1 Phase Change, Nucleation, and Cavitation

1.1 Introduction

This first chapter will focus on the mechanisms of formation of two-phase mixtures of vapor and liquid. Particular attention will be given to the process of the creation of vapor bubbles in a liquid. In doing so we will attempt to meld together several overlapping areas of research activity. First, there are the studies of the fundamental physics of nucleation as epitomized by the books of Frenkel (1955) and Skripov (1974). These deal largely with very pure liquids and clean environments in order to isolate the behavior of pure liquids. On the other hand, most engineering systems are impure or contaminated in ways that have important effects on the process of nucleation. The later part of the chapter will deal with the physics of nucleation in such engineering environments. This engineering knowledge tends to be divided into two somewhat separate fields of interest, cavitation and boiling. A rough but useful way of distinguishing these two processes is to define cavitation as the process of nucleation in a liquid when the pressure falls below the vapor pressure, while boiling is the process of nucleation that ocurs when the temperature is raised above the saturated vapor/liquid temperature. Of course, from a basic physical point of view, there is little difference between the two processes, and we shall attempt to review the two processes of nucleation simultaneously. The differences in the two processes occur because of the different complicating factors that occur in a cavitating flow on the one hand and in the temperature gradients and wall effects that occur in boiling on the other hand. The last sections of this first chapter will dwell on some of these complicating factors.

1.2 The Liquid State

Any discussion of the process of phase change from liquid to gas or vice versa must necessarily be preceded by a discussion of the liquid state. Though simple kinetic theory understanding of the gaseous state is sufficient for our purposes, it is necessary to dwell somewhat longer on the nature of the liquid state. In doing so we shall follow Frenkel (1955), though it should also be noted that modern studies are usually couched in terms of statistical mechanics (for example, Carey 1992).

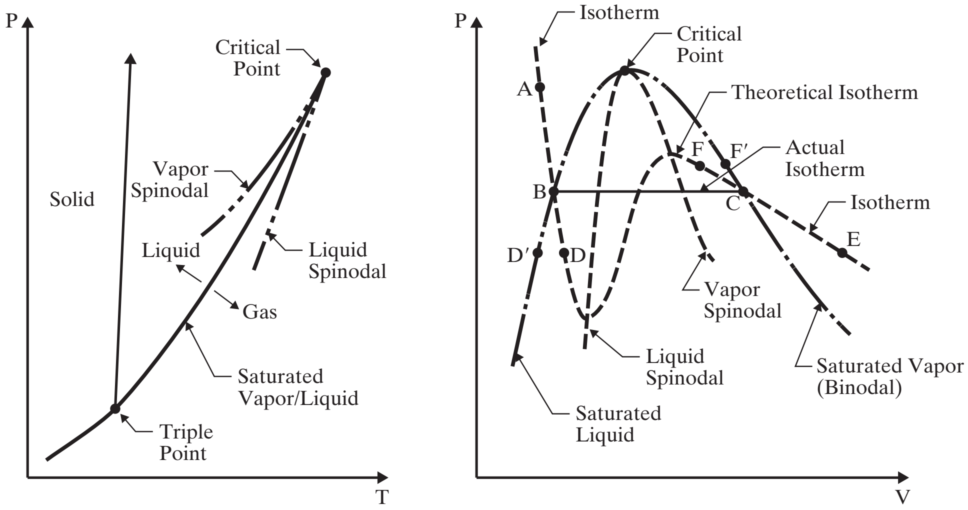

Figure 1.1 Typical phase diagrams.

Our discussion will begin with typical phase diagrams, which, though idealized, are relevant to many practical substances. Figure 1.1 shows typical graphs of pressure, p, temperature, T, and specific volume, V, in which the state of the substance is indicated. The triple point is that point in the phase diagram at which the solid, liquid, and vapor states coexist; that is to say the substance has three alternative stable states. The saturated liquid/vapor line (or binodal) extends from this point to the critical point. Thermodynamically it is defined by the fact that the chemical potentials of the two coexisting phases must be equal. On this line the vapor and liquid states represent two limiting forms of a single "amorphous" state, one of which can be obtained from the other by isothermal volumetric changes, leading through intermediate but unstable states. To quote Frenkel (1955), "Owing to this instability, the actual transition from the liquid state to the gaseous one and vice versa takes place *not* along a *theoretical* isotherm (dashed line, right, Figure 1.1), but along a horizontal isotherm (solid line), corresponding to the splitting up of the original homogeneous substance into two different coexisting phases..." The critical point is that point at which the maxima and minima in the theoretical isotherm vanish and the discontinuity disappears.

The line joining the maxima in the theoretical isotherms is called the vapor spinodal line; the line joining the minima is called the liquid spinodal line Clearly both spinodals end at the critical point. The two regions between the spinodal lines and the saturated (or binodal) lines are of particular interest because the conditions represented by the theoretical isotherm within these regions can be realized in practice under certain special conditions. If, for example, a pure liquid at the state A (Figure 1.1) is depressurized at constant temperature, then several things may happen when the pressure is reduced below that of point B (the saturated vapor pressure). If sufficient numbers of nucleation sites of sufficient size are present (and this needs further discussion later) the liquid will become vapor as the state moves

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horizontally from B to C, and at pressure below the vapor pressure the state will come to equilibrium in the gaseous region at a point such as E. However, if no nucleation sites are present, the depressurization may lead to continuation of the state down the theoretical isotherm to a point such as D, called a "metastable state" since imperfections may lead to instability and transition to the point E. A liquid at a point such as D is said to be in tension, the pressure difference between B and D being the magnitude of the tension. Of course one could also reach a point like D by proceeding along an isobar from a point such as D′ by increasing the temperature. Then an equivalent description of the state at D is to call it superheated and to refer to the difference between the temperatures at D and D′ as the superheat.

In an analogous way one can visualize cooling or pressurizing a vapor that is initially at a state such as F and proceeding to a metastable state such as F′ where the temperature difference between F and F′ is the degree of subcooling of the vapor.

1.3 Fluidity and Elasticity

Before proceding with more detail, it is valuable to point out several qualitative features of the liquid state and to remark on its comparison with the simpler crystalline solid or gaseous states.

The first and most obvious difference between the saturated liquid and saturated vapor states is that the density of the liquid remains relatively constant and similar to that of the solid except close to the critical point. On the other hand the density of the vapor is different by at least 2 and up to 5 or more orders of magnitude, changing radically with temperature. Since it will also be important in later discussions, a plot of the ratio of the saturated liquid density to the saturated vapor density is included as Figure 1.2 for a number of different fluids. The ratio is plotted against a non-dimensional temperature, $\theta = T/T_C$ where T is the actual temperature and T_C is the critical temperature.

Second, an examination of the measured specific heat of the saturated liquid reveals that this is of the same order as the specific heat of the solid except at high temperature close to the critical point. The above two features of liquids imply that the thermal motion of the liquid molecules is similar to that of the solid and involves small amplitude vibrations about a quasi-equilibrium position within the liquid. Thus the arrangement of the molecules has greater similarity with a solid than with a gas. One needs to stress this similarity with a solid to counteract the tendency to think of the liquid state as more akin to the gaseous state than to the solid state because in many observed processes it possesses a dominant fluidity rather than a dominant elasticity. Indeed, it is of interest in this regard to point out that solids also possess fluidity in addition to elasticity. At high temperatures, particularly above 0.6 or 0.7 of the melting temperature, most crystalline solids exhibit a fluidity known as creep. When the strain rate is high, this creep occurs due to the nonisotropic propagation of dislocations (this behavior is not like that of a Newtonian liquid and cannot be characterized by a simple viscosity). At low strain rates, high-temperature creep occurs due simply to the isotropic migration of molecules

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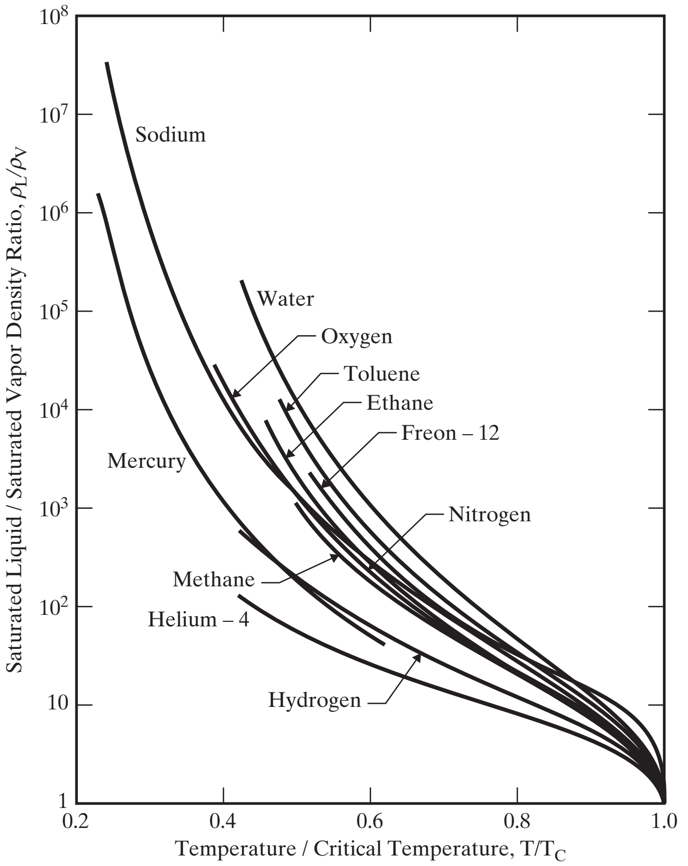

Figure 1.2 Ratio of saturated liquid density to saturated vapor density as a function of temperature for various pure substances.

within the crystal lattice due to the thermal agitation. This kind of creep, which is known as diffusion creep, is analogous to the fluidity observed in most liquids and can be characterized by a simple Newtonian viscosity.

Following this we may ask whether the liquid state possesses an elasticity even though such elasticity may be dominated by the fluidity of the liquid in many physical processes. In both the liquid and solid states one might envisage a certain typical time, t_m, for the migration of a molecule from one position within the structure of the substance to a neighboring position; alternatively one might consider this typical time as characterizing the migration of a "hole" or vacancy from one position to another within the structure. Then if the typical time, t, associated with the applied force is small compared with t_m, the substance will not be capable of permanent deformation during that process and will exhibit elasticity rather than fluidity. On the other hand if $t \gg t_m$ the material will exhibit fluidity. Thus, though the conclusion is overly simplistic, one can characterize a solid as having a large t_m and a liquid as having a small t_m relative to the order of magnitude of the typical time, t, of the applied force. One example of this is that the earth's mantle behaves to all intents and purposes as solid rock in so far as the propagation of seismic waves is concerned, and yet its fluid-like flow over long geological times is responsible for continental drift.

The observation time, t, becomes important when the phenomenon is controlled by stochastic events such as the diffusion of vacancies in diffusion creep. In many cases the process of nucleation is also controlled by such stochastic events, so the observation time will play a significant role in determining this process. Over a longer period of time there is a greater probability that vacancies will coalesce to form a finite vapor pocket leading to nucleation. Conversely, it is also possible to visualize that a liquid could be placed in a state of tension (negative pressure) for a significant period of time before a vapor bubble would form in it. Such a scenario was visualized many years ago. In 1850, Berthelot (1850) subjected purified water to tensions of up to 50 atmospheres before it yielded. This ability of liquids to withstand tension is very similar to the more familiar property exhibited by solids and is a manifestation of the elasticity of a liquid.

1.4 Illustration of Tensile Strength

Frenkel (1955) illustrates the potential tensile strength of a pure liquid by means of a simple, but instructive calculation. Consider two molecules separated by a variable distance s. The typical potential energy, Φ, associated with the intermolecular forces has the form shown in Figure 1.3. Equilibrium occurs at the separation, x_o, typically of the order of $10^{-10}m$. The attractive force, F, between the molecules is equal to $\partial\Phi/\partial x$ and is a maximum at some distance, x_1, where typically x_1/x_o is of the order of 1.1 or 1.2. In a bulk liquid or solid this would correspond to a fractional volumetric expansion, $\Delta V/V_o$, of about one-third. Consequently the application of a constant tensile stress equal to that pertinent at x_1 would completely rupture the liquid or solid since for $x > x_1$ the attractive force is insufficient to counteract that tensile force. In fact, liquids and solids have compressibility moduli, κ, which are usually in the range of 10^{10} to 10^{11} $kg/m\,s^2$ and since the pressure, $p = -\kappa(\Delta V/V_o)$,

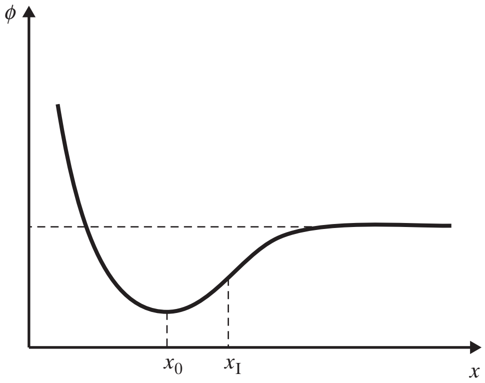

Figure 1.3 Intermolecular potential.

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it follows that the typical pressure that will rupture a liquid, p_T, is -3×10^9 to -3×10^{10} $kg/m\,s^2$. In other words, we estimate on this basis that liquids or solids should be able to withstand tensile stresses of 3×10^4 to 3×10^5 atmospheres! In practice solids do not reach these limits (the rupture stress is usually about 100 times less) because of stress concentrations; that is to say, the actual stress encountered at certain points can achieve the large values quoted above at certain points even when the overall or globally averaged stress is still 100 times smaller. In liquids the large theoretical values of the tensile strength defy all practical experience; this discrepancy must be addressed.

It is valuable to continue the above calculation one further step (Frenkel 1955). The elastic energy stored per unit volume of the above system is given by $\kappa(\Delta V)^2/2V_o$ or $|p|\Delta V_o/2$. Consequently the energy that one must provide to pull apart all the molecules and vaporize the liquid can be estimated to be given by $|p_T|/6$ or between 5×10^8 and 5×10^9 $kg/m\,s^2$. This is *in agreement* with the order of magnitude of the latent heat of vaporization measured for many liquids. Moreover, one can correctly estimate the order of magnitude of the critical temperature, T_C, by assuming that, at that point, the kinetic energy of heat motion, kT_C per molecule (where k is Boltzmann's constant, 1.38×10^{-23} $kg\ m^2/s^2K$) is equal to the energy required to pull all the molecules apart. Taking a typical 10^{30} molecules per m^3, this implies that T_C is given by equating the kinetic energy of the thermal motions per unit volume, or $1.38\times10^7\times T_C$, to $|p_T|/6$. This yields typical values of T_C of the order of $30\rightarrow300^\circ K$, which is in accord with the order of magnitude of the actual values. Consequently we find that this simplistic model presents a dilemma because though it correctly predicts the order of magnitude of the latent heat of vaporization and the critical temperature, it fails dismally to predict the tensile strength that a liquid can withstand. One must conclude that unlike the latent heat and critical temperature, the tensile strength is determined by weaknesses at points within the liquid. Such weaknesses are probably ephemeral and difficult to quantify, since they could be caused by minute impurities. This difficulty and the dependence on the time of application of the tension greatly complicate any theoretical evaluation of the tensile strength.

1.5 Cavitation and Boiling

As we discussed in Section 1.2, the tensile strength of a liquid can be manifest in at least two ways:

1. A liquid at constant temperature could be subjected to a decreasing pressure, p, which falls below the saturated vapor pressure, p_V. The value of (p_V-p) is called the tension, Δp, and the magnitude at which rupture occurs is the tensile strength of the liquid, Δp_C. The process of rupturing a liquid by decrease in pressure at roughly constant liquid temperature is often called cavitation.
2. A liquid at constant pressure may be subjected to a temperature, T, in excess of the normal saturation temperature, T_S. The value of $\Delta T = T - T_S$ is the

superheat, and the point at which vapor is formed, ΔT_C, is called the critical superheat. The process of rupturing a liquid by increasing the temperature at roughly constant pressure is often called boiling.

Though the basic mechanics of cavitation and boiling must clearly be similar, it is important to differentiate between the thermodynamic paths that precede the formation of vapor. There are differences in the practical manifestations of the two paths because, although it is fairly easy to cause uniform changes in pressure in a body of liquid, it is very difficult to uniformly change the temperature. Note that the critical values of the tension and superheat may be related when the magnitudes of these quantities are small. By the Clausius-Clapeyron relation,

$$\left(\frac{dp}{dT}\right)_{\substack{saturation\\conditions}} = \frac{L}{T\left[\rho_V^{-1} - \rho_L^{-1}\right]} \tag{1.1}$$

where ρ_L, ρ_V are the saturated liquid and vapor densities and L is the latent heat of evaporation. Except close to the critical point, we have $\rho_L \gg \rho_V$ and hence $dp/dT \approx \rho_V L/T$. Therefore

$$\Delta T_C \approx \Delta p_C \cdot \frac{T}{L\rho_V} \tag{1.2}$$

For example, in water at $373K$ with $\rho_V = 1\ kg/m^3$ and $L \approx 2 \times 10^6\ m^2/s^2$ a superheat of $20K$ corresponds approximately to one atmosphere of tension. It is important to emphasize that Equation (1.2) is limited to small values of the tension and superheat but provides a useful relation under those circumstances. When Δp_C and ΔT_C are larger, it is necessary to use an appropriate equation of state for the substance in order to establish a numerical relationship.

1.6 Types of Nucleation

In any practical experiment or application weaknesses can typically occur in two forms. The thermal motions within the liquid form temporary, microscopic voids that can constitute the nuclei necessary for rupture and growth to macroscopic bubbles. This is termed homogeneous nucleation. In practical engineering situations it is much commoner to find that the major weaknesses occur at the boundary between the liquid and the solid wall of the container or between the liquid and small particles suspended in the liquid. When rupture occurs at such sites, it is termed heterogeneous nucleation.

In the following sections we briefly review the theory of homogeneous nucleation and some of the experimental results conducted in very clean systems that can be compared with the theory.

In covering the subject of homogeneous nucleation, it is important to remember that the classical treatment using the kinetic theory of liquids allows only weaknesses of one type: the ephemeral voids that happen to occur because of the thermal motions of the molecules. In any real system several other types of weakness are possible. First, it is possible that nucleation might occur at the junction of the liquid and a solid boundary. Kinetic theories have also been developed to cover such heterogeneous nucleation and allow evaluation of whether the chance that this will occur is larger or smaller than the chance of homogeneous nucleation. It is important to remember that heterogeneous nucleation could also occur on very small, sub-micron sized contaminant particles in the liquid; experimentally this would be hard to distinguish from homogeneous nucleation.

Another important form of weaknesses are micron-sized bubbles (microbubbles) of contaminant gas, which could be present in crevices within the solid boundary or within suspended particles or could simply be freely suspended within the liquid. In water, microbubbles of air seem to persist almost indefinitely and are almost impossible to remove completely. As we discuss later, they seem to resist being dissolved completely, perhaps because of contamination of the interface. While it may be possible to remove most of these nuclei from a small research laboratory sample, their presence dominates most engineering applications. In liquids other than water, the kinds of contamination which can occur in practice have not received the same attention.

Another important form of contamination is cosmic radiation. A collision between a high energy particle and a molecule of the liquid can deposit sufficient energy to initiate nucleation when it would otherwise have little chance of occurring. Such, of course, is the principal of the bubble chamber (Skripov 1974). While this subject is beyond the scope of this text, it is important to bear in mind that naturally occurring cosmic radiation could be a factor in promoting nucleation in all of the circumstances considered here.

1.7 Homogeneous Nucleation Theory

Studies of the fundamental physics of the formation of vapor voids in the body of a pure liquid date back to the pioneering work of Gibbs (Gibbs 1961). The modern theory of homogeneous nucleation is due to Volmer and Weber (1926), Farkas (1927), Becker and Doring (1935), Zeldovich (1943), and others. For reviews of the subject, the reader is referred to the books of Frenkel (1955) and Skripov (1974), to the recent text by Carey (1992) and to the reviews by Blake (1949), Bernath (1952), Cole (1970), Blander and Katz (1975), and Lienhard and Karimi (1981). We present here a brief and simplified version of homogeneous nucleation theory, omitting many of the detailed thermodynamical issues; for more detail the reader is referred to the above literature.

In a pure liquid, surface tension is the macroscopic manifestation of the intermolecular forces that tend to hold molecules together and prevent the formation of large holes. The liquid pressure, p, exterior to a bubble of radius R, will be related to the interior pressure, p_B, by

$$p_B - p = \frac{2S}{R} \tag{1.3}$$

where S is the surface tension. In this and the section which follow it is assumed that the concept of surface tension (or, rather, surface energy) can be extended down to bubbles or vacancies a few intermolecular distances in size. Such an approximation is surprisingly accurate (Skripov 1974).

If the temperature, T, is uniform and the bubble contains only vapor, then the interior pressure p_B will be the saturated vapor pressure $p_V(T)$. However, the exterior liquid pressure, $p = p_V - 2S/R$, will have to be less than p_V in order to produce equilibrium conditions. Consequently if the exterior liquid pressure is maintained at a constant value just slightly less than $p_V - 2S/R$, the bubble will grow, R will increase, the excess pressure causing growth will increase, and rupture will occur. It follows that if the maximum size of vacancy present is R_C (termed the critical radius or cluster radius), then the tensile strength of the liquid, Δp_C, will be given by

$$\Delta p_C = 2S/R_C \tag{1.4}$$

In the case of ephemeral vacancies such as those created by random molecular motions, this simple expression, $\Delta p_C = 2S/R_C$, must be couched in terms of the probability that a vacancy, R_C, will occur during the time for which the tension is applied or the time of observation. This would then yield a probability that the liquid would rupture under a given tension during the available time.

It is of interest to substitute a typical surface tension, $S = 0.05\ kg/s^2$, and a critical vacancy or bubble size, R_C, comparable with the intermolecular distance of $10^{-10}\ m$. Then the calculated tensile strength, Δp_C, would be $10^9\ kg/m\ s^2$ or $10^4\ atm$. This is clearly in accord with the estimate of the tensile strength outlined in Section 1.4 but, of course, at variance with any of the experimental observations.

Equation (1.4) is the first of three basic relations that constitute homogeneous nucleation theory. The second expression we need to identify is that giving the increment of energy that must be deposited in the body of the pure liquid in order to create a nucleus or microbubble of the critical size, R_C. Assuming that the critical nucleus is in thermodynamic equilibrium with its surroundings after its creation, then the increment of energy that must be deposited consists of two parts. First, energy must be deposited to account for that stored in the surface of the bubble. By definition of the surface tension, S, that amount is S per unit surface area for a total of $4\pi R_C^2 S$. But, in addition, the liquid has to be displaced outward in order to create the bubble, and this implies work done on or by the system. The pressure difference involved in this energy increment is the difference between the pressure inside and outside of the bubble (which, in this evaluation, is Δp_C, given by Equation (1.4)). The work done is the volume of the bubble multiplied by this pressure difference, or $4\pi R_C^3 \Delta p_C/3$, and this is the work done by the liquid to achieve the displacement implied by the creation of the bubble. Thus the net energy, W_{CR}, that must be deposited to form the bubble is

$$W_{CR} = 4\pi R_C^2 S - \frac{4}{3}\pi R_C^3 \Delta p_C = \frac{4}{3}\pi R_C^2 S \tag{1.5}$$

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It can also be useful to eliminate R_C from Equations (1.4) and (1.5) to write the expression for the critical deposition energy as

$$W_{CR} = 16\pi S^3/3(\Delta p_C)^2 \tag{1.6}$$

It was, in fact, Gibbs (1961) who first formulated this expression. For more detailed considerations the reader is referred to the works of Skripov (1974) and many others.

The final step in homogeneous nucleation theory is an evaluation of the mechansims by which energy deposition could occur and the probability of that energy reaching the magnitude, W_{CR}, in the available time. Then Equation (1.6) yields the probability of the liquid being able to sustain a tension of Δp_C during that time. In the body of a pure liquid completely isolated from any external radiation, the issue is reduced to an evaluation of the probability that the stochastic nature of the thermal motions of the molecules would lead to a local energy perturbation of magnitude W_{CR}. Most of the homogeneous nucleation theories therefore relate W_{CR} to the typical kinetic energy of the molecules, namely kT (k is Boltzmann's constant) and the relationship is couched in terms of a Gibbs number,

$$Gb = W_{CR}/kT \tag{1.7}$$

It follows that a given Gibbs number will correspond to a certain probability of a nucleation event in a given volume during a given available time. For later use it is wise to point out that other basic relations for W_{CR} have been proposed. For example, Lienhard and Karimi (1981) find that a value of W_{CR} related to kT_C (where T_C is the critical temperature) rather than kT leads to a better correlation with experimental observations.

A number of expressions have been proposed for the precise form of the relationship between the nucleation rate, J, defined as the number of nucleation events occurring in a unit volume per unit time and the Gibbs number, Gb, but all take the general form

$$J = J_O e^{-Gb} \tag{1.8}$$

where J_O is some factor of proportionality. Various functional forms have been suggested for J_O. A typical form is that given by Blander and Katz (1975), namely

$$J_O = N\left(\frac{2S}{\pi m}\right)^{\frac{1}{2}} \tag{1.9}$$

where N is the number density of the liquid (molecules/m^3) and m is the mass of a molecule. Though J_O may be a function of temperature, the effect of an error in J_O is small compared with the effect on the exponent, Gb, in Equation (1.8).

1.8 Comparison with Experiments

The nucleation rate, J, is given by Equations (1.8), (1.7), (1.6), and some form for J_O, such as Equation (1.9). It varies with temperature in ways that are important to