

Radius and Transition Temperature

Dependent Equation Chapter 1 Section 1 Nucleation Bulk Tension Factor of Water Droplets

Mingheng Fu

School of Mechanical Engineering, North China Electric Power University, Baoding 071003,
China.

13702697394@163.com

Abstract: Nucleation bulk tension factor (NBTF) of water droplets is variable with various curvature radius of droplets, the degrees of temperature and different pressure outside the surface of droplets. A simple model for NBTF of pure water droplets, free of any adjustable parameter, is presented by the curvature radius of droplets and the liquid-vapor transition temperature. It is shown that the present model for the water droplet offers not only a qualitative but even an excellent quantitative agreements with computer simulations for water droplets. This work is really significant for two-phase wet steam flow with spontaneous condensation where slight adjustments of surface tension of water will modify the nucleation parameters quite significantly.

Keywords: Surface tension, Nucleation bulk tension factor, Water droplets.

1. INTRODUCTION

The liquid-vapor surface energy density or surface tension γ , a fundamental property of water droplets, naturally corresponds with the reversible work to form a new liquid surface per unit area 1. It's true that the surface tension γ of a certain water droplet, in addition to curvature radius, depends on the temperature T, pressure P and the composition of the two coexisting bulk phases. When considering the two-phase wet steam flow with spontaneous condensation, the composition of the two coexisting bulk phases reminds being the single water steam medium and the transition pressure P is closely related to the transition temperature T_b ; namely, the transition temperature T_b of the bulk vapor phase is a single-valued function of the transition pressure P. Therefore, the surface tension $\gamma(R, T_b)$, for a pure working medium of water steam, is determined by the transition temperature T_b and the curvature radius of droplets. Under the existing technology, the surface tension of small droplets, especially in magnitude between nanometer and micrometer, fails to be obtained in experiment. Thus, the common

method, named Molecular Dynamics (MD), is adopted to calculating the surface tension under different circumstances. However, the arbitrary values of small droplets with various radii have not yet been widely established on the basis of the transition temperature and the curvature radii of droplets.

In the classical nucleation theory (CNT) where the surface tension is often treated as the bulk one, the nucleation rate, in the exponential term, grows cubically as a function of surface tension, which will cause the calculation results deviate from the experimental results⁸. Combining the idea of Gibbs, Tolman³ illustrated that the surface tension must change its value with various droplet curvature radii when the radius R_s of the surface tension of the droplet did not correspond to the equimolar radius r_e . Furthermore, Koenig⁴, Benson⁵, Pummer⁶, Kegel⁷ went deeper on the theory of the size-dependent surface tension γ and predicted a decrease in surface tension with the droplet radius dropping its values. However, a united agreement has not been established to describe the numerical relationship between the surface tension γ and the factors impacting it.

To control the intensity of the homogeneous condensation event, nucleation bulk tension factor NBTF is introduced in the classical homogeneous condensation nucleation rate expression⁸⁻⁹. It represents a ratio of size-dependent surface tension of small droplets to bulk surface tension. As the surface tension can influence the nucleation rate seriously, the values of NBTF predicted will have a difference to controlling the location of the condensation front, degree of super cooling, wetness fraction and droplet size. Moses undergone changing the values of nucleation rate and demonstrated the nucleation rate do effect greatly the results of Computer Fluid Dynamics (CFD) simulation¹⁰. In spite of the complex function of surface tension of water droplets, Sriram highlighted the fact that NBTF is really vital for condensing flows in steam turbines by comparing the numerical simulations with the experiment results with different values of certain NBTF¹¹. However, it's rude to treat NBTF as a certain value since the surface tension of water droplets varies with the transition temperature and the curvature radii of droplets. In addition, the transition temperature and the curvature radii of droplets will change the value of NBTF in return.

Naturally the structure and energy differences between solid and liquid are small in comparison with those between solid and gas or between liquid and gas. Lu deduced a model and the results of model agree well with the computer simulation results of water droplets when assuming that the nanocrystal has the same structure as that of the corresponding bulk one¹². However, all the transition enthalpy used in the model is equal to those of certain material under an atmosphere pressure. Thus, the model isn't able to describe the variety of the surface tension when the liquid-vapor transition enthalpy change its value under different transition temperature, especially in two-phase wet steam flow with spontaneous condensation.

In this paper, the function of transition enthalpy E_0 is deduced using the method of polynomial fitting because the process of derivation in former model used by Lu¹² are not able to restrict that the transition temperature must be a certain value under an atmosphere pressure. On such a basis, a simple model of NBTF is developed explicitly to account for the values of NBTF

under various transition temperature and curvature radius of working medium. And the new model predictions for $\gamma (R, T_b)$ or NBTF have been reached a well agreement with the available results of computer simulation for water. The work makes a contribution to determining the surface tension or NBTF in CNT, which is significant for two-phase wet steam flow with spontaneous condensation.

2. MODEL

With regard to surface tension at a certain transition temperature, the surface tension $\gamma (R, T_b)$ related to the size of water droplet and the transition temperature can degenerate to a size-dependent $\gamma (R)$ only. When assuming that the nanocrystal has the same structure as that of the corresponding bulk as well as the natural rule that the structure and energy of solid and liquid varies little in comparison with those between solid and gas or between liquid and gas¹², the size-dependent surface tension $\gamma (R)$ and the bulk one γ_0 can be shown as the form,

$$\frac{\gamma (R)}{\gamma_0} = [1 - \frac{1}{4R / h - 1}] \exp(-\frac{2S_b}{3R_{idg}} \frac{1}{4R / h - 1}) \quad (1)$$

Where

$$S_b = E_0 / T_b \quad (2)$$

Where, S_b is the bulk value of solid-vapor transition entropy with E_0 and T_b being the bulk solid-vapor transition enthalpy and transition temperature. R is the curvature radius of the droplet and R_{idg} is the ideal gas constant. The h here is defined as the O-H bond length.

As a natural consideration, the E_0 can be treated as the ethalpy of vaporisation because the value of enthalpy in fusion is small in comparison of that in vaporization. In light of this consideration as well as a water molecule consists of three atoms, the ethalpy in vaporisation function E_0 based on the data of ethalpy in vaporisation of water¹³ in various transition temperature can be given using the method of polynomial fitting , where the polynomial order is selected as four.

$$E_0 \approx (\text{Interpret} + A * T_b + B * T_b^2 + C * T_b^3 + D * T_b^4) * M / 3 \quad (3)$$

Where the $M=0.01801514\text{kg/mol}$ represents the molar mass of water and T_b is the bulk liquid-vapor transition temperature. At the same time, the values of Interpret, A, B, C and D are shown in Table 1.

Table 1. Several Values of the Equation (3)

Interpret	A	B	C	D
2457.29	-2.69E-2	-3.25E-2	1.55E-4	-2.84E-7

Combining equations 1 and 2 as well as the definition of NBTF, there is

$$NBTF = \frac{\gamma(R, T_b)}{\gamma_0(T_b)} = \left[1 - \frac{1}{4R/h - 1}\right] \exp\left(-\frac{2E_0/T_b}{3R_{idg}} \frac{1}{4R/h - 1}\right) \quad (4)$$

Where the expression of E0 and the relative values of parameters has been shown in equation (3) and Table 1.

3. RESULTS AND DISCUSSION

In light of equation (4), comparisons of $\gamma(R, T_b)/\gamma_0(T_b)$ for water droplets with different transition temperature T_b and coexisting temperature T between the results of computer simulation and those of current model calculation are given in Figures 1, 2, and 3. The parameters related to equation (4) have been listed in Table 2.

Table 2. Several Values of Parameters for Establishing the Curves of Three Figures

	H [nm]	T_b [k]	T [k]	$\gamma_0(T)$ [mJ/m ²]
Figure1	0.096 ¹⁸	373 ¹⁵	300 ¹⁵	75.0 ¹⁵
Figure2	0.096 ¹⁸	373 ¹⁶	298 ¹⁶	66.0 ¹⁶
Figure3	0.096 ¹⁸	300 ¹⁷	300 ¹⁷	59.5 ¹⁷

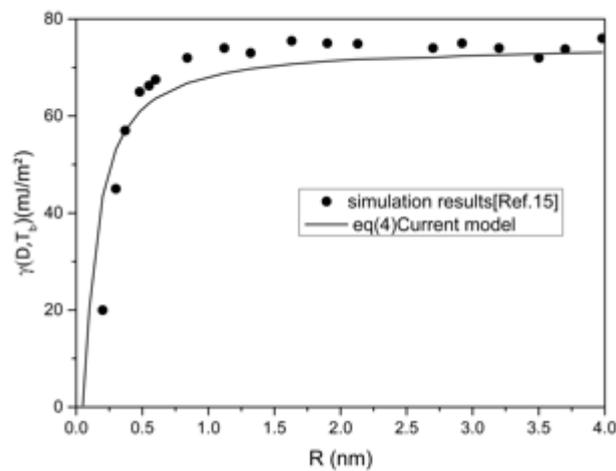


Figure 1. The radius dependence of $\gamma(R, T_b)$ with $T_b=373K$ and $T=300K$ for water15

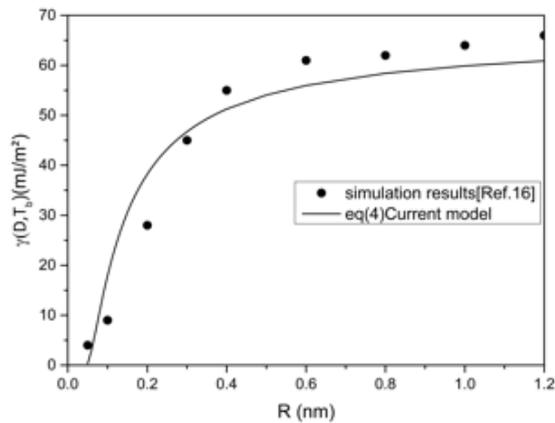


Figure 2. The radius dependence of $\gamma(R, T_b)$ with $T_b=373K$ and $T=298K$ for water16

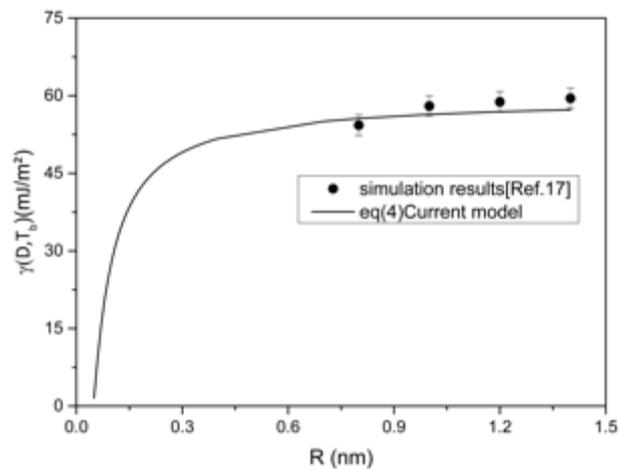


Figure 3. The radius dependence of $\gamma(R, T_b)$ with $T_b=300\text{K}$ and $T=300\text{K}$ for water17

In Figure 1, the Monte Carlo method, to get the relative surface tension of computer simulation results, is carried out by Samsonov15 at room temperature $T=300\text{K}$ with bulk surface tension remaining 75mJ/m^2 and under atmosphere pressure which means the transition temperature of bulk water corresponds with $T_b=373\text{K}$. According to the results of computer simulation in Figure 2, the effective surface tension of water16 is shown at temperature $T=298\text{K}$, and the transition temperature $T_b=373\text{K}$ with the surface tension $\gamma_0=66.0\text{mJ/m}^2$ when the curvature radius approach infinity. In Figure 3, the surface tension17 is examined via non-equilibrium MD simulation in NVT ensemble. In terms of the simulation, the transition temperature and coexisting temperature remains the same as 300K and the bulk surface tension mentioned in the passage is regarded as 59.5mJ/m^2 .

It's evident that the current model agrees well with the results of computer simulation of water droplets though there do exist some deviation. And the agreement corroborates the validity of the assumption in equation (4).

As shown in Figures 1-3, the value of $\gamma(R, T_b)$ falls off as the radii of water droplets decrease when being a certain transition temperature and coexisting temperature which have a great influence on the bulk surface tension $\gamma(T)$. This can be explained naturally because being an energetic difference between the surface molecules and the interior molecules of the droplets, the surface tension $\gamma(R, T_b)$ decreases as the energy of interior molecules comes closed with that of surface molecules when the radius of water droplets is really small.

Though the transition temperature T_b is not equal to the coexisting temperature T in Figure 1 and Figure 2. There is no influence on the values of NBTf since the equation (4) shown above has no association with the coexisting temperature. Furthermore, the concept of coexisting temperature is the same as the transition temperature when considering in the two-phase wet steam flow with spontaneous condensation. And the related equation predictions agree well with the simulation results in Figure 3 where $T_b=T$.

Though the tendency of the current model matches well with the simulation results, the current model, compared in three Figures, has the same trend that the equation predictions are slightly bigger than that of simulation at the beginning and slightly smaller than that afterwards. This might be the appearance that the deviations of deducing equation (1) which can be derived from Lindemann's criterion¹⁹ could accumulate. What's more, the MD simulation of water can not get the truth of surface tension of water because current methods still exist some misunderstanding about the physical geometry of water molecule. However, the current model predictions, though there do exist some deviation, still fit well with the results of computer simulation as in Figure 1, 2 and 3.

In the two-phase wet steam flow with spontaneous condensation, the surface tension of water droplet is really significant for the calculation of nucleation rate which grows cubically in the exponential term as a function of surface tension. As the transition pressure corresponds one-to-one with the transition temperature, the surface tension of water droplet only depends on transition temperature and the curvature radius of droplets, which is reflected the same arguments as the equation (4). As a natural phenomenon, the water droplets with a critical radius first appears during the beginning process of spontaneous condensation and grows its size along with process undergoing deeper. When the curvature radius of droplets become bigger as the droplets grow, the NBTF should vary from a small value to 1 but it can't reach but approach 1 because the curvature radii of droplets, compared with the bulk one, would not be infinity in spontaneous condensation, which is in sympathy with the equation (4).

Sriram¹¹ demonstrates that the values of the fixed NBTF will change its values to meet the experimental data when the total temperature in numerical simulation remains diverse. At the same time, the reason has not been presented. In light of the results of numerical simulation shown in reference 11, the best fixed value of NBTF meeting the results of experiments tends to get larger and varies from 0.85 to 0.95 when the total temperature increases in the entrance of Laval nozzle with the same total pressure. It can be explained by our model in equation (3) and (4) because the transition enthalpy E_0 decreases its value while transition temperature T_b increases. As the mathematical relationship shown in equation (4), NBTF, with other conditions remained constant, will increase its values as the values of T_b raises and the E_0 reduces at the same time.

In terms of the well agreement shown between our equation predictions of surface tension and the results of computer simulation, the simple model of NBTF shows a huge potential in predicting the nucleation parameters in flow field, which is really vital for the two-phase wet steam flow with spontaneous condensation. And further study can be aimed at inserting the model to calculate the nucleation parameters in complex process with two-phase wet steam flow with spontaneous condensation.

4. CONCLUSION

In summary, the function of transition enthalpy E_0 , associated with the experimental transition temperature, is established using polynomial fitting. On the basic function of E_0 , a simple

model for NBTF of pure water droplets is developed by the radius of droplets and the liquid-vapor transition temperature. Reasonable agreements show the present model predictions reaches a well agreement with the results of computer simulations for water droplets. What's more, the equation of NBTF might be significant for two-phase wet steam flow with spontaneous condensation and the trends of the best fixed value of NBTF meeting the results of experiments can be explained by our model.

REFERENCES

- [1] Gibbs, J. W. The Collected Works; Longmans, Green and Company: New York, 1928; Vol. 1.
- [2] Bakhtar F, Young J B, White A. J, et al. Classical Nucleation Theory and its Application to Condensing Steam Flow Calculations [J].Journal of Mechanical Engineering Science, 2005, 219: 1315-1333.
- [3] Richard C. Tolman. The Effect of Droplet Size on Surface Tension [J]. The Journal of Chemical Physics, 1949, 17:333-337.
- [4] Koenig F O. On the Thermodynamic Relation between Surface and Curvature [J]. Journal of Chemical Physics. 1950, 18:449.
- [5] Benson G C, Shuttleworth R. The Surface Energy of Small Nuclei [J]. Journal of Chemical Physics. 1951, 19:130-131.
- [6] Plummer P L M, Hale B N. Molecular Models for Pre-Nucleation Water Clusters [J]. Journal of Chemical Physics. 1972, 56:4329-4334.
- [7] Kegel W. On the Variation of the Interfacial Tension with Cluster Size in Connection to Homogeneous Nucleation from the Vapor Phase [J]. Journal of Chemical Physics. 1995, 102: 1094-1095.
- [8] Gerber, A. G., 2008, "Inhomogeneous Multifluid Model for Prediction of Nonequilibrium Phase Transition and Droplet [J] Journal of Fluids Engineering, pp 031402-1-031402-11, Vol 130.
- [9] Moore, M. J., Walters, P. T., Crane, R. I. and Davidson, B. J., 1973, "Predicting the Fog-Drop Size Wet-Steam Turbines", pp. 101-109, Inst. of Mechanical Engineers (UK), Conf. on heat and fluid flow in steam and gas turbine plant, University of Warwick, paper C37/73.
- [10] Moses, C. A., Stein, G. D., 1978, "On the Growth of Steam Droplets Formed in a Laval Nozzle Using Both Static Pressure and Light Scattering Measurements", pp. 311-312, Vol. 10, Journal of Fluids Engineering.
- [11] Sriram A T, Moraga Francisco, Mistry Hiteshkumar. Numerical Sensitivity Studies on Nucleation of Droplets in Steam Turbine[C].ASME Power Conference, 2011, Power2011-55269.
- [12] Haiming Lu, Qing Jiang. Size-Dependent Surface Tension and Tolman's Length of droplets [J].Langmuir, 2005, 21:779-781.
- [13] Yanfeng Liu, Zhengyang Gao, Xiujun Liang. Heat Transfer [M].China: North China Electric Power University, 2013; p269.

- [14] Water Molecular Weight. <http://www.convertunits.com/molarmass/Water>.
- [15] V. M. Samsonov, A. N. Bazulev and N. Yu. Sdobnyakov. Rusanov's Linear Formula for the Surface Tension of Small Objects [J]. PHYSICAL CHEMISTRY. 2003, 389:83-85.
- [16] Hideaki Takahashi, Akihiro Morita. A Molecular Dynamics Study on Inner Pressure of Microbubbles in Liquid Argon and Water [J]. Chemical Physics Letters. 2013, 573:35-40.
- [17] Christian Sendner etc. Interfacial Water at Hydrophobic and Hydrophilic Surfaces: Slip, Viscosity, and Diffusion [C]. American Chemical Society. 2009.
- [18] Michael etc. A New General Purpose Quantum Mechanical Molecular Model [J]. J. Am. Chem. Soc. 1985, 107, 3902.
- [19] H. M. Lu and Q. Jiang. Size-dependent Surface Energies of Nanocrystals [J]. J. Phys. Chem. 2004, 108, 5617-5619.
- [20] Frank G. Shi. Size-dependent Thermal Vibration and Melting in Nanocrystals [J]. J. Mater. Res. 1994, 1307-1313.
- [21] Alan F. Wright etc. First-principles calculation of the Mg (0001) surface relaxation [J]. Surface Science. 1994, 302, 215-222.
- [22] Alejandro, Angel Rubio. A Molecular Dynamics study of water nucleation using the TIP4P/2005 model [J]. The Journal of Chemical Physics. 2011, 244505, 1-13.
- [23] Q. Jiang, J.C. Li, B.Q. Chi. Size-dependent Cohesive Energy of Nanocrystals [J]. SCIENCE DIRECT. 2002, 366:551-554.