

Süperdoymdaki Buhar İçinde Damlacık Oluşumunun Serbest Enerji Değişimi

Nuretdin Eren, Nihal Buyukcizmeci, Rıza Oğul

Department of Physics, University of Selcuk, Kampus, Konya, Turkey.

e-mail: rogul@selcuk.edu.tr

Öz: Süperdoymuş bir buhar içinde damlacık oluşumu sırasında saf bir numunenin davranışı ve yarı sıvı-gaz faz eğrisi altındaki kararlı bölgedeki büyük genlikli yoğunluk dalgalanmaları sonucunda buhar fazından damlacıklar oluşumu süreçleri araştırılmıştır. Fisher modeli temelinde, çeşitli doyma oranları için, kritik su damlacıklarının oluşumu esnasındaki serbest enerji değişimleri damlacık yarıçapının bir fonksiyonu olarak hesaplanmıştır. Damlacık yüzeyinin küresel şekil alması ile yüzey serbest enerjisi ile bağlantılı olan toplam entropinin azalmasını tanımlayan geometrik terimin kritik damlacık oluşumlarını tanımlayan toplam serbest enerjide anlamlı değişmelere neden olduğu gözlenmiştir.

Anahtar kelimeler: Süperdoyma oranı, damlacık oluşumu, doyma yoğunluğu.

Free Energy Change of Droplet Formation in a Supersaturated Vapor

Abstract: The behavior of the pure substances during the condensation of liquid droplets in a supersaturated vapor and, the mechanism of homogeneous nucleation of vapor to liquid droplets that may occur as a result of large amplitude density fluctuations within the coexistence line in the metastable region have been investigated. The free energy change accompanying the formation of a critical water drop is calculated as a function of droplet radius for various saturation ratios on the basis of Fisher's model. It is observed that a geometric term due to the fact that the surface of a drop relaxes to spherical shape which reduces the total entropy associated with the surface free energy, produces significant changes in total free energy change of critical droplet formation.

Keywords: Supersaturation ratio, droplet formation, saturation density.

1. Introduction

Here in this study we discuss only the behavior of the pure substances during the condensation of liquid droplets in a supersaturated vapor, so that the processes by which condensation is initiated are homogeneous. This is important not only for our understanding of physical processes involved in condensation or liquid fracture but also for natural and industrial processes. Metastable fluid states are observed both

theoretically and experimentally in the liquid-gas phase transition region, where the fluids have very distinguishing properties (Schmidt et al., 1997; Ogul, 1998; Kalikmanov and van Dongen, 1995; Goodman et al., 1984; Ogul and Atav, 2003; Fisher, 1982; Abraham, 1979; Vicentini et al., 1985). It is instructive to investigate the thermodynamic properties of fluids under extreme conditions of low densities and high temperatures. Besides their general interest

for the abovementioned applications, these studies are also very important for our understanding of the behavior of heat fluxes in thermal systems.

The development of density inhomogeneities in any initially homogeneous matter can be classified as spinodal decomposition and nucleation of droplets. Spinodal decomposition occurs as a result of growth of small amplitude fluctuations to such an extent that the matter is disrupted and it breaks up within the isothermal spinodal line. During the nucleation of localized region, however, droplets may be formed as a result of large amplitude fluctuations everywhere within the coexistence line. In this paper, we shall concentrate on investigating the free energy change accompanying the formation of a critical water drop in the framework of Fisher's droplet model (Fisher, 1967), rather than presenting empirical corrections for calculating nucleation rate in order to make a comparison with experimental data.

2. Material and Methods

2.1. Phase Instabilities Below the Critical Point

The main purpose of this study is to explore the physical mechanisms leading to formation of liquid droplets as a result of density fluctuations in the phase transition region. For orientation, we point out the fact that the phase diagram is determined by van

der Waals-type equation of state. The locus of the points satisfying the condition that $(\partial P/\partial n)_T = 0$, forms the spinodal line in the n-T plane, where P denotes the pressure, T the temperature and n the molecule number density. In other words, one may determine the dynamically unstable region by means of the bulk modulus B,

$$B = -V \frac{\partial P}{\partial V} = n \left(\frac{\partial P}{\partial n} \right)_T \quad (1)$$

where B is positive because an increase in pressure causes a decrease in volume. This condition for the spinodal line can be applied only to a single component liquid. For a multicomponent liquid, the corresponding criteria is considerably more complicated. At the equilibrium density the bulk modulus is positive $(\partial P/\partial n)_T > 0$, and the liquid matter is stable to small-amplitude, long-wavelength density fluctuations. The liquid matter will be dynamically unstable when the bulk modulus is negative $(\partial P/\partial n)_T < 0$. As the density decreases, matter enters a metastable region where it is thermodynamically unstable with respect to separation into liquid and gas phases. However, the matter in this region is stable to small long-wavelength density fluctuations. This is because the bulk modulus is still positive in the metastable region. When the bulk modulus is zero $(\partial P/\partial n)_T = 0$, metastable region ends, and matter becomes unstable to

small density fluctuations. In this paper, we will not pretend to give a detailed account of the relation between spinodal line and the homogeneous nucleation, instead we refer the reader to Abraham (1979), Lienhard and Karimi (1981), where it was shown that the limit of homogeneous nucleation lies very close to the spinodal line.

The coexistence line in n - T plane can be determined by equating the pressure and chemical potentials of liquid and gas phases as $P(n_1, T) = P(n_2, T)$ and $\mu(n_1, T) = \mu(n_2, T)$. The critical temperature T_c is determined by $(\partial P / \partial n)_T = 0$ and $(\partial^2 P / \partial n^2)_T = 0$. Phase diagram has an inflection point at T_c . In other words, at the critical temperature T_c the surface between the two phases disappears (this is because the surface tension vanishes at T_c), and only the gas phase is possible above this temperature. The corresponding vapor pressure and density are called critical pressure P_c and critical density n_c , respectively. In this paper, we shall primarily concentrate on the droplet formation as a result of the nucleation of localized region in between coexistence and spinodal line, where the density is significantly less than critical density n_c .

2.2. Nucleation and Droplet Formation

We shall now discuss droplet and bubble formations. By a droplet we mean a

small volume of liquid phase at equilibrium surrounded by the vapor phase of the liquid; by a bubble we mean a small volume of vapor trapped by a thin film with two surfaces on each side of the film. Homogeneous nucleation of bubbles is formally very similar to the homogeneous nucleation of droplets. In the nucleation of liquid droplets, the subcritical droplets are in mechanical equilibrium with the surrounded vapor phase (but not in thermodynamic equilibrium until critical size r^* is reached). In the homogeneous nucleation of bubbles, however, the vapor phase in a bubble is in thermodynamic equilibrium with the surrounding liquid, but not in mechanical equilibrium until the critical size is reached. Droplet formation occurs in the portion of the region between the isothermal spinodal line and the coexistence line where the densities are less than the critical density (metastable vapor), while bubble formation can occur in the portion of the region between isothermal spinodal line and the coexistence line for the densities greater than the critical density (metastable liquid). Because of the similarity, we deliberately set aside the bubble formation and concentrate on the derivations for the nucleation of critical droplets: The probability of formation of a droplet can be estimated by calculating the free energy change ΔG accompanying the formation of the drop of radius r and containing A molecules. This

probability is proportional to $\exp(-\Delta G^*/kT)$. In other words the rate of nucleation at which critical droplets grow to become supercritical is given by

$$J = K \exp(-\Delta G^*/kT). \quad (2)$$

where k is the Boltzmann constant, T is the temperature and the constant K is determined from kinetic theory (Fisher, 1967). On the other hand, we should remark here that the rate of nucleation at which critical droplets grow to become supercritical, strongly depends upon the free energy change of critical droplet formation ΔG^* . Small variations in K are negligible because the behavior of J is dominated by the exponent ΔG . Therefore, it is usually satisfactory to consider the values of ΔG in the study of nucleation process. Here in this study, we have also considered ΔG to study homogeneous nucleation of vapor to liquid droplets.

For our present purposes, let us concentrate on calculation of the total free energy change ΔG in creating a liquid droplet in the framework of Fisher's droplet model (Fisher, 1967). In this model, we assume that the droplet is essentially of uniform density and spherical so that we have $r = r_0 A^{1/3}$ with $V = (\frac{4}{3}\pi r^3)$, where A represents number of molecules in drop, r the radius and V the volume of droplet. In

our derivation, ΔG will consist of the following three terms.

The first term is the well known surface free energy: The liquid droplets tend to have spherical shape, because a sphere has the smallest surface/volume ratio, among the geometrical objects. We can calculate the work of creating a droplet of radius r in a supersaturated vapor. When the radius of a spherical droplet changes from r to $r + dr$ the change in surface area will be

$$dA = 4\pi(r + dr)^2 - 4\pi r^2 = 8\pi r dr \quad (3)$$

The work we need to change the surface area by an infinitesimal amount dA can be written

$$dW = \sigma(T) dA \quad (4)$$

where the temperature dependent coefficient $\sigma(T)$ is called the surface tension. Integrating Eq.(4.2), we can identify the work of surface formation

$$W_1 = \sigma(T) 4\pi r^2 \quad (5)$$

This work can be interpreted as the free energy change for the formation of liquid/vapor interface. The exact relation between the surface tension of a saturated fluid and equation of state (a relation between P-n-T), was derived by Van der Waals. The current literature contains many equations of state that represent thermodynamic data over a wide range of the values of P and T in the phase transition region (Shamsundar and Lienhard, 1993; Reid et al., 1987; Koyuncu et al., 2002;

Fletcher, 1993). Some of these equations are valid only for liquids, some only for vapors, and they produce separate correlation for different thermodynamic properties. Theoretical and experimental predictions for $\sigma(T)$ indicate that the surface tension declines with increasing temperature and vanishes at the critical temperature, where the surface between two phases disappears. There exist various approximations to predict a reasonable relation between $\sigma(T)$ and T/T_c (Guggenheim, 1945).

The second term is arising from the transition from vapor to liquid: The vapor phase can be prepared in the supersaturated state of metastable region and then droplets of liquid phase will be prepared outside the coexistence line. In order to study the evolution of a liquid droplet formation, we choose two points in the vapor and liquid phases, where the pressures of liquid and gas phases are equal but the densities are different. For a sufficiently slow process in a system of the Gibbs free energy G , volume V , pressure P , entropy S , number of particle N and chemical potential μ , we have the relation,

$$dG = VdP - SdT + \mu dN \quad (6)$$

Assuming that the number of particles N is conserved we can write down $dG = VdP$ at fixed T . One may calculate the vapor pressure of a pressurized liquid by using the fact that at equilibrium we have

$\mu_g = \mu_\ell$, and for any change that preserves equilibrium $d\mu_g = d\mu_\ell$. If the pressure P on the liquid is increased by dP , the chemical potential of the liquid changes by $d\mu_\ell = VdP$ and the chemical potential of the vapor changes by $d\mu_g = Vdp$ where dp is the change in its vapor pressure p . If we use the ideal gas relationship $pV = NkT$ then we can write

$$d\mu_g = (NkT/p)dp \quad (7)$$

$$d\mu_\ell = VdP. \quad (8)$$

Using the fact that $d\mu_g(T, P) = d\mu_\ell(T, P)$, and performing the integration with respect to the fact that when there is an additional pressure ΔP on the liquid, the vapor pressure will be p_2 (when there is no additional pressure acting on the liquid, the pressure experienced by the liquid is equal to the normal vapor pressure p_1); then we obtain

$$NkT \int_{p_1}^{p_2} \frac{dp}{p} = \int_{p_1}^{p_1 + \Delta P} VdP \quad (9)$$

$$W_2 = VnkT \ln(p_2 / p_1) = V\Delta P \quad (10)$$

where p_2 / p_1 is called supersaturation ratio denoted by S_0 and $N = nV = n(4/3)pr^3$. This equation represents the free energy change for the transfer at constant temperature and pressure of a droplet from the vapor into the liquid phase. In the context of molecular physics it is a good approximation to use the ideal gas

relationship between chemical potential and pressure at fixed T. However, one should bear in mind that this generally will not be a very good approximation for a nearly degenerate Fermi gas. Summation of the contributions from Eq.(5) and (10) will give the total free energy change to create a droplet

$$\Delta G_1 = 4\pi r^2 \sigma - \left(\frac{4}{3}\pi r^3\right)nkT \ln S_0. \quad (11)$$

The third term is a geometric term which can be added to take into account of

$$\Delta G_2 = 4\pi r^2 \sigma - \left(\frac{4}{3}\pi r^3\right)nkT \ln S_0 + 3kT\tau \ln(r/r_0) \quad (13)$$

The first term on the right-hand side of (13) gives the change in free energy on formation the liquid/vapor interface, the second term arises from the transition from vapor to liquid and the third term is the geometric term where we have used the fact that $A = (r/r_0)^3$ for the numerical calculations. In the classical or van der Waals-like limit the critical exponent is given by $\tau=7/3$ and we find that $r_0=1.925^\circ A$ for water drops. Differentiation of (13) with respect to r, yields

$$8\pi\sigma r^* - 4\pi nkT \ln S_0 r^{*2} + \frac{3kT\tau}{r^*} = 0 \quad (14)$$

A critical size droplet can only exist if it can attain a size greater than the critical

the fact that the surface closes on itself which reduces the total entropy associated with the surface free energy, which was suggested by Fisher (1967) for the first time as

$$W_3 = kT\tau \ln A \quad (12)$$

with $r = r_0 A^{1/3}$ and $V = (\frac{4}{3}\pi r^3)$, where we

assume that droplets are of uniform density. As a result of the contribution by W_3 , Eq.(11) will be of the form

radius r^* . When $r < r^*$ droplets will tend to evaporate particles (or breakup) to get rid of their surface energy, therefore instead of growing it evaporates. Whereas if $r > r^*$, they tend to grow by accumulating particles from the vapor and thereby lowering the free energy. This means that the droplet reaches more stable levels with additional molecules.

Variation of the free energy change ΔG^* as a function of the critical radius r^* obtained from Eq.(13) for water is shown in Fig.1. In this figure, we have also shown the results obtained from Eq.(11) to see the effect of geometric term given by Eq.(12). This approach in terms of the free energy change was also applied for a nucleonic liquid-gas phase transitions in nuclear

reactions (Goodman et al., 1984). Recently, Fisher's model has been successfully applied to heavy ion collisions to calculate discoverable quantities such as nucleonic vapor pressure, evaporation enthalpy and surface energy (Elliott et al., 2002). However, in order to make a comparison with experimental results and the predictions of theoretical approaches such as Fisher's model and density functional theory, one should perform the measurements of the nucleation rate. Therefore, the empirical corrections to the classical approaches may be used to investigate the variation of the rate of nucleation in terms of supersaturation ratio and temperature (see for example Dillmann and Meier (1991), Wolk and Strey (2002) and references therein).

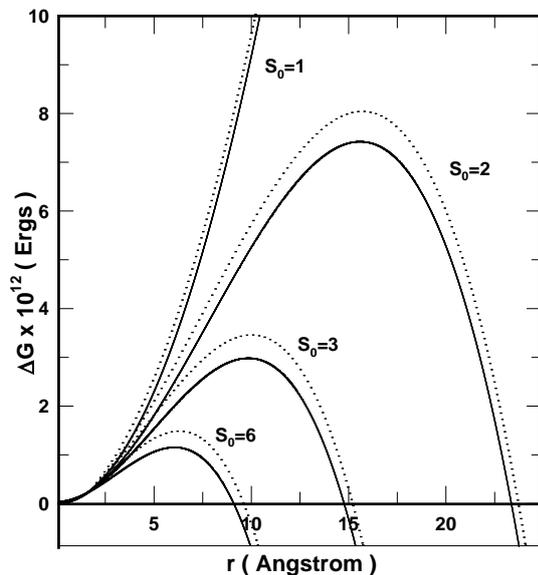


Figure 1. Free energy change of droplet formation as a function of droplet radius, for various saturation ratios at $T=293$ (K) for water. Solid and dotted lines represent the results obtained from Eqs.(11) and (13), respectively.

3. Results and Discussion

It is instructive to study homogeneous nucleation of water vapor to liquid droplets for our understanding of the basis of most of the theoretical treatments of heterogeneous nucleation. The results of our calculations for water are presented in Fig.1. Free energy changes of droplet formation as a function of droplet radius are calculated from Eq.(11) and Eq.(13). As can be seen from this figure when $S_0 = 1$, the curve refers to unsaturated vapor that means there is no droplet formation. The results for water obtained from Eq.(11) follow the same trend with those given in Boucher (1969). A geometric term $\tau kT \ln A$ due to the fact that the surface relaxation to a spherical shape reduces the total entropy associated with the surface has been taken into account through Eq. (13). As can be seen from Fig.1, this geometric term produce significant changes in the process of droplet formation by means of surface free energy. We haven't seen the present application for water anywhere else. When $S_0 = 2$, Eq.(13) produces a free energy deviation of greater than 8 % from that obtained from Eq.(11). As can be seen from the figure, this deviation increases with increasing supersaturation ratio. When $S_0 = 5$, for example, we find a deviation of % 25. However, this effect may be negligible for the values $S_0 < 2$, where $r^* >$

15 Å. It is also important to emphasize that the region of $r < r_0$ is inaccessible due to the finite volume of molecules, which was not considered in the previous studies. When the radius is $r = 15.65 \text{ Å}$ we have $S_0 = 2$, whereas when $r = 10 \text{ Å}$, $S_0 = 3$. The calculations for $S_0 > 5$, is unreliable because in this region radius of a droplet is less than 7 Å (approximately 50 molecules) and the basis of the calculation is suspect. This is because the connection between statistical mechanics and thermodynamics is usually established in the limits of large number of molecules. A similar calculation can be performed for nucleation of bubbles in water liquid under negative pressure. In Fig.2, we present the variations of supersaturation ratio as a function of radius of droplets at 293 K. It is seen from this figure that surface free energy by means of Eq.(12) is very effective at small values of critical radius r^* .

Our purpose in this paper is not to examine the experimental data in detail, but a cursory glance at the literature, however, shows that various experimental techniques have been used for the measurement of nucleation rates over extended ranges of J , T and S_0 (see for example Wolk and Strey (2002) and references therein). In these studies, empirical correction functions to the

classical nucleation theory have been used to predict nucleation rates, and a good agreement between nucleation theory and experiment is observed. As for the spinodal decomposition for water, experimental results are quite difficult to obtain particularly in the neighborhood of the spinodal limit of water liquid under tension. In this respect, we can cite Poole et al. (1993), for details.

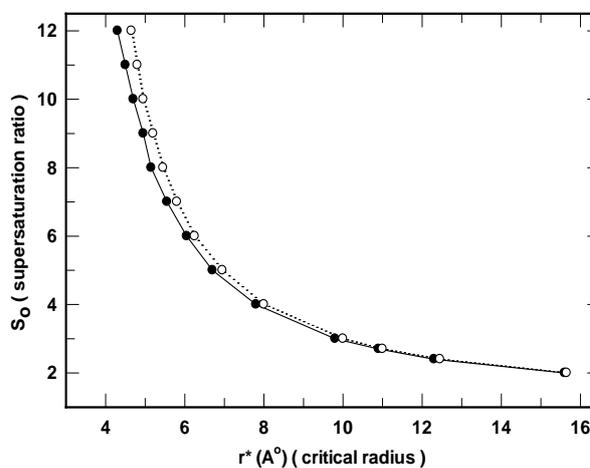


Figure 2. Variation of supersaturation ratio with critical radius at 293 (K) for water droplets. Solid and dotted lines represent the results obtained from the differentiations of Eqs.(11) and (13), respectively.

In summary, we have presented a transparent derivation of the mechanism for the critical droplet formation process in a classical (non-quantal) approach on the basis of Fisher's model, and applied the results for water. We should point out that we consider only pure bulk material, so that the processes are homogeneous. This is possible in the laboratory, but in the outside world nucleation is initiated by minute dust particles or other kinds of foreign matter, so

that the process is heterogeneous. These particles provide a surface to which water molecules can attach and grow to the droplets. In the case of droplets of water in the moist air at room temperature the nucleation is initiated at $S_0 \leq 1.01$, by suspended foreign particles, and progressively at higher S_0 values are reached. In the absence of foreign particles (pure water), initial drops will tend to evaporate at such small values of S_0 due to

an initial tendency to condense is overcome by a heightened tendency to evaporate.

In conclusion, it is seen from Fig.2 that a geometric term given by Eq.(12) produces significant changes in the surface free energy, which is crucial especially for the small values of r^* . Therefore, further analysis of the free energy change of the droplet formation would be worthwhile to provide better predictions for the nucleation rates.

References

- Abraham FF (1979). On the thermodynamic, structure and phase stability of the nonuniform fluid state,, *Physics Reports* 53, 93–156.
- Boucher EA (1969). Nucleation, Zettlemoyer A C (ed.). p. 535. Dekker, New York.
- Dillmann A, Meier GEA (1991). A refined droplet approach to the problem of homogeneous nucleation from the vapor phase, *The Journal of Chemical Physics* 94, 3872–3884.
- Elliott JB, Moretto LG, Phair L (2002). Liquid to vapor phase transition in excited nuclei, *Physical Review Letters* 88, 042701- 042704.
- Fisher ME (1967). Theory of condensation and critical point, *Physics* 3, 255–283.
- Fisher ME (1982). Proceedings of the School on Critical Phenomena, Stellenbosch, South Africa, edited by F.J.W. Hahne (Springer-Verlag, Berlin, 1983), Vol. 186, Chap. 1.
- Fletcher NH (1993). Van der waals equation and nucleation theory, *European Journal of Physics* 14, 29–35.
- Goodman AL, Kapusta JI, Mekjian AZ (1984). Liquidgas phase instabilities at subnuclear densities, *Physical Review C* 30, 851–865.
- Guggenheim E (1945). The principle of corresponding states, *The Journal of Chemical Physics* 13, 253–261.
- Kalikmanov VI, van Dongen MEH (1995). Semiphenomenological theory of homogeneous vapor-liquid nucleation, *The Journal of Chemical Physics* 103, 4250–4255.
- Koyuncu M, Demirtas A, Ogul R (2002). Excess properties of liquid mixtures from the perturbation theory of Barker-Henderson, *Fluid Phase Equilibria* 193, 87–95.
- Lienhard JH, Karimi A (1981). Homogeneous nucleation and the spinodal line, *Journal of Heat Transfer* 103, 61–64.
- Ogul R (1998). On the spinodal instabilities at subnuclear densities, *International Journal of Modern Physics E* 7, 419–424.
- Ogul R, Atav U (2003). Investigating the droplet formation in a nucleonic vapor, *Physica Scripta* 67, 34–36.
- Poole PH, Sciortino F, Essmann U, Stanley HE (1993). Spinodal of liquid water, *Physical Review E* 48, 3799-3817.
- Reid RC, Prausnitz JM, Poling BE (1987). The properties of gases and liquids. McGraw-Hill, New York.
- Schmidt M, Kusche R, Kronmüller W, Issendorff B, Haberland H (1997). Experimental determination of the melting point and heat capacity for a free cluster of 139 sodium atoms, *Physical Review Letters* 79, 99-102.
- Shamsundar N, Lienhard JH (1993). Equation of state and spinodal lines-a review, *Nuclear Engineering and Design* 141, 269–287.
- Vicentini A, Jacucci G, Pandharipande VR (1985). Fragmentation of hot classical drops, *Physical Review C* 31, 1783-1793.
- Wolk J, Strey R (2002). Emprical function for homogeneous water nucleation rates, *The Journal of Chemical Physics* 117, 4954-4960.