



# SUPERHEATING LIMIT OF BOILING *n*-HEXANE SPINODAL DECOMPOSITION VERSUS NUCLEATION PROCESS

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**Key Word Index**—Nucleation; equation of state; spinodal decomposition.

Two predicative theories for superheating limits of a boiling liquid are considered in this work. In the nucleation picture, classical homogeneous nucleation theory is used to calculate superheating temperature at various pressures. In spinodal decomposition picture, stability limits are taken as the superheating temperature. A perturbed-hard chain equation of state was developed and used for the purpose of calculating mechanical stability limit. Calculations are done for the case of normal hexane at different pressures and compared with experimental results. Classical nucleation theory gives good prediction at negative and smaller pressures. While near critical pressure, spinodal picture seems to be more accurate.

## INTRODUCTION

When a liquid is heated under constant pressure it will eventually reach the liquid-vapor equilibrium point where the chemical potential of the two phases  $\mu$  and  $\mu^*$  are equal. Usually, a superheating limit of the liquid can often be observed, in which the metastable region  $\mu > \mu^*$  can be reached. Experimental investigations of superheating behavior were first done by Moore<sup>1)</sup>, Wakashima and Takata<sup>2)</sup>, and later extensively by Skripov and co-workers<sup>3-5)</sup>. If care was taken in excluding all impurities, a characteristic superheating temperature limit can be observed, for given pressure, to within 1°. At superheating limit, a sharp "ping" can be heard when the liquid vaporizes explosively.

Scientific explanations of the superheating of liquid generally follow two distinctly different approaches. One approach is that of homogeneous nucleation theory<sup>6-10)</sup>, in which the kinetic limit of the formation of critical nuclei is considered. Because the exponential dependence

of nucleation rate of energy barrier of nucleus formation, a superheating temperature of liquid can be calculated at which rapid increases of nucleation rate commences. Nucleation rate theory has been applied to the prediction of superheating by many authors<sup>11,12)</sup>.

The second approach considers the mechanical stability limit of the system. According to Gibbs thermodynamic criterion, metastable region requires that  $(\frac{\partial P}{\partial V})_T < 0$ . The superheating limit corresponds to the limit  $(\frac{\partial P}{\partial V})_T = 0$ , *e.g.* the minimum in the Van der Waals "loop". Such limit is called spinodal limit. Outside this limit, any small density fluctuation will lead to "explosive" growth of new phase. The states between equilibrium point and metastable limit are the metastable states. Such approaches have been considered by several authors<sup>17-19)</sup> before. Obviously, one needs a very good equation of state for the purpose. Recent advances<sup>20)</sup> in statistical thermodynamics have produced very ac-

curate equation of state for normal liquids. Particularly, Prausnitz<sup>21,22</sup> has developed a Perturbed Hard-Chain theory for fluids containing polyatomic molecules. The theory generalizes Van der Waals theory to include both rotational and vibrational degrees of freedom. It has been shown to be particularly useful for normal hydrocarbons. We shall use this theory in this paper to consider the spinodal limit.

It is obvious that, the spinodal limit should provide an upper bound to the nucleation temperature. But one can doubt whether one observes nucleation or spinodal decomposition in an actual experimental superheating limit. Most people believe that homogeneous nucleation was observed in liquid system because it is "rapid". However, recently there are some doubts about this view. At high pressure, near critical point, it may happen that dynamical processes in liquid may become so slow that nucleation becomes too slow to be observed. One has the possibility of going all the way to spinodal limit.

It is the purpose of this paper to examine both approaches for the system *n*-hexane for which plenty accurate thermodynamic data are available. We have been able to build accurate equation of state based on perturbed Hard-Chain theory for *n*-hexane. We then apply both classical Volmer-Döring nucleation theory and mechanical stability criterion for the system. The results are compared with experimental superheating data.

### SPINODAL LIMIT

In this section, we calculate the mechanical stability limit of Van der Waals "loop", *e. g.*

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad (1)$$

The superheated liquid states are found on *P-V* isotherm between the saturated liquid and the minimum on the Van der Waals "loop". This limit is where any small density fluctuation will lead to immediate phase separation—spinodal decomposition. For this purpose, we need accurate equation of states for polyatomic liquids. Recently, Prausnitz<sup>21,22</sup> developed Perturbed Hard-Chain Theory (PHC) based on generalization of the classical Van der Waals theory. The equation of state gives, especially good liquid densities and vapor pressure. For normal hydrocarbons and polymers, PHC uses only three adjustable parameters while taking into account of vibrational-rotational degrees of freedom of polyatomic molecules. We will use PHC for normal hexane; by fitting vapor pressure and critical point data we can get the three adjusting parameters.

Like the classic Van der Waals theory, PHC builds the equation of state by separating contributions into two parts (a) the reference hard-chain (b) the perturbation to internal energy due to attractive force. The compressibility factor of the real liquid *Z* is related to that of a reference hard-chain system, *Z<sub>0</sub>*, by

$$Z = Z_0 - \frac{a}{RTv}, \quad Z = \frac{Pv}{RT} \quad (2)$$

where *v* is molar volume, *a* is the analog Van der Waals (VDW) constant.

*Z<sub>0</sub>* is calculated by Carnahan-Starling equation of state<sup>23</sup> with Prigogine's correction of vibration-rotational degrees of freedom<sup>24</sup>. *3C* is the total numbers of external degrees of freedom. The result is

$$Z_c = 1 + C \frac{(\tau/\bar{v}) - 2(\tau/\bar{v})^2}{(1 - \tau/\bar{v})^2} \quad (3)$$

Here  $\bar{v}$  is the reduced volume given by

$$\bar{v} = \frac{v}{rv^*} \quad (4)$$

$v^*$  is the closed-packed volume per segment of a  $r$ -segment molecule.

$$\tau = \sqrt{2} \pi / 6 \quad (5)$$

The VDW constant " $a$ " was given by Prausnitz<sup>21)</sup> as

$$a = -R \left( \frac{\epsilon q}{k} \right) (rv^*)^4 \sum_{n=1}^4 \sum_{m=1}^M \left( \frac{mA_{nm}}{\bar{v}^{m-1}} \right) \frac{1}{\bar{T}^{n-1}} \quad (6)$$

where  $\epsilon q$  is energy parameter,  $k$  is the Boltzman Constant,  $T$  is the reduced temperature

$$\bar{T} = \frac{c k T}{\epsilon q} \quad (7)$$

$A_{nm}$  are tabulated constants given by Prausnitz. The three fitting parameters are  $\epsilon q$ ,  $rv^*$  and  $c$ .

For data reduction, we use primarily vapor pressure and critical point data; this is consistent with our purpose of gaining accurate description of the two phase region. Therefore, PVT data were not used. For vapor pressure data of *n*-Hexane, we used the values compiled by J. H. Weber<sup>25)</sup>. The isotherms of PHC are calculated for temperatures below critical point, and saturated vapor pressures were calculated by Maxwell's Construction. The results of the fitting are  $\epsilon q/k = 612.4^\circ K$ ,  $rv^* = 87.33 \text{ cm}^3/\text{mole}$  and  $C = 1.91$ . Calculated saturation pressures are listed in Table 1 and compared with experimental data; the root mean square deviation is 2.38% over the temperature range of  $T = 400^\circ K$  to critical point. The fittings are somewhat better

Table 1. Vapor Pressure of *n*-Hexane

$T$ ( $^\circ K$ )	$P$ (calc) (atm)	$P$ (exp)* (atm)
400	4.38	4.56
420	6.60	6.75
440	9.72	10.03
460	13.92	13.99
480	19.12	19.49
500	26.27	26.35

\* Experimental values are interpolated from data of references (5), (25).

in the higher temperature range. The calculated critical point is  $P_c = 28.9 \text{ atm}$  and  $T_c = 507.4^\circ K$ , compared with experimental value of  $P_c = 29.8 \text{ atm}$  and  $T_c = 507.8^\circ K$ . The results of the calculated vapor pressure are shown in Fig. 1 together with experimental data.

After the equation of state is found, it is straightforward to apply the condition Eq. (1) to obtain the spinodal limit which gives the limit to metastable region. The results are shown in Fig. 2. One can see that the mechanical limit does provide an upperbound to superheating and approach experimental superheating at higher pressure.

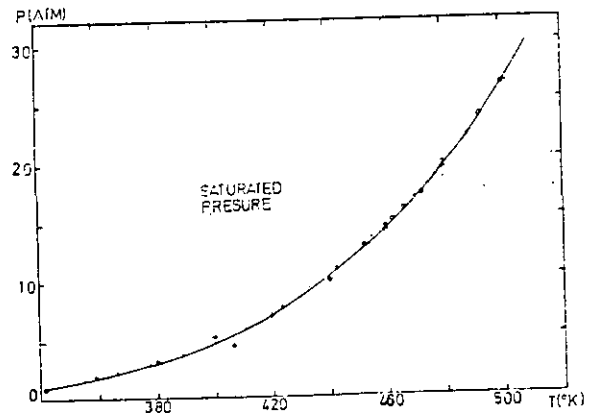


Fig. 1. Saturated Pressure of *n*-Hexane.

- Experimental data from reference (5)
- Experimental data from reference (25)
- + Calculated from perturbed Hard-Chain theory

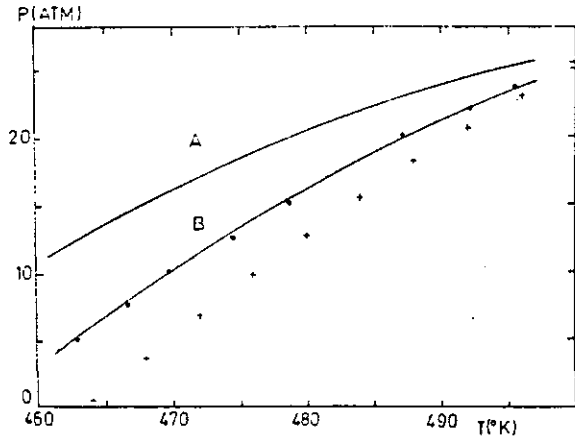


Fig. 2. Superheating limit of *n*-Hexane.

- Experimental data from reference (4).
- Calculated from classical nucleation theory
- + Calculated from mechanical stability limit of the Perturbed Hard-Chain theory equation of state
- A Equilibrium vapor pressure
- B Best fit to the "●" points

### NUCLEATION LIMIT

According to classical nucleation theory<sup>11)</sup>, limit of superheating occurs at a point where the nucleation rate rises very sharply. Kagan<sup>12)</sup> has derived an expression for  $I$ , the rate of nucleation, *i.e.*, number of critical nuclei per unit volume per unit time which continue to grow to macroscopic size

$$I = I_0 \exp(-E^*/kT) \quad (8)$$

where  $E^*$  is the potential barrier to be crossed.  $E^*$  is given by a thermodynamic analysis as<sup>13)</sup>

$$E^* = \frac{4\pi}{3} \sigma r_c^2 \quad (9)$$

$\sigma$  is the surface tension and  $r_c$  is the radius of critical bubble given by

$$P_c = P_0 + \frac{2\sigma}{r_c} \quad (10)$$

$P_0$  is the ambient pressure and  $P_c$  is the

equilibrium pressure inside the critical size bubble. Usually, saturated pressure  $P_s$  is measured under its own pressure which is different from  $P_c$  (under higher pressure  $P_0$ ).  $P_c$  can be estimated from  $P_s$  from the relation

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{v_l}{RT} \quad (11)$$

$f$  is the fugacity and  $v_l$  is the molar volume of the liquid. Integrating Eq. (11), yields

$$\ln \frac{f_c}{f_s} = \ln \frac{P_c}{P_s} = \frac{P_c - P_s}{P_s} = \frac{v_l(P_c - P_s)}{RT} \quad (12)$$

Therefore,

$$\begin{aligned} P_c - P_0 &\approx (P_s - P_0) \left(1 - \frac{v_l P_s}{RT}\right) \\ &= (P_s - P_0) \left(1 - \frac{Z v_l}{v_g}\right) \end{aligned} \quad (13)$$

With Eqs. (9), (10), (13), the energy barrier height in the exponential term of Eq. (8) can be calculated from surface tension data and saturation pressure.

For the pre-exponential kinetic factor  $I_0$ , we use the result of Kagan in the form of

$$I_0 = \frac{1}{2} N_0 v_l \sqrt{\sigma/kT} \quad (14)$$

$$v_l = \sqrt{8kT/\pi m}$$

$m$  is molecular mass and  $N_0$  is Avogadro's number.

Since  $I$  rises very sharply at the nucleating point, one can choose an arbitrary rate  $I = 10^3$  nuclei/(cm<sup>3</sup>·sec) as the critical nucleating rate at the observed nucleating point. With this criterion,  $E^*/kT$  is about 60. The degree of superheating is not sensitive to the choice of critical nucleation rate, even if  $I$  is increased by a factor of  $10^4$ , change of nucleation tem-

perature is only about 1°K.

For saturation pressure, we use the values obtained from previous section. The surface tensions of *n*-hexane are calculated from experimental data as<sup>29</sup>

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^{11/3}$$

$$\sigma_0 = 52.33 \text{ dyne/cm} \quad (15)$$

$T_c$  is critical temperature.

The calculated superheating limits are shown in Fig. 2 together with those calculated from section II. The crosses are the spinodal limits, circles are calculated from nucleation theory and dots are the experimental data of Skripov<sup>29</sup>.

## RESULT AND DISCUSSIONS

From Fig. 2, one can see classical nucleation theory agrees very well the experimental superheating limits for temperature below  $T/T_c = 0.95$  ( $T = 483^\circ\text{K}$  here). The mechanical stability limit provides upper bound to the superheating limit, which is expected. The agreement with nucleation theory for temperature above  $T/T_c = 0.95$  is less clear cut; there are two experimental data of superheating temperature higher than that predicted by classical nucleation theory. This may indicate a transition from kinetic limit (Nucleation theory) to mechanical stability (spinodal decomposition) situation. Theoretically, one would expect the kinetic process will slow down near critical point. If one gets near enough to the critical region, the nucleation process may be slow enough that is not observed; then the spinodal decomposition picture will be the proper one. However, due to lack of enough data, one can not really say very much at

this point. Further investigation of boiling near critical region is certainly very desirable. One should note here that there are several other examples<sup>27-29</sup> in the literature shows that experimental superheating is larger than that predicted by nucleation theory. Often they do not receive much attention under prevailing believe that nucleation theory works "well". We would like to suggest that the alternative spinodal decomposition process should be looked into more carefully. Unlike in vapor condensation, nucleation processes are comparatively slower in boiling and they may not happen in an actual superheating situation.

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