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Thermodynamics of micro-droplets: studies on the lattice gas model

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THERMODYNAMICS OF MICRO-DROPLETS:
STUDIES ON THE LATTICE GAS MODEL

by

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B.S., University of Montana, 1976

Presented in partial fulfillment of the requirements
for the degree of Master of Science

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ABSTRACT

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Thermodynamics of Micro-Droplets: Studies On the Lattice Gas Model  
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Director: George W. Woodbury, Jr.  

The classical theory of homogeneous nucleation assumes that a certain size droplet must form as an initial step in the condensation of a pure liquid from its vapor. This droplet is characterized by a sharp interface, high interior density, and surface tension equal to that of a plane interface. Mechanically stable droplets are assumed to exist at all radii from \( r = 0 \) to \( r = \infty \).

The assumption that bulk properties hold for microscopic droplets has not been well justified. It is the purpose of our study to calculate the thermodynamic potential of very small droplets from first principles. Investigation of this thermodynamic potential will reveal whether the assumptions lying at the heart of the classical theory of homogeneous nucleation are indeed justified.

The method used to calculate the thermodynamic potential was to apply the cluster variation method to a two dimensional triangular lattice gas model. The thermodynamic potential was written in a detailed form allowing a complete characterization of microscopic droplets.

It was found that, in agreement with the classical theory, a special droplet, called the critical droplet, must form as an initial step in the condensation process. The properties of this special droplet differed markedly from the classical predictions. It was found that the critical droplet is considerably more diffuse than the classically predicted droplet. The most striking result of the calculations was that droplets smaller than the critical droplet do not exist. Therefore, a fundamental change in the standard kinetic scheme for homogeneous nucleation is indicated.
ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

It is commonly observed that as a pure gas is cooled, it will condense at the boiling point of the liquid. Closer inspection reveals that the condensation process begins at inhomogeneities such as foreign particles or container walls. In the absence of such nucleation sites, a droplet of the pure liquid must form as an initial step and then grow to form bulk liquid. This condensation mechanism, called homogeneous nucleation, occurs with difficulty. Two of the most important reasons for this difficulty are: (a) to serve as a nucleation site, a droplet must form by random fluctuations, and (b) once formed, a droplet may not be stable with respect to the gas phase. The stability of the droplet, as will be demonstrated later, is dependent on its size. Therefore, the condensation of a pure vapor occurs at temperatures well below the equilibrium boiling point. This phenomenon is known as supercooling or supersaturation.

To investigate the structure of a droplet suitable as a nucleation site and to appreciate the problems associated with this droplet's growth, we next look at the thermodynamic potential which arises from the standard simple thermodynamic treatment of droplets.

Consider a droplet of the liquid suspended in the gas at pressure $P_g$. This droplet is in mechanical equilibrium with the vapor but
constrained in such a way that it will neither evaporate nor undergo condensation. Let $N_d$ and $N_g$ be the number of particles in the drop and the gas respectively. A feature of this system, when it is at equilibrium is:

$$0 = dU - T dS + P_g dV$$

where $U$ is the energy of the system, and $T$, $S$, and $V$ are, respectively: temperature, entropy, and volume. It follows that

$$\Phi = U - TS + P_g V$$

is the thermodynamic potential for the system under conditions of fixed $T$ and $P_g$. The Helmholtz free energy, $F = U - TS$, is made up of contributions from the droplet and from the gas. The droplet is taken to include the interface region. Therefore,

$$F = F_{\text{drop}} + F_{\text{gas}}$$

Then $F_{\text{drop}}$ can be rewritten as:

$$F_{\text{drop}} = F_x(T, P_g) + \Delta F$$

where $F_x(T, P_g)$ is the free energy of $N_d$ molecules of bulk liquid under the stated conditions of temperature and pressure and $\Delta F$ is the free energy change necessary to convert $N_d$ molecules of bulk liquid to a drop. That is, $\Delta F$ is the reversible work in forming the drop. This work is taken to be $\sigma A$, where $\sigma$ is the surface tension and $A$ is the surface area of the drop. Combining this with equations (2), (3), and (4) gives

$$\Phi = F_x(T, P_g) + F_g(T, P_g) + P_g V + \sigma A$$

For a bulk fluid of $N$ particles, the chemical potential is given by:
\[ \mu N = F + PV \]

Therefore, equation (5) may be rewritten as

\[ \Phi = \mu_g (T, P_g) N_g + \mu_l (T, P_g) N_l + \sigma A \] (7)

where \( N_g \) is the number of gas particles and \( N_l \) is the number of particles in the drop. And finally, equation (7) may be written in terms of the drop radius \( r \), the liquid density \( \rho_l \), and the total number of molecules \( N = N_l + N_g \)

\[ \Phi = \mu_g (T, P_g) N + (\mu_l (T, P_g) - \mu_g (T, P_g)) \rho_l \frac{4\pi r^3}{3} + 4\pi r^2 \sigma \] (8)

This form of \( \Phi \) is particularly convenient to use in describing droplet growth. When the gas is supersaturated, \( \mu_g \) is greater than \( \mu_l \) and \( \Phi \) behaves as \( Ar^2 - Br^3 + C \) where \( A \) and \( B \) are positive numbers. Therefore, \( \Phi \) passes through a maximum (see Figure 1) at \( r^* \) (given by \( r^* = 2A/3B \)), which is called the "critical droplet" radius.

Since \( \Phi \) spontaneously tends to a minimum under conditions of fixed \( T \) and \( P_g \), Figure 1 shows that drops smaller than the critical droplet tend to evaporate while larger drops grow through condensation. Thus the barrier to homogeneous nucleation is the formation of the critical droplet.

This behavior is also predicted by the Young-Laplace equation for the pressure differential across a curved surface. Let \( P_l \) and \( P_g \) be the pressures on the inside and outside of the droplet respectively. The Young-Laplace equation, which is the condition for mechanical stability of the drop, states:

\[ P_l - P_g = 2\sigma/r \] (9)
Figure 1. $\phi$ vs. $r$.

For a plane interface ($r = \infty$), this reduces to the ordinary equilibrium condition that $P_L = P_g$. However, if the droplet is sufficiently small, the pressure on the inside of the droplet is so high that the droplet is unstable with respect to the gas phase. Therefore a gas may be supersaturated with respect to bulk liquid and yet be less than saturated with respect to small droplets. We are again led to the idea that small droplets tend to disperse while large droplets tend to grow and that there is a critical droplet in meta-stable equilibrium with the supersaturated gas.

To find the radius of the critical droplet, $\left(\frac{\partial \phi}{\partial r}\right)$ is set equal to zero giving:
\[ r* = -2\sigma / \{ \rho_g [\mu_l(T,P_g) - \mu_g(T,P_g)] \} \]  
(10)

The chemical potential difference is evaluated by applying the Gibbs-Duhem equation at constant temperature, \( \rho d\mu = dP \). Then,

\[ \mu_l(T,P_g) - \mu_g(T,P_g) = \int_{P_\infty}^{P_g} \left( \frac{1}{\rho_l} - \frac{1}{\rho_g} \right) dP \]  
(11)

where \( P_\infty \) is the vapor pressure of the bulk liquid and we have used the fact that \( \mu_l(T,P_\infty) = \mu_g(T,P_\infty) \). If the liquid is considered to be incompressable and the vapor ideal, the integration gives

\[ \mu_l(T,P_g) - \mu_g(T,P_g) = \frac{1}{\rho_l} (P_g - P_\infty) - kT \ln(P_g/P_\infty) \]  
(12)

Since the first term on the right side of equation (12) is generally negligible compared with the second, equation (12) for the critical droplet size becomes:

\[ r* = 2\sigma / \{ \rho_l kT \ln(P_g/P_\infty) \} \]  
(13)

Equation (13) is the well known Gibbs-Thompson equation, which relates the size of the critical drop to the degree of supersaturation, \( P_g/P_\infty \). Note that as the degree of supersaturation is increased, the size of the critical drop decreases and the critical drop is more readily formed through fluctuations.

The simplest form of homogeneous nucleation theory, first proposed by Volmer and Weber\(^3\) and later modified by Becker and Doring\(^4\), is a form of transition state theory where the rate of condensation is pictured as the rate at which molecules hit critical droplets, thus becoming trapped in the liquid phase. In this theory, the rate equation contains two factors, one for the concentration of the critical droplets; the other, a standard kinetic factor.
describing the rate at which molecules impinge on a sphere of radius \( r^* \). The more sensitive factor is the concentration of critical droplets, which is taken to be proportional to \( \exp(-\Phi(r^*)/kT) \), where \( \Phi(r^*) \) is the thermodynamic potential of the critical droplet.

Several assumptions have been made in the development of the classical theory of nucleation, some about the kinetic nature of the problem and others relating the thermodynamic potential. The theory is generally quite insensitive to the kinetic assumptions but quite sensitive to the thermodynamic potential. Assumptions which have been made, whether explicitly or implicitly, in our development of the thermodynamic potential are:

1) The interface between the liquid and gas is sharp so that the radius of curvature and surface area of the drop are well defined.
2) The density inside the drop is constant and equal to the density of the bulk liquid.
3) The surface tension is independent of the radius of curvature.
4) The chemical potential of the supersaturated gas is a well defined, continuous function of the pressure.
5) Mechanically stable drops exist at all radii from \( r = 0 \) to \( r = \infty \).

Because these assumptions have been made, the only information about the critical droplet available from the classical theory is the radius. In order to obtain more information about droplet growth and structure, it is necessary to make the thermodynamic potential more detailed. That is, let \( \Phi \) depend on interface thickness, interior density, and the number of particles. Then it is not necessary to build in mechanical stability by introducing an assumed surface tension. Rather, a well defined geometry will correspond to a minimum in the thermodynamic potential and we will find out
whether or not a specific droplet structure is stable. We may then ask, using the more detailed form for the thermodynamic potential, does the notion of a well defined critical droplet arise? From our work, we hope to determine whether or not a critical droplet exists in a well defined model, and if it does, to find its interior density, interface thickness, and radius. Then it may be determined whether any changes in the classical theory of homogeneous nucleation theory are required.

The idea of expressing the thermodynamic potential as a function of the detailed structure parameters of the interface was first suggested by van der Waals in his work on plane interfaces. Cahn and Hilliard have extended this method by expressing the thermodynamic potential near the critical point as a power series in the density gradient. Their work on plane interfaces shows that the interface thickness becomes infinite as the critical temperature is approached. They then applied this same series expansion method to droplets. The major result of this treatment is that the structure of the critical droplet is dependent on the degree of supersaturation. At low supersaturation, the critical droplet compares very closely to the classical droplet in all properties of the droplet such as the work required to form the nucleus, the radius of the critical drop, densities inside and outside the drop, etc. At higher supersaturation, the critical droplet differs from the classical droplet in several ways. For example, the work in forming the critical droplet is less than that predicted for the classical droplet, the pressure and density at the center of the
droplet are less than in the classical droplet, the radius of the droplet is less than the radius of the classical droplet at first, but passes through a minimum and then increases with increasing supersaturation, and the thickness of the interface is, in general, greater than that of a plane interface between two equilibrium phases. These trends in the properties of the critical droplet each approach a limit at the maximum degree of supersaturation. That is, at the limit of supersaturation, the work required to form the critical droplet approaches zero, the density at the center of the droplet approaches the density of the bulk supersaturated gas outside the droplet, the radius becomes infinite, and the droplet is not homogeneous. This is to say that random fluctuations in the density of a supersaturated gas are more likely to result in the formation of a critical droplet, and therefore cause condensation to occur, as the degree of supersaturation increases.

Yang, Fleming, and Gibbs developed the method further by expanding the Helmholtz free energy in a power series of density derivatives and minimizing this free energy expression. Using this approach, they have provided a microscopic formulation of the surface tension and a differential form of the Young-Laplace equation, and generalized the method to include the presence of an external field.

The above methods are characterized by a series expansion of the thermodynamic potential in terms of the density gradient. This expansion limits the utility of the method to temperatures near the critical temperature where the interface thickness is large. This
limitation can be avoided by using a lattice model and calculating the thermodynamic potential from first principles. This approach has been used by Ono and Kondo\(^9\) who applied the Bragg-Williams approximation\(^10\) to an inhomogeneous system to determine the equilibrium density profile for a plane interface. Parlange\(^11\) has used the lattice approach, applying the Bethe approximation\(^12\), to arrive at the general difference equations for the thermodynamic potential at temperatures well below the critical temperature. He has, however, restricted his solutions to these equations to temperatures near the critical temperature where the difference equations can be replaced by differential equations.

Our approach to this problem will be to generalize the cluster variation method\(^13,14,15\) to make it applicable to droplets, calculate the thermodynamic potential as a function of the detailed structure of the droplet and investigate the behavior of this potential as it relates to the theory of homogeneous nucleation.
CHAPTER II

DESCRIPTION OF THE METHOD

In a lattice gas model\textsuperscript{16}, particles may be located only at specific sites, determined by the geometry of the lattice. Figure 2 shows two-dimensional square and triangular lattices. Each site may be unoccupied or occupied by one particle and the energy depends on the occupation pattern, according to the choice of the model. A site density is then defined as the average occupancy of a site in a large collection of identical lattices. Because each lattice site has a maximum occupancy of one, the site density is numerically equal to the probability that the site is occupied.

(a) Square

(b) Triangular

Figure 2. Two dimensional lattices
The approximation method chosen for our work is the Bethe (or quasi-chemical) approximation, which is one of a class of approximations known as the cluster variation method. The attraction of this method for our problem is the fact that thermodynamic relations are directly related to the bulk density in the case of a uniform system. For a non-uniform system, it is relatively easy to relate thermodynamic functions to local densities. The approach taken here is to relate the thermodynamic potential to local densities in the droplet, then to examine the potential as droplet parameters are varied.

In this paper, the cluster variation method will be explained only briefly. For a more detailed treatment, see references 11,14,15,17,18. A general outline of the steps involved is as follows:

1) The geometry of the lattice is chosen. In two dimensions, common choices are the square and triangular lattices as shown in Figures 2a and 2b.

2) A "basic figure" is chosen. For the two dimensional triangular lattice, possible choices are a) the point - (*), b) the bond (*-*), c) the triangle (**) etc. The size of the basic figure determines the accuracy of the approximation.

3) List all possible configurations of the basic figure and its subfigures (formed by overlap of two basic figures) by distributing particles on the lattice sites of the figures. For example, a site may be empty (o) or filled (*), a bond may be empty (o-o), half filled (o-*), or completely filled (*-*).

4) Consistency conditions are written for the probabilities of all configurations of all figures. For example, the probabilities of the configurations of the bond must be consistent with the probabilities of the sites contained in the bond.

5) The configurational free energy of the system is written in terms of these probabilities.
6) The configurational free energy is minimized with respect to the independent probabilities other than the site densities. This minimization results in a set of simultaneous, non-linear algebraic equations.

7) Solve the system of equations developed in step 6. This results in expressions for the probabilities of the basic figure and its subfigures in terms of the site densities.

8) The resulting free energy is used to construct the thermodynamic potential, which in turn is the starting point for numerical work.

As a specific example of the cluster variation method, we will next go through the eight steps listed above as they apply to our research.

1) The lattice chosen for our work is the two dimensional triangular lattice (Figure 2b), with nearest neighbor interactions. That is, the interaction energy between two particles is:

\[ \omega = -\varepsilon \text{ if the particles occupy adjacent sites on the lattice} \]
\[ \omega = 0 \text{ otherwise} \]

2) The basic figure chosen is the bond. It has been shown that the choice of this basic figure, with nearest neighbor interactions, is equivalent to the Bethe approximation.

3) Let the probability that a figure is in a specific configuration be denoted by \( p(C) \). That is, the probability that site \( i \) is filled is written: \( p(*i) \). Then the probabilities of the various bond configurations are:

\[ p(*i-*j) = \text{probability that the nearest neighbor sites } i \text{ and } j \text{ are both filled} \]
\[ p(o_i-*j) = \text{probability that site } i \text{ is empty while site } j \text{ is filled} \]
\[ p(*i-o_j) = \text{probability that site } j \text{ is empty while site } i \text{ is filled} \]
\[ p(o_i-o_j) = \text{probability that sites } i \text{ and } j \text{ are both empty} \]
and the probabilities of the subfigures, in this case individual sites, are:

\[ p(*)_i = \text{probability that site } i \text{ is filled} \]
\[ p(o_i) = \text{probability that site } i \text{ is empty} \]

4) Consistency and normalization conditions leave only two independent probabilities which we take to be:

\[ p(*)_i \equiv \rho_i \text{ and } p(*)_i = \chi_{ij} \]

Then:

\[ p(*)_i - o_j = \rho_i - \chi_{ij} \]
\[ p(o_i - *)_j = \rho_j - \chi_{ij} \]
\[ p(o_i - o_j) = 1 - \rho_i - \rho_j + \chi_{ij} \]

and

\[ p(o_i) = 1 - \rho_i \]

5) The configurational free energy is

\[ F' = U' - TS' \]

where

\[ U' = \sum_C p(C) U'(C) \]

and

\[ S' = -k \sum_C p(C) \ln(p(C)) \]

where \( U'(C) \) is the energy of configuration \( C \) of the lattice system.

(We are using primes on \( F, U \) and \( S \) to denote just the configurational contributions to these quantities.) Using the cluster variation method with the bond as the basic figure, the configurational free energy is approximated by:

\[ F' = \sum_{ij} \left[ -\varepsilon \chi_{ij} \right] - T \left[ \sum_{ij} S_b(ij) \right] - 5 \sum_i S_s(i) \]

where

\[ S_b(ij) \equiv -k \left[ \chi_{ij} \ln \chi_{ij} + (\rho_i - \chi_{ij}) \ln(\rho_i - \chi_{ij}) + (\rho_j - \chi_{ij}) \ln(\rho_j - \chi_{ij}) \right. \]
\[ + \left. (1 - \rho_i - \rho_j + \chi_{ij}) \ln(1 - \rho_i - \rho_j + \chi_{ij}) \right] \]

\[ (15a) \]

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and \( S_g(i) \equiv -k[\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)] \) (15b)

where \( \sum_{ij} \) is a sum over all bonds in the lattice system and \( \sum_i \) is a sum over all sites.

6) The configurational free energy as written in step 5) is minimized with respect to \( \chi_{ij} \). This minimization results in:

\[
0 = -\varepsilon + kT \ln \frac{X_{ij}(1 - \rho_i - \rho_j + \chi_{ij})}{(\rho_i - \chi_{ij})(\rho_j - \chi_{ij})} \tag{16}
\]

Note that \( \chi_{ij} \) depends only on \( \rho_i \) and \( \rho_j \); consequently all bond probabilities depend only on the densities of the two sites in the bond and we will write \( \chi_{ij}(\rho_i, \rho_j) \) to express the functional dependence of \( \chi_{ij} \) on the two site densities.

7) This equation is a quadratic in \( \chi_{ij} \) and, therefore, has two roots, only one of which has physical significance.

Then, \( \chi_{ij} = \frac{-b - (b^2 - 4ac)^{1/2}}{2a} \) (17)

where \( a = \exp(\varepsilon/kT) - 1 \)

\[ b = \rho_i + \rho_j - 1 - (\rho_i + \rho_j)\exp(\varepsilon/kT) \]

and \( c = \rho_i \rho_j \exp(\varepsilon/kT) \)

8) The free energy is now obtained for a given density pattern form equations (15) and (17). This is incorporated into our thermodynamic potential (see Appendix I) for the droplet, which has the form:

\[
(\Psi - \Psi^\infty) = (F'_i - F'_g) - kT \ln(Z) \sum_i (\rho_i - \rho_\infty) \tag{18}
\]

where \( \rho_\infty \) is the density in a uniform (supersaturated) gaz, \( Z \) is its activity, and \( F'_g \) is the corresponding free energy. The set of
densities $\rho_i$ represents the droplet system with $F$ as the corresponding free energy. Values of $\rho_i$ are high in the droplet region and approach asymptotically the density $\rho_\text{g}$ outside the droplet. When equation (18) is combined with equation (15) we obtain:

$$
(\Psi - \Psi_\infty) = \sum_{i,j} \epsilon (\chi_{i,j}(\rho_i \rho_j) - \chi_{i,j}(\rho_\text{g} \rho_\text{g}))
$$

$$
- T \sum_{i,j} \left( S_b(\rho_i \rho_j) - S_b(\rho_\text{g} \rho_\text{g}) \right) - 5 \sum_i \Sigma \left( S_s(\rho_i) - S_s(\rho_\text{g}) \right)
$$

$$
- kT \ln(Z) \sum_{i} (\rho_i - \rho_\text{g})
$$

In our research, we used two methods of determining the critical droplet structure. The first was to choose $\ln(Z)$ corresponding to a supersaturated gas and solve for the critical droplet parameters (as outlined below), and the second was a direct investigation of the dependence of $(\Psi - \Psi_\infty)/kT$ on droplet parameters.

In calculating the thermodynamic potential, three parameters must be specified, the temperature variable $\epsilon/kT$, the activity $Z$, and the density of the supersaturated vapor $\rho_\text{g}$. $\epsilon/kT$ was chosen by examining $\ln(Z)$ as a function of density in homogeneous systems (i.e., $\rho_i = \rho_j$ for all $i$ and $j$) for various values of $\epsilon/kT$. Below the critical temperature, the graph of $\ln(Z)$ exhibits a van der Waals loop indicating a phase transition as shown in Figure 3. The equilibrium liquid and gas densities are given by the Maxwell equal areas construction as shown in Figure 4. After choosing a value of $\epsilon/kT$, a value of $\ln(Z)$ is chosen from the region corresponding to a supersaturated gas. This region is bounded by the equal areas tie-line and the local maximum in the graph of $\ln(Z)$ vs. $\rho$ (see Figure 4).
Figure (3). $\ln(Z)$ vs. $\rho$ at various temperatures in a homogeneous system. Values of the temperature variable, $\varepsilon/kT$, are in parentheses.
Finally, a value for $\rho_g$ is determined for the chosen values of $\epsilon/kT$ and $\ln(Z)$.

To solve for the critical droplet structure, it is first recognized that the critical droplet corresponds to the droplet for which $\frac{\partial (\psi - \psi_\infty)}{\partial \rho_i} = 0$ at all sites in the lattice. For the model we have chosen, we have (from equation (18)),

$$\frac{\partial (\psi - \psi_\infty)}{\partial \rho_i} = \frac{\partial F'}{\partial \rho_i} - kT \ln(Z) = 0 \quad \text{for all } i \quad (20)$$

It has been argued that it should be possible to use the difference equation resulting from equation (20) to solve for the density profile of the critical droplet. An acceptable solution has a high density at the center of the droplet and asymptotically approaches the bulk supersaturated gas density far from the center of the droplet. We could not find such a solution. For a given temperature, activity and interior density the difference equation produces a profile, but none could be found with the proper asymptotic behavior, regardless of the choice of $\ln(Z)$ and $\rho_o$, where $\rho_o$ is the initial density at the central point of the droplet (see Figure 5). This approach was, therefore, abandoned in favor of constructing the thermodynamic potential as an explicit function of the droplet structure parameters. This approach has the added attraction of providing considerably more information about the critical and near critical droplets.
C. Calculation of the Thermodynamic Potential

Various sets of $\varepsilon/kT$, $\ln(Z)$, and $\rho_g$ were chosen according to the procedure outlined above. As all of these sets displayed the same qualitative features, one set was chosen for complete analysis: $\varepsilon/kT = 1.20$, $\ln(Z) = -3.27640$, and $\rho_g = 0.100$. For comparison, the value of $\varepsilon/kT$ at the critical point is 0.8109\textsuperscript{20}. These parameters correspond to a supersaturation ratio of $P_g/P_\infty = 1.616$. The droplet profile was then modeled by:

$$\rho_i = ((\rho_{\text{int}} - \rho_g)/2.0) (-\tanh(\frac{X-R}{\Delta L})) + (\rho_{\text{int}} + \rho_g)/2.0 \quad (21)$$
where $\rho_{\text{int}}$ is the high density limit in the liquid region, $x$ is the distance from the center of the drop to the site $i$, $r$ is the radius of the drop, and $\Delta l$ is a measure of the interface thickness. Figure 6 shows two density profiles having the same $\rho_{\text{int}}$, $\rho_g$, and $r$ but different $\Delta l$. It should be noted that if $\Delta l$ is large, the density at the center of the droplet will not be equal to $\rho_{\text{int}}$ but will have the value

$$\rho_0 = \frac{1}{2} \left( (\rho_{\text{int}} - \rho_g) + (\rho_{\text{int}} + \rho_g) \right)$$

as shown in Figure 6b. The distances $x$, $r$, and $\Delta l$ are all in units of the lattice spacing. When equation (21) is substituted into equation (19), we obtain an expression for $(\Psi - \Psi_\infty)$ as a function of $\rho_{\text{int}}$, $\Delta l$, and $r$.

Once the above variables, that is, $\varepsilon/kT$, $\ln(Z)$, $\rho_g$, $N_d$, $r$, and $\Delta l$, are chosen the droplet is completely specified and the thermodynamic potential can be calculated. The programs required are included in Appendix 3 with a brief explanation. The data generated by these programs are then read and plotted as $(\Psi - \Psi_\infty)/kT$ vs. $r$ holding $\Delta l$ and $N_d$ fixed. A typical plot is shown in Figure 7.
Figure (6a). Two density profiles having $r = 5.0$ as modeled by equation (21).

Figure (6b). Model droplet profile when $\Delta l$ is of the same magnitude as $r$. Here $r = 2.0$ and $\Delta l = 3.0$. 

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CHAPTER III

RESULTS

Figure 7 shows that a droplet of 19 particles has a local minimum in \((\Psi - \Psi_\infty)/kT\) between \(\Delta \lambda = 1.4\) and 1.8 for \(r\) between 2.2 and 2.4, indicating a mechanically stable droplet. All droplets investigated with \(N_d \geq 17\) displayed such a minimum, but for \(N_d\) less than 17 there is no local minimum in the thermodynamic potential indicating that these droplets \((N_d < 17)\) would disappear by expanding, with a concomitant decrease in \(\rho_o\), until the density inside the droplet became equal to the density of the bulk supersaturated gas.

In order to locate the minimum in \((\Psi - \Psi_\infty)/kT\) for each \(N_d\) more exactly, contours of \((\Psi - \Psi_\infty)/kT\) in the \((r, \Delta \lambda)\) surface were plotted. Typical contours are shown for \(N_d = 16\) and \(N_d = 17\) in Figures 8a and 8b respectively. Using this method, we were able to locate local minima to within \(\pm 0.01\). The structure parameters for droplets with \(N_d \geq 17\) are listed in Table I. These data are plotted in Figure 9 as \((\Psi - \Psi_\infty)/kT\) vs. \(r\). A maximum in the thermodynamic potential for mechanically stable droplets occurs for \(N_d = 17\), identifying this as the critical droplet.

The surface tension is also available. The thermodynamic potential was defined: (see equation (18))

\[
\Psi = F' - kT(\ln(Z))N
\]

or equivalently,

\[
\Psi = F - \mu N
\]
Figure (8b). Contours of $(\psi - \psi_{\infty})/kT$ above the $(r, \Delta \ell)$ plane for $N_d = 17$. 
<table>
<thead>
<tr>
<th>$N_d$</th>
<th>$\rho_o$</th>
<th>$\Delta l$</th>
<th>$r$</th>
<th>$(\Psi - \Psi^\infty)/kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0.5696</td>
<td>2.088</td>
<td>2.440</td>
<td>0.70605</td>
</tr>
<tr>
<td>18</td>
<td>0.6174</td>
<td>1.880</td>
<td>2.520</td>
<td>0.69082</td>
</tr>
<tr>
<td>19</td>
<td>0.6583</td>
<td>1.759</td>
<td>2.561</td>
<td>0.66057</td>
</tr>
<tr>
<td>20</td>
<td>0.6892</td>
<td>1.670</td>
<td>2.618</td>
<td>0.61706</td>
</tr>
<tr>
<td>21</td>
<td>0.7161</td>
<td>1.620</td>
<td>2.660</td>
<td>0.56123</td>
</tr>
<tr>
<td>22</td>
<td>0.7446</td>
<td>1.560</td>
<td>2.725</td>
<td>0.49395</td>
</tr>
<tr>
<td>23</td>
<td>0.7698</td>
<td>1.540</td>
<td>2.780</td>
<td>0.32800</td>
</tr>
<tr>
<td>24</td>
<td>0.7885</td>
<td>1.500</td>
<td>2.820</td>
<td>0.230659</td>
</tr>
<tr>
<td>25</td>
<td>0.8075</td>
<td>1.480</td>
<td>2.860</td>
<td>0.12475</td>
</tr>
<tr>
<td>26</td>
<td>0.8257</td>
<td>1.460</td>
<td>2.920</td>
<td>0.01092</td>
</tr>
<tr>
<td>27</td>
<td>0.8362</td>
<td>1.440</td>
<td>2.960</td>
<td>-0.11031</td>
</tr>
<tr>
<td>28</td>
<td>0.8528</td>
<td>1.420</td>
<td>3.020</td>
<td>-0.23835</td>
</tr>
<tr>
<td>29</td>
<td>0.8614</td>
<td>1.400</td>
<td>3.060</td>
<td>-0.37276</td>
</tr>
<tr>
<td>30</td>
<td>0.8712</td>
<td>1.400</td>
<td>3.100</td>
<td>-0.51264</td>
</tr>
<tr>
<td>31</td>
<td>0.8842</td>
<td>1.400</td>
<td>3.168</td>
<td>-0.65805</td>
</tr>
<tr>
<td>32</td>
<td>0.8870</td>
<td>1.384</td>
<td>3.210</td>
<td>-0.80815</td>
</tr>
<tr>
<td>33</td>
<td>0.8973</td>
<td>1.376</td>
<td>3.270</td>
<td>-0.96283</td>
</tr>
<tr>
<td>34</td>
<td>0.8995</td>
<td>1.374</td>
<td>3.320</td>
<td>-1.12174</td>
</tr>
<tr>
<td>35</td>
<td>0.9046</td>
<td>1.374</td>
<td>3.560</td>
<td>-1.97020</td>
</tr>
<tr>
<td>40</td>
<td>0.9282</td>
<td>1.360</td>
<td>3.820</td>
<td>-2.89191</td>
</tr>
<tr>
<td>45</td>
<td>0.9355</td>
<td>1.340</td>
<td>4.280</td>
<td>-4.88662</td>
</tr>
<tr>
<td>55</td>
<td>0.9482</td>
<td>1.320</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Then, from equation (2),

\[ \psi - \psi_\infty \approx \phi - \phi_\infty - N_d \mu \]  

(24)

If we assume \( \phi - \phi_\infty \) is given by the simple thermodynamic theory, then from equation (12).

\[ \psi - \psi_\infty \approx (\mu_\ell - \mu_g) \rho_\ell V_d + \sigma A \]  

(25)

where \( V_d \), the volume of the droplet, and \( A \) the surface area are modified for the dimensionality of the lattice (see Appendix 1). According to equation (25), if \( (\psi - \psi_\infty)/V_d \) is plotted vs. \( A/V_d \), the slope is \( \sigma \). The approximate equation (25) motivates us to define the surface tension as the linear coefficient in the power series expansion of \( (\psi - \psi_\infty)/V_d \) in the variable \( A/V_d \), that is:

\[ \sigma = \lim_{A/V_d \to 0} \frac{d[(\psi - \psi_\infty)/V_d]}{d(A/V_d)} \]

Figure 10 shows that \( (\psi - \psi_\infty)/V_d kT \) vs. \( A/V_d \) is a straight line until the size is very close to that of the critical droplet; then significant deviations occur. The value of the surface tension \( (\sigma/kT) \) taken from this curve, is 0.3907 in units of reciprocal lattice length.

Figures 11 and 12 show that the interior density and interface thickness respectively, approach their bulk limits as droplet size increases. The equilibrium liquid density, obtained from the plot of \( \ln(Z) \) vs. \( \rho \) is 0.955. This compares favorably with the apparent limit of \( \rho_0 \) as \( r \) becomes large.

**DISCUSSION**

The Bethe approximation applied to a two dimensional triangular lattice, in accordance with the classical theory, predicts a critical
Figure (10). \((\psi - \psi_\infty)/kTr^2\) vs. \(1/r\). Data are listed in Table I.
droplet. By writing the thermodynamic potential in a detailed form, we were able to characterize the critical droplet and compare the results with the classical theory.

In the classical picture, the critical droplet has a sharp interface, an interior density equal to the density of the bulk liquid and a surface tension equal to that of a plane interface. The radius of the critical droplet may be calculated from the two dimensional analog of equation (13) using the value of $\sigma/kT$ obtained from the straight line portion of Figure 10. Before using equation (13), however, a value for $\rho_L(\ln(P_g/P_\infty))$ must be obtained. Two methods are available for obtaining $\rho_L(\ln(P_g/P_\infty))$. The first is from a straightforward calculation of $P_g$ and $P_\infty$ from:

$$PV = \mu N - F = NkT(\ln(Z)) - F'$$

or

$$P/kT = \rho L(\ln(Z)) - F'/kTV$$

Then using the equilibrium liquid density for $\rho_L$ in units of the lattice spacing, $L$, (see Appendix 2 for the connection between $d$, the unit distance defined by the unit cell volume and the more convenient unit of lattice spacing, $L$.) we find:

$$B \equiv \rho_L(\ln(P_g/P_\infty)) = 0.5296 L^{-2}$$

Finally, using equation (13), $r^* = 0.7378 L$. The second method of obtaining $B$ is from the intercept of Figure 10. The equation of the least squares line fitting the straight line portion of the graph is
\[
\frac{(\Psi - \Psi_\infty)}{kT} = 2.4551(1/r) + (-0.84195)
\]

Comparing this with:
\[
\frac{(\Psi - \Psi_\infty)}{kT} = 2\pi(\sigma/kT)(1/r) - \text{B}\pi
\]

We see:
\[-\text{B}\pi = -0.84195\]

or
\[\text{B} = 0.2680 \text{ L}^{-2}\]

This results in \(r^* = 1.4578 \text{ L}\). The classical value of \((\Psi - \Psi_\infty)/kT\) can be calculated from equations (25) and (12). Using \(\text{B} = 0.5296 \text{ L}^{-2}\) and \(r^* = 0.7378 \text{ L}\), we find \((\Psi - \Psi_\infty)/kT = 0.90556\). Using \(\text{B} = 0.2680 \text{ L}^{-2}\) and \(r^* = 1.4578\), \((\Psi - \Psi_\infty)/kT = 1.7893\). This discrepancy points out the weakness of assuming that bulk properties hold for the critical droplet.

As a result of our calculation, we found the critical droplet to be considerably more diffuse than predicted by the classical theory. That is, we found \(r^*\) to be \(2.440 \text{ L}\) (as compared to \(0.7378 \text{ L}\) or \(1.4578 \text{ L}\)) with an interface thickness of \(2.088 \text{ L}\) (compared to the bulk limit of \(1.30 \text{ L}\)) and an interior density of \(0.65772 \text{ L}^{-2}\) (compared to the bulk liquid density of \(1.1027 \text{ L}^{-2}\)). The calculated value of \((\Psi - \Psi_\infty)/kT\) is \(0.70605\). The classical predictions of \((\Psi - \Psi_\infty)/kT\) are \(0.90556\) and \(1.7893\). Because the concentration of critical droplets is proportional to \(\exp(-\Psi/kT)\), our calculations indicate that critical droplets are higher in concentration than predicted by the classical theory.

The surprising result of our calculation is the qualitative picture that the critical droplet cannot form by the addition of
particles to mechanically stable, sub-critical droplets in thermal equilibrium with the system because, in this approximation, no such droplets exist. This result is consistent with recent molecular dynamics calculations on small clusters in a supersaturated vapor done by Zurek and Schieve\textsuperscript{21}. Therefore, some other path is required. This is an important result because the standard kinetic schemes for homogeneous nucleation are based on the existence and growth of sub-critical droplets in an essential way\textsuperscript{20}, indicating that a fundamentally different approach to homogeneous nucleation is required.
BIBLIOGRAPHY


APPENDIX I

Development of the Thermodynamic Potential.

Using the grand canonical ensemble, where \( T \) - the temperature of the system, \( V \) - the volume, and \( \mu \) - the chemical potential are all fixed, the probability of a configuration \( (C) \) is:

\[
p(C) = \frac{Z^N(C) \exp(-U'(C)/kT)}{\Xi}
\]

(A1)

where \( Z = \exp(\mu/kT)(\Delta L/\Lambda)^n \)

(A2)

and \( \Xi = \sum C^N(C) \exp(-U'(C)/kT) \)

In the expression for \( Z \), the activity, \( \Delta L^n \) is the cell volume for the lattice; \( \Lambda \) is the thermal deBroglie wavelength, \( (2\pi m kT/h^2)^{1/2} \); \( n \) is the dimensionality of the lattice; and \( N(C) \) and \( U(C) \) are the number of particles and the energy, respectively, for a configuration.

For our study of nucleation in a supersaturated gas, we wish to develop an expression for the probability of a droplet relative to the probability of a supersaturated gas. Therefore, we define \( \{g\} \) to be the set of all configurations corresponding to a uniform supersaturated gas at a density \( \rho_g \). Then: \( p(\{g\}) = \) the probability of a supersaturated gas.

\[
p(\{g\}) = \sum_{CC\{g\}} p(C)
\]

(A3)

where \( \sum_{CC\{g\}} \) denotes the summation of all states belonging to the set \( \{g\} \).

Let \( p(C|\{g\}) = p(C)/p(\{g\}) \)

(A4)
and
\[ F'(\{g\}) = \sum_{C \in \{g\}} p(C|\{g\})U(C) - TS(\{g\}) \] (A5)

where
\[ S'(\{g\}) = -k \sum_{C \in \{g\}} p(C|\{g\})\ln p(C|\{g\}) \] (A6)

Using equations (A1), (A2), (A3), and (A4), we may write equation (A6) as:
\[ S(\{g\}) = -k \sum_{C \in \{g\}} p(C|\{g\})\ln \left[ \frac{Z^N(C)\exp(-U(C)/kT)}{p(\{g\})} \right] \] (A7)

and the expression for \( F'(\{g\}) \), equation (A5) simplifies to:
\[ F'(\{g\}) = kT(\langle N \rangle \ln Z - \ln \Xi - \ln p(\{g\})) \] (A8)

where \( \langle N \rangle = \sum_{C \in \{g\}} p(C|\{g\})N(C) \)

and after rearrangement,
\[ p(\{g\}) = \frac{Z^{\rho g V} \exp(-F'(\{g\})/kT)}{\Xi} \] (A9)

where the relation \( \langle N \rangle = \rho g V \) has been used.

We next develop an expression for the probability of a drop embedded in a supersaturated vapor at density \( \rho g \).

The system is characterized by \( \rho g, N_d, V_d, N, A, V, \) and \( T \), where \( N \) is the total number of particles in the system, \( N_d = N - \rho g V \), \( V_d \) is the volume of the drop, and \( A \) is the surface area of the drop. The volume and surface area of the drop will be dependent on the dimensionality of the lattice. That is, in three dimensions the volume of a sphere is \( V = \frac{4}{3} \pi r^3 \) where \( r \) is the radius of the sphere, and the surface area is \( A = 4\pi r^2 \). In two dimensions, the analogous equations are \( V = \pi r^2 \) and \( A = 2\pi r \). Then, let \( \{D\} \) be defined as the set of all configurations characterized by \( \rho g, N_d, V_d, A, N, V, \) and \( T \). Following the same procedure as above, we find:
Finally, from equations (A9) and (A10), the probability of a drop relative to a uniform supersaturated vapor, is written:

$$p(D) = \frac{Z\rho g V + N_d}{\Xi} \exp(-F'(D)/kT)$$  

(A10)

$$Q = \frac{p(D)}{p(g)} = \exp[-F'(D) - F'(g)/kT - N_d \ln(Z)]$$  

(A12)

If we define

$$\Psi = F(D) - (\rho g V + N_d)kT \ln(Z)$$

and

$$\Psi_\infty = F(g) - (\rho g V)kT \ln(Z)$$

we see from equation (A12) that the thermodynamic potential we wish to examine is:

$$(\Psi - \Psi_\infty)/kT = (F'(D) - F'(g))/kT - N_d \ln(Z)$$  

(A13)
The natural unit to express density is determined by the volume of the unit cell. This allows us to place one particle on one site by setting $\rho_1 = 1$. This is not a convenient unit to use in measuring distances. Therefore, we develop the relationship between $d$, the distance determined by the unit cell, and $L$, the lattice spacing.

The unit cell for the two dimensional triangular lattice is shown below.

The "volume" of this unit cell is given by

$$d^2 = 12\left(\frac{1}{2}\right)\left(\frac{L}{2}\right)\left(\frac{L}{2}\tan \theta\right)$$

and, since $\theta = 30^\circ$,

$$d^2 = \frac{12 L^2}{8\sqrt{3}}$$
APPENDIX 3

The programs listed here were used in the calculation of \( (\psi - \psi_\infty)/kT \). Variables used are defined in the comment statements. The main program calculates the interior density of the droplet having radius RAD and interface thickness THICK such that the specified value for \( N_d \) is obtained. This is done by an interval halving routine in the subroutine package. The droplet parameters are then written into FOR23.DAT. THICK is incremented in line 110 with the maximum value determined by the line following line 110. RAD is incremented in line 150 with the maximum value determined in the next line.

The subroutine CHEMPO reads data from FOR23.DAT, calculates \( (\psi - \psi_\infty)/kT \) for the specified droplet, and writes all droplet parameters, \( (\psi - \psi_\infty)/kT \), and the first and second differences of \( (\psi - \psi_\infty)/kT \) on the lineprinter and the droplet parameters and \( (\psi - \psi_\infty)/kT \) into FOR24.DAT. Key variables in CHEMPO are EPS — the value of \( \epsilon/kT \); XMU — the value of \( \ln(Z) \); SUM — the accumulator for the summation of \( \rho_i - \rho_g \); SUMSIT — the accumulator for the site entropies, SUMXIJ — the accumulator for the summation of \( \chi_{ij} \); SUMENT — the accumulator for the summation of bond entropies, and PHI — the final value of \( (\psi - \psi_\infty)/kT \). All summations were done in one sixth of the entire lattice. A hexagonal shape was chosen for the droplet so that the final value of PHI is six times the sum of the proper accumulators.
The program finds parameters for droplets containing a specified number of particles. The droplet profile is modeled by a hyperbolic tangent. Parameters controlling the profile are: radius of the drop; thickness of the interface; and point - the density at the center of the drop. Note: If the interface thickness is large and the radius is small, the central site will not have the density of point. Rather, the density will be calculated in the subroutine XNEXPT. The values of \( \epsilon/K_T, \mu/K_T, \) and \( R_{0(EXT)} \) are chosen to be consistent with each other.

```fortran
C --------------- FOR 2-DIM. TRIANGULAR LATTICE ---------------
C THIS PROGRAM FINDS PARAMETERS FOR DROPLETS CONTAINING
C A SPECIFIED NUMBER OF PARTICLES. SUBROUTINE PACKAGE
C MUST BE LOADED ALONG WITH THIS PROGRAM. DROPLET PROFILE
C IS MODELED BY A HYPERBOLIC TANGENT. PARAMETERS CONTROLLING
C THE PROFILE ARE: RAD - RADIUS OF THE DROP; THICK -
C THE THICKNESS OF THE INTERFACE; AND POINT - THE DENSITY
C AT THE CENTER OF THE DROP. (NOTE: IF THE INTERFACE
C THICKNESS IS LARGE AND THE RADIUS IS SMALL, THE CENTRAL
C SITE WILL NOT HAVE THE DENSITY OF POINT. RATHER,
C THE DENSITY WILL BE CALCULATED IN THE SUBROUTINE XNEXPT.
C THE VALUES OF \( \epsilon/K_T, \mu/K_T, \) AND \( R_{0(EXT)} \) ARE CHOSEN TO
C BE CONSISTENT WITH EACH OTHER.
C
COMM/A/AVE,HI,RAD,THICK,FOEXT,F01
COMMON/C/L,YLO,YMIC,YHI,CMU
DIMENSION R0(50)
C I IS THE NUMBER OF PARTICLES PER DROP IN THE FIRST SET
C OF DROPLETS, 12 IS THE NUMBER IN THE LAST SET.
C PROGRAM WILL CALCULATE 12-I SETS OF DROPLETS.
I=36; I=36
C IN THE LOOP I IS THE NUMBER OF PARTICLES PER DROP
DO 200 I=11,12
C INITIALIZE NECESSARY VARIABLES. CMU IS CHECK VALUE FOR
C INTERVAL HALVING ROUTINE
CMU=FLOAT(I)
RAD=0.50; TOL=0.001
FOEXT=0.10
THICK=0.20
C INTERVAL HALVING ROUTINE NEEDS SOME STARTING POINTS
XMID=0.6; XLO=0.3; XHI=0.99; YLO=POINT(XLO); YHI=POINT(XHI)
YMID=POINT(XMID); L=0
C XLO, XMID, & XHI ARE THREE VALUES FOR INITIAL DENSITY
C YLO, YMID, YHI ARE THE CORRESPONDING VALUES FOR # OF
C PARTICLES PER DROP
IF(YLO-CMU)*(YHI-CMU) GT 20, 10, 110
10 IF(YLO-CMU).LT.TOL)GO TO 15
WRITE(23,715)XHI,YHI,RAD,THICK;NUM=NUM+1;GO TO 100
15 WRITE(5,715)XLO,YLO,RAD,THICK
WRITE(23,715)XLO,YLO,RAD,THICK;NUM=NUM+1;GO TO 100
20 XMID=ROMID(XLO,XMID,XHI)
YMID=POINT(XMID)
IF(ABS(YMIC-CMU)-TOL).LE.0.0)GO TO 100
100 CONTINUE
F01=(XMIC-FOEXT)/2.*(-TANH(-RAD/THICK))+(XMIC+FOEXT)/2.
WRITE(23,715)XMID,YMIC,RAD,THICK,F01;NUM=NLM+1
C INCREASE THICK AND START OVER
THICK=THICK+0.20
IF(THICK.GT.5.0)GO TO 150; GO TO 2
```

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C INCREASE R.A. AND START OVER. THICK MUST BE RESET.
150 RAL=RAD+0.10
IF(RAD.LE.7.)GO TO 1
WRITE(5,720)NUM,CMU
200 CONTINUE
CLOSE(UNIT=23,ACCESS='SEGIN',MODE='ASCII')
CALL CHEMFO(NUM,11)
690 FORMAT(' R.A.&THICK')
700 FORMAT(' POINTS')
705 FORMAT(F)
710 FORMAT(' NO SOLUTION APPARENT')
715 FORMAT(5(F14.8))
720 FORMAT(' TOTAL OF',15,' DROPLETS WITH',F8.4,' PARTICLES')
730 FORMAT(4X,' POINT',6X,' PARTICLE',5X,' RADIUS',6X,
1'THICKNESS',5X,' R.O(C)')
END
FUNCTION TO CALCULATE THE ENTROPY OF A BONE HAVING SITE DENSITIES OF FO(I), FO(J)
FUNCTION SECNC(XIJ, FOI, FOJ)
SECNC= XIJ * ALOG(XIJ) + (FOI - XIJ) * ALOG(FOI - XIJ) + (FOJ - XIJ) * ALOG(FOJ - XIJ)
RETURN
END

FUNCTION TO CALCULATE THE ENTROPY OF A SITE WITH DENSITY FO
FUNCTION SSITE(FC)
SSITE= FO * ALOG(FO) + (1.0 - FO) * ALOG(1.0 - FO)
RETURN
END

FUNCTION XFIGGR(FO1, FO2)
COMMON/E/ECHS
A=ECHS*1.0
E=(FO1+FO2-1.0)-(FO1+FO2)*ECHS
C=ECHS*FO1*FO2
XFIGGR=(-E- SQRT(E*E-4.0*A*C))/(2.0*A)
RETURN
END

FUNCTION XNEXPT(X)
COMMON/A/AVE, HI, RAD, THICK, ROEXT, FO1
XNEXPT=HI* (-TANH((X-RAD)/THICK)) + AVE
PRINT 5, 900
RETURN
END

INTERVAL HALVING ROUTINE
FUNCTION ROMID(XLO, XMID, XHI)
COMMON/L/L, YLO, YMID, YHI, CMU
IF((YMID-CMU)*(YHI-CMU))S, 10, 15
5 XLO=XMID; YLO=YMID; XMID=(YMID+XHI)/2.0; GO TO 20
10 WRITE(S, 800) XMID
GO TO 20
15 XHI=XMID; YHI=YMID; XMID=(XLO+XMID)/2.0
20 L=L+1
ROMID=XMID
CALCULATE NUMBER OF PARTICLES IN 2-DIM HEXAGONAL DROP
FUNCTION POINT(POINT)
COMMON/A/AVE,HI,RAD,THICK,ROEXT,R01
P=2.*E;Z=(POINT-ROEXT)*5.*E
DO 50 L=1,28
X=FLOAT(L)
P=-E*X*(TANH((X-RAD)/THICK)-1.*E)+P
CONTINUE
P=-E*(TANH((E.0-RAD)/THICK)-1.*E)+P
POINT=P
RETURN
END

CALCULATE NUMBER OF PARTICLES IN 3-DIM DROP ON CUBIC LATTICE
FUNCTION DENCEE(POINT)
DIMENSION RO(15,15,15)
COMMON/A/AVE,HI,RAD,THICK,ROEXT
COMMON/CUBIE/ RO,POINTS
POINTS=0.0
AVE=(POINT+ROEXT)/2.0
HI=(POINT-ROEXT)/2.0
DO 100 I=1,15
DO 100 J=1,15
DO 100 K=1,15
N=1;COREC=1.0
IF(I.EQ.1)N=N+1
IF(J.EQ.1)N=N+1
IF(K.EQ.1)N=N+1
GO TO(40,10,20,30)N
10 COREC=0.500;GO TO 40
20 COREC=0.250;GO TO 40
30 COREC=0.125;GO TO 40
40 Z1=FLOAT(I-1);Z2=FLOAT(J-1);Z3=FLOAT(K-1)
X=SQRZ(Z1*Z1+Z2*Z2+Z3*Z3)
RO(I,J,K)=XEXP(X)
POINTS=POINTS+COREC*(RO(I,J,K)-ROEXT)
CONTINUE
DENCEE=8.*0*POINTS
RETURN
END
THIS PROGRAM READS DATA FOR THE LTOPS FOUND BY THE MAIN
PROGRAM. IT THEN CALCULATES PHI-PHI(INF). OUTPUT
IS TO THE LINE PRINTER AND FOR24.CAT. THE DATA FILE
IS USED IN THE FLOATING ROUTINES.

SUBROUTINE CH@MFO(NICE,NFT)
COMMON/E/ECHS
COMMON/H/AVE,HI,FAL,THICK,FOEXT,FO1
COMMON/L,L,YLO,YMIE,YHI,CHU
DIMENSION FO(50)
NUM=0
NUM=NUM+1
READ(3,800,END=550,ERR=516)FOINT,POINTE,FAL,THICK,FO1
IF(INT(POINT/0.01)*NE.NPT)GO TO 2
NFT=NFT+1
C STRANGE VALUES FOR FTEMP AND STEMPE GUARANTEE THAT UNDEFINED
VALUES ARE NOT PRINTED.
FTEMP=-999999999.9999999
STEMPE=-5.
WRITE(3,820)
2 N=30 ! SIZE OF ARRAY USED
EPS=1.2;ROEXT=0.10
XMU=-3.2764000
ECHS=EXP(EPS)
XIJINF=XFIGGR(FOEXT,ROEXT)
SSINF=SSITE(ROEXT)
SEINF=SBOND(XIJINF,ROEXT,ROEXT)
5 CONTINUE
C LOAD ARRAY AND TAKE SITE ORIENTED SUMS
HI=(FOINT-ROEXT)/2.0
AVE=(FOINT+ROEXT)/2.0
SUM=0.0
SUMSIT=0.0
SUMXIJ=0.0
SUMENT=0.0
DO 10 I=1,N+1
X=FLOAT(1)
RO(I)=XNEXPT(X)
SUMSIT=SUMSIT+X*(SSITE(RO(I))-SSINF)
SUM=SUM+X*(RO(I)-ROEXT)
10 CONTINUE
SUMMU=(SUM+(FO1-FOEXT)/6.0)*XMU
SUMSIT=5.0*(SUMSIT+(SSITE(RO1)-SSINF)/6.0)
C WORK OVER THE BONDS, TAKING POINT 1,1 AS A SPECIAL POINT
XIJI1=XFIGGR(RO1,RO(1))
XIJI1=XFIGGR(RO(1),RO(1))
XIJI2=XFIGGR(RO(1),RO(2))
SUMXIJ=SUMXIJ+(XIJI1+XIJI1+2.0*XIJI2-4.0*XIJIINF)
SUMENT=SUMENT+(SEOND(XIJI1,RO1,RO(1))SEOND(XIJI1,RO(3),RO(1))
1+2.0*SEOND(XIJI2,RO(1),RO(2))-4.0*SEINF)
C NOW GET THE REST OF THE BONDS
C
I=0
EC 20  I=2,N  
X=FLOAT(1)  
XIJIH=XFIGGR(RO(I),RO(I-1))  
XIJI=XFIGGR(RO(I),RO(I))  
XIJK=XFIGGR(RO(I),RO(I+1))  
SUMXIJ=SUMXIJ+(XIJIH+X*XJIJI+2.*X*XIJK-(3.*X+1)*XIJNI)  
SUMENT=SUMENT+SEONI(XIJIH,FO(I),FO(I-1))+X*SEONI(XIJI,FO(I), 
1,FO(I))+2.0*X*SEONI(XIJK,FO(I),FO(I+1))-(5.*X+1)*SEINF  
Z  CONTINUE  
C  
C  SUMXIJ=-EPS*SUMXIJ  
PHI=6.0*(SUMXIJ+SUMENT-SUMSIT-SUMMU)  
C  FLIF WILL BE THE FIRST DIFFERENCE, SLIF THE SECOND DIFFERENCE.  
FDIF=PHI-FTEMP  
SLIF=TEMP-FDIF  
FTEMP=PHI  
STEMP=FLIF  
C  FLAG POINTS TO EVERY FDIF GREATER THAN 0  
IF(FDIF.GT.0.0)FLAG=' <--->'  
500  WRITE(3,815)NUM,POINTS,RAD,THICK,POINT,PHI,RO1,FDIF,SLIF  
C  1,FLAG  
WRITE(24,825)FAL,THICK,PHI,POINTS  
FLAG='  '  
IF(NUM.LE.NICE)GO TO 1  
510  WRITE(5,805)NUM  
550  NUM=NUM-1  
WRITE(5,810)NUM,POINTS  
800  FORMAT(5F14.8)  
805  FORMAT( ' READ OUT ERROR AT RECORD # ',I4)  
810  FORMAT( ' DONE WITH ',I5, ' DROPLETS WITH ',F8.4, ' PARTICLES' )  
820  FORMAT( '1 NUM. PARTICLES',3X,' RAD',3X,' THICK', 
1,6X,' RO(INT)',7X,' PHI/KT RO(0)',7X,' FIRST DIFF.'  
2,6X,' SECOND DIFF.' ))  
825  FORMAT(4F14.8)  
RETURN  
END