength value close to the absolute metastable limit at which nucleation by one molecule cluster is possible. A tensile strength value less than the absolute metastable limit of 160 MPa for water may be obtained due to the stretching of liquid under negative pressure.

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Nomenclature

A	: Interfacial area
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
J_n	: Nucleation rate of n-mer cluster per unit volume
k_B	: Boltzmann constant
m	: Mass of molecule
n	: Number of molecules in a cluster

N	: Number density = ρ_m/m or number of molecules
P	: Pressure
P_∞	: Vapor pressure
R	: Radius of bubble or radius of nucleus
t_{nucl}	: Duration of nucleation process
t_l	: Lag time for bubble nucleation
T	: Temperature of liquid
T_f	: Melting temperature of liquid
V_{nucl}	: Volume of nucleated phase
v	: Usual molecular volume of liquid
v_m	: Effective molecular volume of liquid
Z	: Coordination number
Z_f	: Zeldovich nonequilibrium factor

Greek letter

α	: Polarizability of a liquid molecule
β	: Accommodation coefficient
ΔH_{vap}	: Enthalpy of evaporation
ΔH_f	: Enthalpy of fusion
ϵ_o	: Potential parameter of London dispersion attraction
ϵ_m	: Energy needed to separate a pair of molecules
ρ	: Density
ρ_m	: Density of liquid
ρ_c	: Critical density of liquid
σ	: Interfacial tension
τ	: Tensile strength of liquid

Subscripts

c	: Critical state or critical cluster
f	: Final or ambient
v	: Vapor
g	: Gas
l	: Liquid

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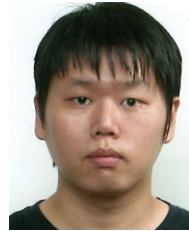
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