NUCLEATION STUDIES IN CONVERGENT NOZZLE

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Synopsis

The problem of instability in condensing flows of steam understand parallel to the care of heat additions to a compressible fluid. For any specific mach number, there is a maximum amount of heat release that the flow can cope with. If the heat release by condensation is more than the heat required to reduce the flow Mach number to unity, then instability occurs. This quantity of heat released is a function of the limiting supercooling attained by the fluid.

A description is given on the theoretical treatment of nucleation in flowing steam employing an equation of state based on the third virial coefficiant. Calculated results covering the pressure range 0.1-1.5 bar in a convergent nozzle of expansion rate $\dot{P} = 1000\ s^{-1}$ are presented.

Notation

A	Area
β	virial coefficient
C	Condensation rate
C_1 & C_2	Constants defined in text
c_p	Specific heat at constant pressure
c_v	Specific heat at constant volume
d_e	Equivalent diameter of duct section
f	$\frac{2d_e}{pu^2} \quad \frac{dp}{dx}$ friction factor or function of...
F	*Helmholtz* function
g	Number of molecules in a cluster
G	*Gibb's* Free Energy
h	Specific enthalpy
I	Nucleation rate
$\tilde{k}$	*Boltzmann's* constant
k	Isentropic exponent
K_1, K_2	Constant defined in text
Kn	*Knudsen* number = $\frac{\tilde{I}}{2n}$
l	Energy released per unit mass of vapour condensing
$\bar{I}$	Mean free path
m_r	mass of a droplet
m	Mass of a molecule
(Ma)	Mach number
N	Square of (Ma)

n_o	Number of molecules per unit volume
P	Pressure
$\dot{p}$	Rate of Expansion $\frac{-1}{p} \frac{dp}{dt}$
q	Condensation coefficient
r	Droplet mean radius
R	Gas constant for water vapour
t	time
T	Temperature
u	Velocity
v	Specific volume
x	Distance along duct axis
X	Simplifying symbol defined by equation state
Y	Simplifying symbol defined by equation of state
Z	Simplifying symbol
λ	Thermal conductivity
ζ	Dryness fraction
ρ	Density
σ	Surface tension

Subscripts

o	Zero pressure of stagnation state
∞	Plane surface
g	Cluster containing g molecules
G	Vapour phase
L	Liquid phase
r	Droplet
s	Saturation

Superscript

*	Critical condition

Introduction

In the low pressure stages of condensing steam turbine when steam expands below the saturation line, at some point in the nozzle, the saturation condition is reached and moisture might be expected to precipitated in the form of fine drops. Research shows that the precipitation of moisture is however delayed beyond the point where saturation is reached. This phenomenon is called limiting supersaturation, and during the period when the vapour pressure is greater than the saturation pressure corresponding to the temperature, state of metastable equilibrium exists. The series of pointt of precipitation state at various pressures is known as the *Wilson* line.

A considerable amount of work has been done on the problems of nucleation, supersaturation, the behaviour of wet steam in steam turbines and the erosion of turbine blade. Computer programs for both convergent and convergent - divergent nozzles has been developed in one and two dimensional form to accomodate the nucleation treatment.

Basic Physical Model

Condensing flows of steam can be regarded as a special case of compressible flows of the parent vapour phase in which the heat addition is the result of the phase change which effect its mass flow rate. Considering the one dimensional steady flow of steam over an incremental axial distance dx along the duct shown in Figure 1 and assuming no slip between the phases, the governing equations of flow can be written as follows;

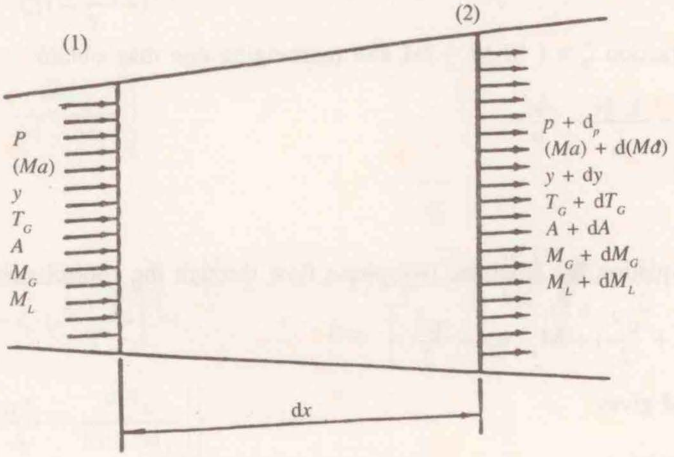

Figure 1: Enlargement of Flow Metal

Mass continuity

$M = M_L + \rho_G Au = \text{Constant}$

differentiating

$$\frac{d\rho_G}{\rho_G} + \frac{du}{u} + \frac{dA}{A} + \frac{dM_L}{M - M_L} = 0 \qquad \text{... (1)}$$

Equation of state

The equation of state adopted is of the form

$$\frac{P}{\rho_G R\, T_G} = 1 + \beta_1 \rho_G + \beta_2 \rho_G{}^2 + \beta_3 \rho_3{}^3$$

Details of the subsequent development of this equation together with an expression describing β's are given in Appendix 1. Differentiation and rearrangement of the equation of state gives

$$\frac{dp}{p} - X\,\frac{d\rho_G}{\rho_G} - Y\,\frac{dT_G}{T_G} = 0 \qquad \text{... (2)}$$

where X and Y are given by equations 16A and 16B.

Vapour phase Mach number

In the present treatment it is algebraically convenient to work in terms of the frozen speed of sound and no physical significance is implied.

Defining

$$N = (Ma)^2 = \frac{u^2}{kp/\rho_G} \qquad \text{... (3)}$$

differentiation gives

$$\frac{dN}{N} = \frac{2d(Ma)}{(Ma)} = \frac{2du}{u} + \frac{d\rho_G}{\rho_G} - \frac{dp}{p}$$

Momentum equation

$$dp = -\frac{f\rho_G u^2 dx}{2d_e} - \frac{M}{A}du$$

Introducing the dryness fraction $\zeta = (M\text{-}M_L)/M$ and rearranging one may obtain

$$\frac{dp}{p} = -\frac{k\ Nf\ dx}{2d_e} - \frac{k\ N}{\zeta} - \frac{du}{u}$$

Energy equation

The steady flow energy equation for adiabatic two phase flow through the control volume is

$$d\left[(M - M_L)(h_G + \frac{u^2}{2}) + M_L(h_L + \frac{u^2}{2})\right] = 0$$

$l = h_G - h_L$, by M gives

$$u\ du + dh_G - \frac{d(l M_L)}{M} = 0$$

The term dh_G may be written:-

$$dh_G = c_p d\ T_G + \left[\upsilon_G - T_G(\frac{\partial \upsilon G}{\partial T_G})_p\right]\ dp$$

c_p may be substituted from equations (20) or (23) and an expression for $\upsilon_G - T_G(\frac{\delta G}{\delta T_G})_p$ obtained by appea to the equation of state giving

$$u_G - T_G(\frac{\partial \upsilon G}{\partial T_G})_p = \frac{I}{\rho G}(1 - \frac{Y}{X})$$

Substitution in equation (6), division by c_p T_G and simplification yields

$$\frac{dT_G}{T_G} + (\frac{k - X}{k})(\frac{X - Y}{Y^2})\frac{dp}{p} + \frac{(k - X)XN}{Y^2}\frac{du}{u} - \frac{d(l M_L)}{M\ c_p T_G} = 0 \quad \text{... (7}$$

Equation 1, 4, 5, 7 are the main flow equations. Combining these with the equation of state, nucleation rate and droplet growth equations, the flow of net steam can now be fully solved.

The quantities dA/A and $\frac{f\ dx}{2d_e}$ may be treated as independent variables; $\frac{d\ M_L}{M}$ is the incremental change in wetness fraction and is calculated from considerations of droplet formation and growth. The resulting expressions for $\frac{dN}{N}, \frac{dT_G}{T_G}$ and $\frac{d\rho_G}{\rho_G}$

$$\frac{dN}{N} = \frac{1}{1 - \frac{N}{\xi}\left[1 + (1-\xi)(\frac{k-X}{Y})\right]}\left\{\left[(\frac{k-X}{Y})(kN+1) + k + 1\right]\frac{fNdx}{2d_e} + (1 + \frac{kN}{\xi})\frac{Y}{X}\frac{d(lM_L)}{MC_pT_G} - \{2 +\right.$$

$$\left.\frac{N}{\xi}\left[(k-1) - (1-\xi)(\frac{k-X}{Y})\right]\}\left[\frac{dA}{A} + \frac{d^ML}{M - M_L}\right]\right\} \quad \ldots (8) \qquad \ldots (8)$$

$$\frac{dT_G}{T_G} = \frac{1}{1 - \frac{N}{\xi}\left[1 + (1-\xi)(\frac{k-X}{Y})\right]}\left\{(\frac{k-X}{Y})(X - Y - kN)\frac{fNdx}{2d_e} + \left[1 - \frac{kN}{X}\right]\frac{d^{(lM)}{}_L}{MC_pT_G} + (\frac{k-X}{Y^2})\right.$$

$$\left.(X + \frac{Y-X}{\xi})N\left[\frac{dA}{A} + \frac{dM_L}{M - M_L}\right]\right\} \qquad \ldots (9)$$

and

$$\frac{d\rho G}{\rho G} = \frac{1}{1 - \frac{N}{\xi}\left[1 + (1-\xi)(\frac{k-X}{Y})\right]}\left\{-\frac{N}{Y}(k - X + Y)\frac{fdx}{2d_e} - \frac{Y}{X}\frac{d(lM_L)}{MC_pT_G} + \frac{N}{\xi}\right.$$

$$\left.\left[1 + (1-\xi)(\frac{k-X}{Y})\right]\left[\frac{dA}{A} + \frac{dM_L}{M - M_L}\right]\right\} \quad \ldots (10) \qquad \ldots (10)$$

The Drop Growth Equations

Direct introduction of the third virial coefficient into the governing equations may be avoided by working in terms of densities instead of pressures. The equations relevant to the present enquiry are as follows

Mass transfer rate

The change in droplet mass due to the capture of molecules from the surrounding vapour is

$$\frac{dm_r}{dt} = \frac{4r\bar{l}\sqrt{8\pi R}}{3(1 + \frac{2.67Kn}{q})}\left(\rho_G\sqrt{T_G} - \rho_s(T_L, r)\sqrt{T_L}\right) \quad \ldots (11) \qquad \ldots (11)$$

Heat transfer rate

The energy balance for the droplet may be written as;

$$\lambda\frac{dm_r}{dt} = \frac{4\pi r\lambda(T_L - T_G}{1 + 3.18\ Kn} \quad \ldots (12) \qquad \ldots (12)$$

Equations (11) & (12) together with (8), (9), (10) and (39) form a complete system. The calculation procedure which is based on the standard Runge-Kutta method is similiar to that used for low pressure steam.

Apart from those given in Appendix 2, the modifications applied to the classical expression for the nucleation rate are those by Courtney (2) and Kantrowitz (3). Following the work of Plummer and Hale (4) the surface free energy of a small cluster is taken to be the same as that for the equivalent flat surface and the condensation coefficient q has taken as unity.

Calculated Results

Generally, the limiting supersaturation could occur at various distances in the nozzle depending on the inlet steam temperature as shown in Figure 4. The higher the inlet temperature to the inlet nozzle, the further downsteam supercool occurs. Supercooling tends to be near a fixed value for a given pressure.

The supersaturation ratio P/Ps increases it value at a lower mass flow rate. The pressures at wilson line decreases with an increased in inlet temperature for a contant inlet pressure.

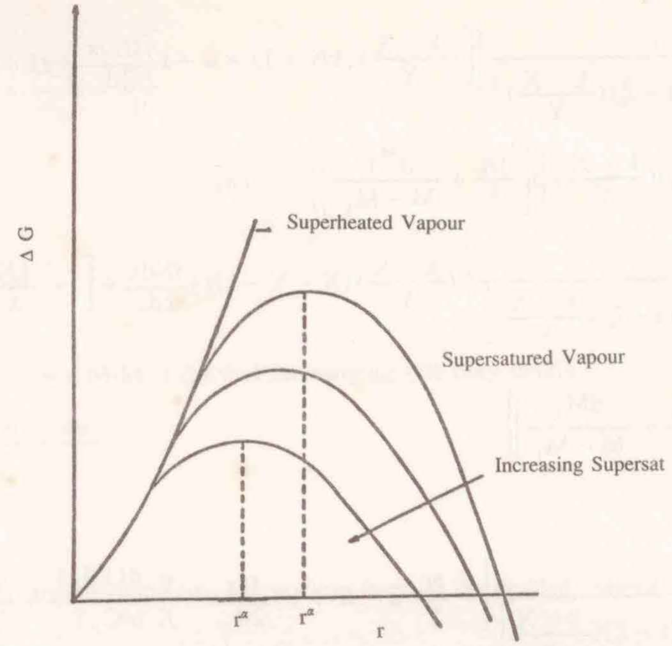

Figure 3

From figure 5, at approximately 2% wetness for example the radius of droplets increases as the pressure and temperature of supercool steam increased. As the steam expands through the nozzle, the velocity at the droplets increases as the pressure and temperature decrease. This is due to the addition heat released by condensation in a sub-sonic steam which accelerates the flow.

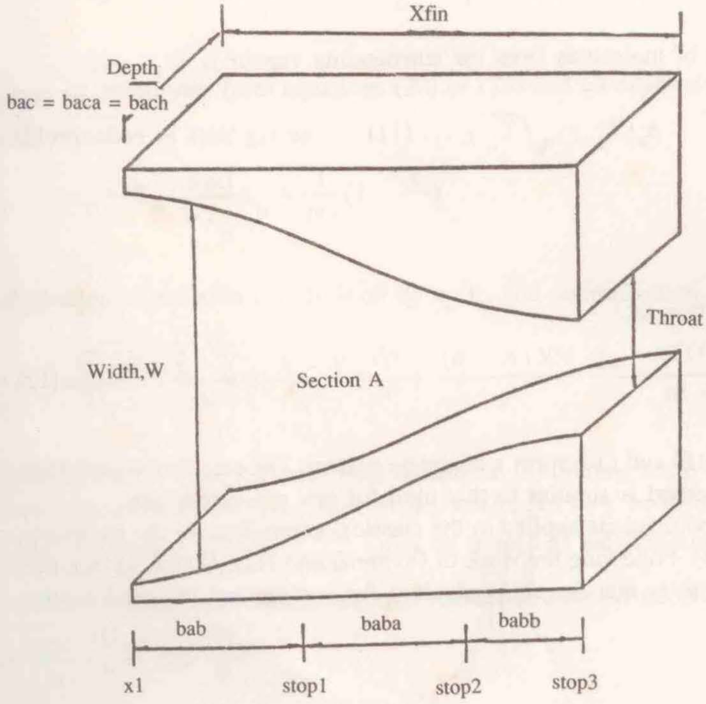

Figure (2a)

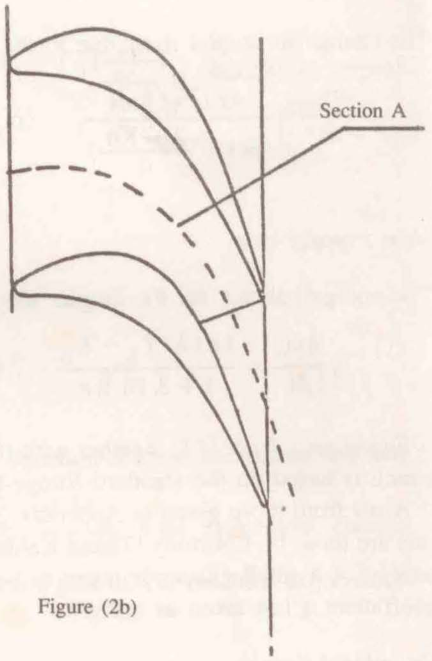

Figure (2b)

It was found that for maximum super cooling supersonic flow gave slightly higher value than the subsonic flow.

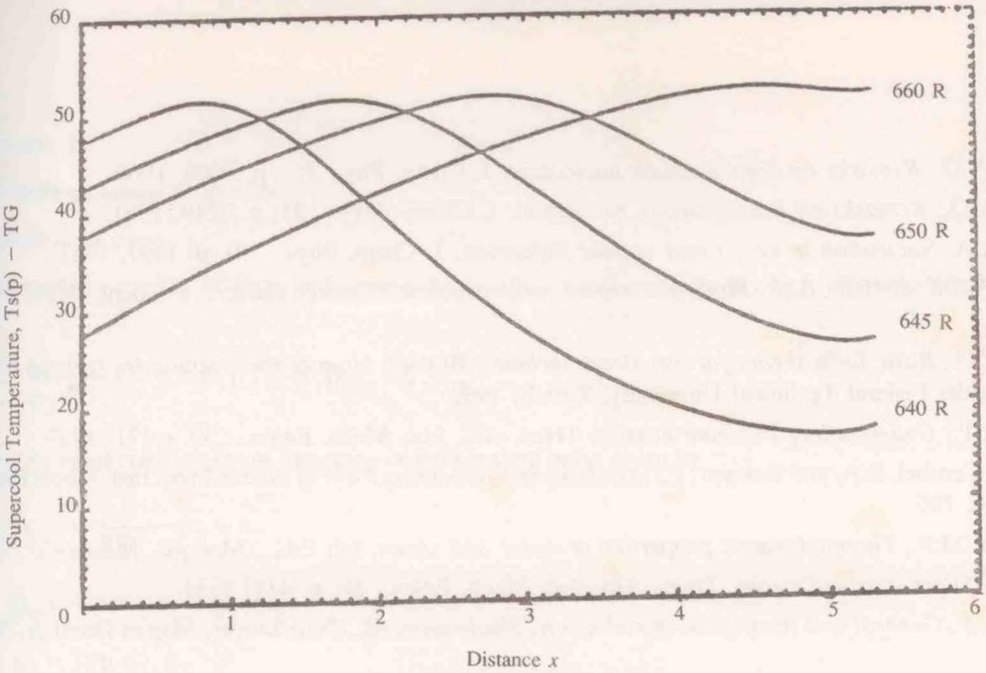

Figure 4: At pressure 20 psi

The wilson line was plotted on the h-s diagram showing the limit at which instability occurs,

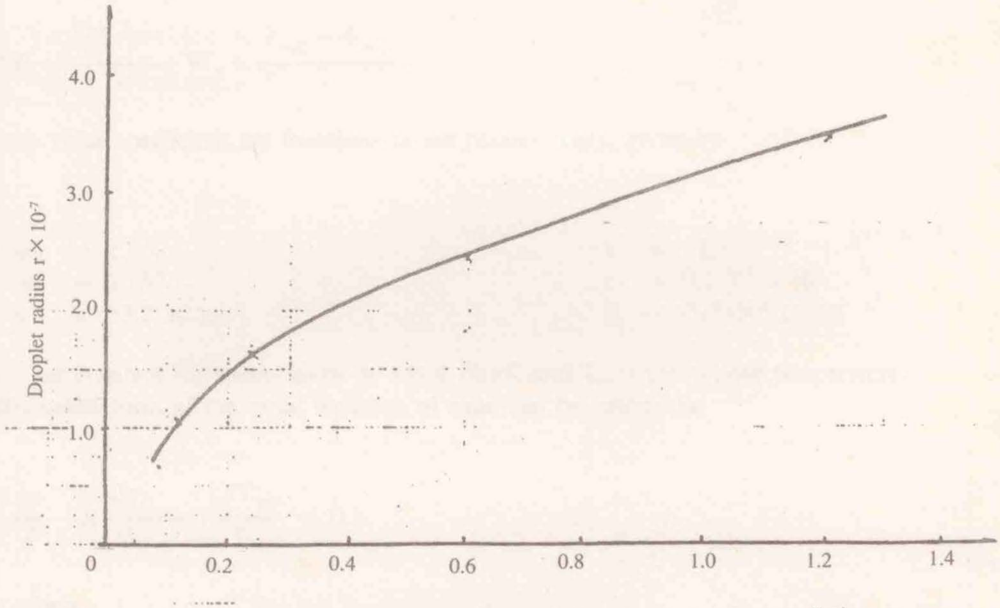

Figure 5: Pressure at Wilson point, P*

Conclusions

The instability of the flow, gives heat addition to the flow when it occurs during the formation of nucleation. This heat addition will result in an increase in Mach number. If the heat addition exceeds beyond which the flow becomes sonic then the flow will be sonic then the flow will be choice due to the increment of mass flow rate. Thus instability of the flow is affected by an increase in heat addition in the flow during nucleation.

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References

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Appendix 1

Derivation of steam properties.

1. Equation of State

The extended equation of state including only the third virial coefficient which was developed by Vukalovitch (8) is

$$\frac{p}{\rho_G R T_G} = 1 + \beta_1 \rho_G + \beta_2 \rho_G{}^2 + \beta_3 \rho_G{}^3 \qquad \text{... (13)}$$

where the virial coefficient are functions of temperature only, given by

$$\beta_1 = -\frac{a}{RT_G} - \phi_1 + b \qquad \text{... (14a)}$$

$$\beta_2 = -b\phi_1 + 4\,\phi_1{}^2 \phi_2 \qquad \text{... (14b)}$$

$$\beta_3 = 32b\,\phi_1{}^2 \phi_2 \qquad \text{... (14c)}$$

$$\theta_1 = \frac{CR}{TG^{W}1}$$

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$$W_1 = \frac{3 + 2_{m1}}{2}, \quad W_2 = \frac{3_{m2} - 4_{m1}}{2}$$

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where,

ml = 1.968
m2 = 2.957
a = 63.2 m^5/kgs^2

k = 22.7
c = 0.3977 x 10^6
b = 0.00085 m^3/kg

R is the gas constant for steam taken as 461.4 J/kgK and T_G is the vapour temperature.
The differential form of the virial equation of state can be written as,

$$\frac{dP}{P} - X\frac{d\rho_G}{\rho_G} - Y\frac{dT_G}{T_G} = 0 \qquad \text{... (15)}$$

where

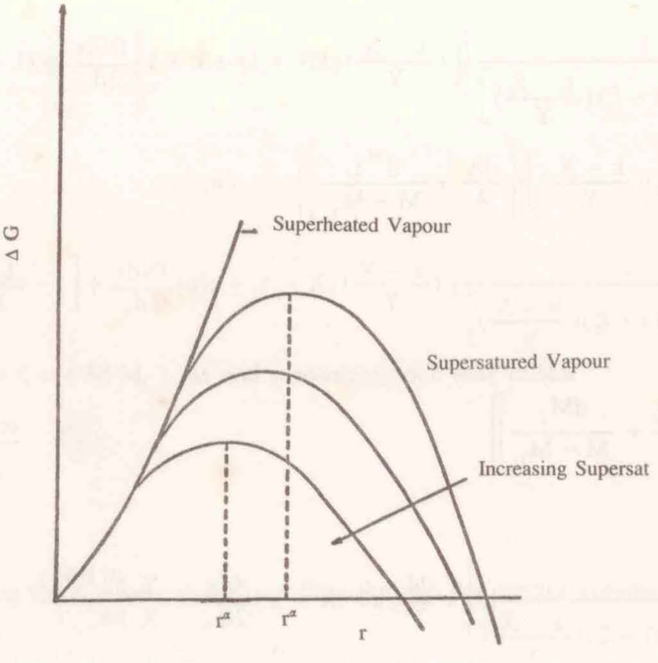
$$X = 1 + \frac{\beta_1 \rho_G + 2\beta_2 \rho_G{}^2 + 3\beta_3 \rho_G{}^3}{1 + \beta_1 \rho_G + \beta_2 \rho_G{}^2 + \beta_3 \rho_G{}^3} \qquad \text{... (16a)}$$

$$Y = 1 + \frac{T_G}{1 + \beta_1 \rho_G + \beta_2 \rho_G{}^2 + \beta_3 \rho_G{}^3}\left[\rho_G \frac{d\beta_1}{dT_G} + \rho_G{}^2 \frac{d\beta_2}{dT_G} + \rho_G{}^3 \frac{d\beta_3}{dT_G}\right] \qquad \text{... (16b)}$$

It can be easily seen that for perfect gas all β's are zero and therefore X and Y tend to unity.

Specific Heat at Constant Pressure

An expression for C_p is obtained by using the thermodynamics relation;



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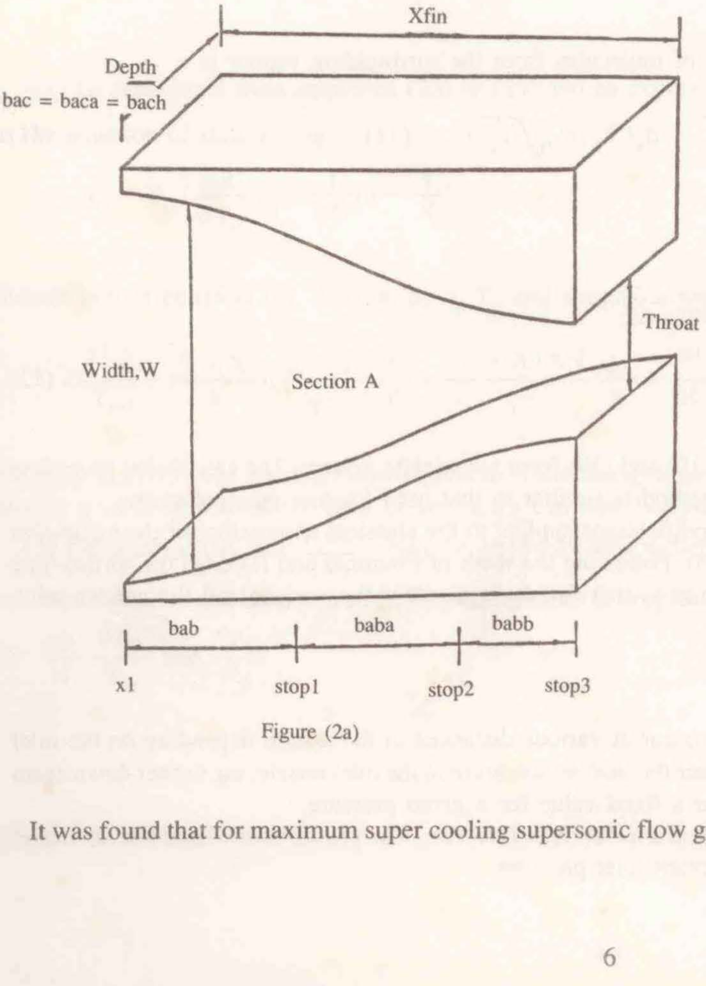

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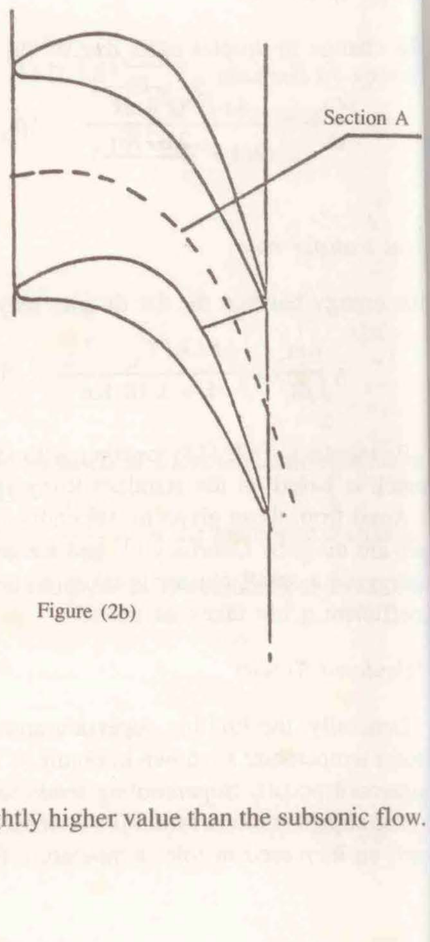

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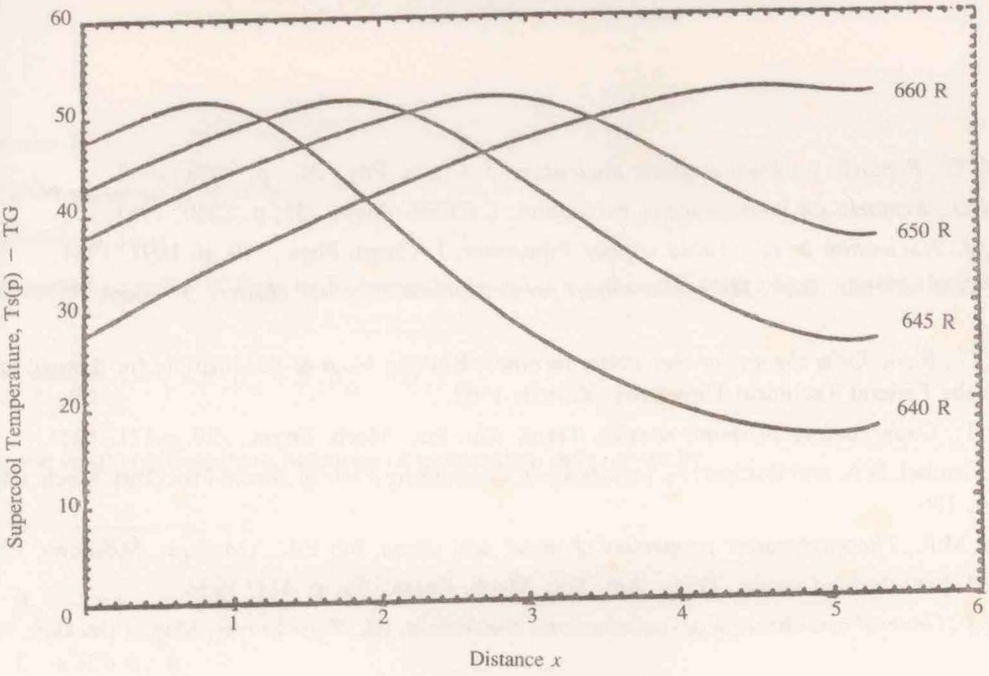

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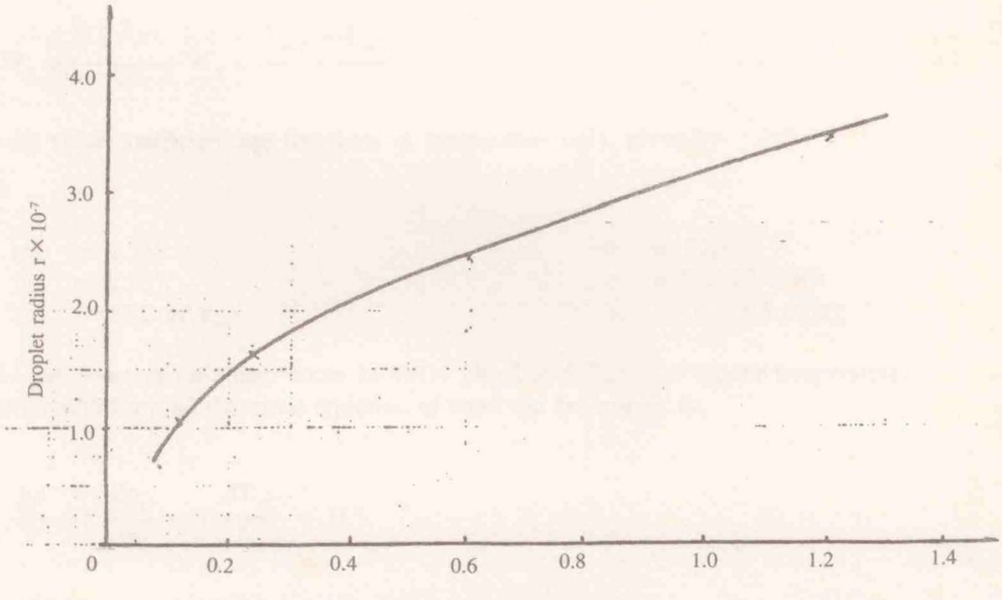

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It can be easily seen that for perfect gas all β's are zero and therefore X and Y tend to unity.

Specific Heat at Constant Pressure

An expression for C_p is obtained by using the thermodynamics relation;

$$(\frac{dh}{dP})_{T_G} = V - T_G(\frac{dV}{dT_G})_P \quad \text{... (17)}$$

Hence,

$$C_p = \frac{\partial}{\partial T_G}\int\left[V - T_G(\frac{\partial V}{\partial T_G}P\right]dp + f_c(T_G) \quad \text{... (18)}$$

The constant of integration f_c (T_G) is determined by setting $P = 0$ in the resulting expression. The final expression for C_p is,

$$C_p = -R\ T_G\left[\frac{1}{T_G}(\frac{1}{V}\frac{d\beta_1}{dT_G} + \frac{1}{2V^2}\frac{d\beta_2}{dT_G} + \frac{1}{3V^3} + \frac{d\beta_3}{dT_G}) + (\frac{1}{v}\frac{d^2\beta_1}{dT_G 2} + \frac{1}{2V^2}\frac{d^2\beta_2}{dT_G 2} + \frac{1}{3V^3}\frac{d^2\beta_3}{dT_G{}^2})\right]$$

$$+ 1.1111 + 0.00071\ T_G + \frac{6992}{T_G{}^2}\ \text{kJ / kgK} \quad \text{... (19)}$$

Specific Heat Capacity At Constant Volume

An expression for C_v is obtain by combining the equation of state with the well established relationship.

$$C_p - C_v = T_G(\frac{\partial P}{\partial T})_V(\frac{\partial V}{\partial T_G}P$$

giving

$$C_v = -2RT_G\left[\frac{1}{T_G}(\frac{1}{V}\frac{d\beta_1}{dT_G} + \frac{1}{2V^2}\frac{d\beta_2}{dT_G} + \frac{1}{v^3}\frac{d\beta_3}{dT_G})\right. \quad \text{... (20)}$$

$$-\frac{1}{2}(\frac{1}{V}\frac{d^2\beta_1}{dT_G{}^2} + \frac{1}{2V^2}\frac{d^2\beta_2}{dT_G 2} + \frac{1}{3V^3}\frac{d^2\beta_3}{dT_G{}^2})$$

$$+ 1.1111 + 0.00071\ T_G + \frac{6992}{T_G{}^2}\ \text{kJ / kgK} \quad \text{... (21)}$$

Isentropic Exponent

The isentropic exponent k is defined by;

$$k = -\frac{V}{P}(\frac{\partial P}{\partial V})_s \quad \text{... (22)}$$

Using Maxwell's relationships and rearranging results in,

$$k = \frac{V}{P}(\frac{\partial P}{\partial V})_{T_G}\frac{C_p}{C_v} \quad \text{... (23)}$$

substitution for $(\frac{\partial P}{\partial V})_{T_G}$ from the equation of state yields.

$$k = \frac{V}{P}\left[R\ T_G\left(\frac{1}{V^2} + \frac{2\beta_2}{V^3} + \frac{3\beta_2}{V^4} + \frac{4\beta_3}{V^5}\right)\right]\frac{C_p}{C_v} \qquad \text{... (24)}$$

A useful relationship for use in the energy equation can be obtained as follows; Equation (20) and (22) can be rewritten as,

$$C_p - C_v = -\frac{T_G}{\rho G^2}\left(\frac{\partial P}{\partial T_G}\right)_{\rho_G}\left(\frac{\partial \rho G}{\partial T_G}\right)_P \qquad \text{... (25)}$$

$$k = \frac{\rho_G}{p}\left(\frac{\partial P}{\partial \rho_G}\right)\frac{C_p}{C_v} \qquad \text{... (26)}$$

Substituting from the definitions of X and Y, simplfying and rearranging yields

$$C_p = \frac{k}{k - X}\,\frac{Y^2}{X}\,\frac{p}{\rho_G T_G} \qquad \text{... (27)}$$

Specific Enthalpy

From the first and second law of thermodynamics,

$$\left(\frac{\partial h}{\partial P}\right)_{T_G} = v - T_G\left(\frac{\partial v}{\partial T_G}\right)_P \qquad \text{... (28)}$$

which can be integrated to give

$$h = \int\left[v - T_G\left(\frac{\partial v}{\partial T_G}{}_P\right)\right] dP + f_h(T_G) \qquad \text{... (29)}$$

It may be shown that,

$$f_h(T_G) = \int f_c(T_G)\, dT + \text{constant} \qquad \text{... (30)}$$

The constant of integration is arbitrary but usual pratice is to set h = 0 at 0°C for the satured liquid. The accepted value of h at 100°C, saturated vapour is then 2676 kJ/kg. Substitution of the equation of state and integration yields;

$$h = -R\ T_G\left[\frac{1}{v}\frac{d\beta_1}{dT_G} + \frac{1}{2v^2}\frac{d\beta_2}{dT_G} + \frac{1}{3v^3}\frac{d\beta_3}{dT_G}\right]$$

$$+ (1.1111\ T_G + 3.5588 \text{ x } 10^{-4} \text{ x } T_G^{\ 2} - \frac{6992}{T_G}) \qquad \text{... (31)}$$

$$+ Pv + 2070.54\ \text{kJ/kg}$$

Specific Entropy

The specific entropy can be found by integrating Maxwell's relationships

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \qquad \text{... (32)}$$

giving

$$s = -\int \left(\frac{\partial v}{\partial T_P}\right) \, dP + f_s\,(T) \qquad \text{... (33)}$$

Using the equation of state, it may be shown that (33) can be integrated by means of a procedure similiar to the one used in specific enthalpy. The final expression for the specific entropy is;

$$s = 0.3153 + 1.1111 \ln T_G + 0.00071\, T_G - \frac{6992}{T_G{}^2}$$

$$+ R\left[\left(\ln v - \frac{\beta_1}{v} - \frac{\beta_2}{2v^2} - \frac{\beta_3}{3v^3}\right) \right.$$

$$\left. - T_G\left(\frac{1}{v}\frac{d\beta_1}{dT_G} + \frac{1}{2v^2}\frac{d\beta_2}{dT_G} - \frac{1}{3v^3}\frac{d\beta_3}{dT_G}\right) \right] \text{kJ/kgK} \qquad \text{... (34)}$$

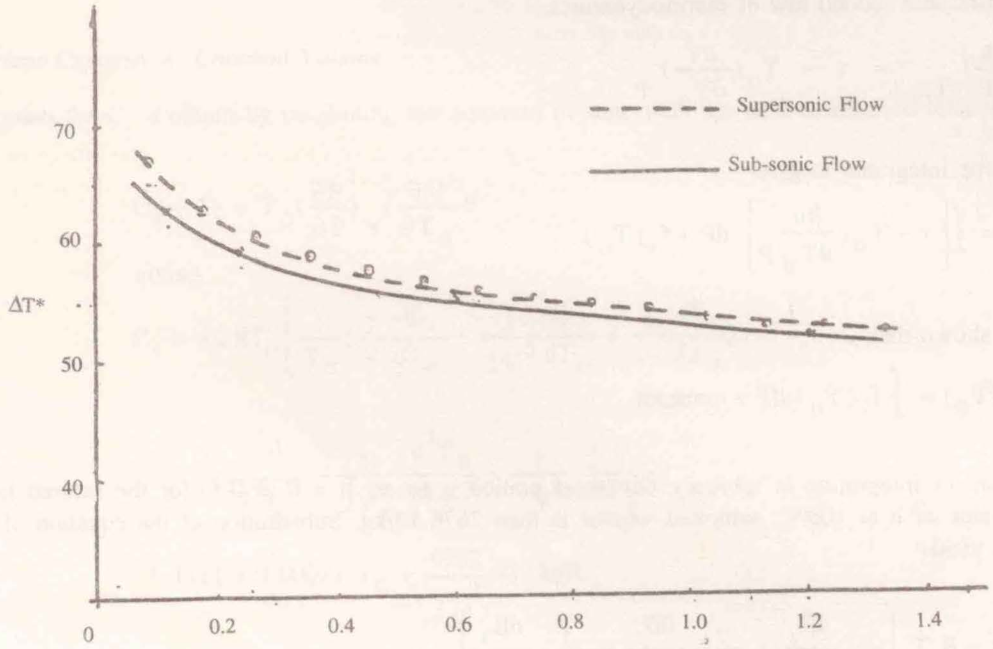

Figure 6: Pressure at Wilson point, P* (bar)

Appendix 2

Nucleation Rate at Low Pressure

1. Critical radius and free energy barrier

It will be seen that in the presence of an available surface, there will be no need for the formation of the droplets. If there is no surface available or the vapour denied the liquid surface, the only way the vapour can condense is to form its own surface by homogeneous nucleation. Its behaviour will be affected by the additional free energy associated with their formation. For the formation of a droplet of radius r, and ignoring any electric charges, the change in free energy due to surface tension, is given by

$$G_r = 4\pi r^2 \sigma \qquad \text{... (35)}$$

where,

σ is the surface tension

r is the radius of droplet.

Hence, the total change in the free energy for a vapour to condense, (when there is no surface) becomes

$$\Delta G = \Delta G_1 + \Delta G_r$$

$$= 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \rho_L \; RT_G \; 1n p_s \frac{P}{(T_G})) \qquad \text{... (36)}$$

For giving vapour conditions, the variations of ΔG with r have a form as shown in Figure 3, ΔG increases initially with increasing r, up to its critical value ΔG occuring at the critical radius r* can be obtained by differentiating equation (36)

$$\frac{d(\Delta G)}{dV} = 0 = 8\pi r \sigma - 4\pi r^2 \rho_L RT \; 1n \frac{p}{p_S(T_G)}$$

$$r^* = \frac{2\sigma}{\rho_L R T_G \; 1n \frac{P}{P_S(T_G)}}$$

or

$$1n \frac{P}{P_S(T_G)} = \frac{2\sigma}{r^* \rho_L R T_G}$$

Equation (37) is known as Kelvin-Helmoltz's equation and for a given supersaturation ratio, gives the size of a critical droplet which be in metastable equilibrium. Droplets larger than this size will achieve a reduction in free energy by capturing molecules and will tend to grow. Smaller droplets will achieve reduction in surface free energy by losing molecules and will tend to evaporate.

This equation is valid for superheated, saturated and supercooled vapour. In the case of saturated vapour, the second term will vanish and the gain of free energy increases with the square of the radius of cluster.

In the case of superheated vapour, the second term is positive and there is a larger gain of free energy for a fluid mass going from vapour into liquid cluster. This does not mean that it is free from embryos of liquid, but is constantly disrupted due to molecular processes.

Thus G* forms can activation barrier to the condensation of pure vapour. On crossing the saturation line, the vapour will initially supercool. The only route by which condensation can proceed is via the fortuitous formation of cluster due to molecular collisions.

2. Steady State Nucleation Rate

In the classical derivation of the expression for nucleation rate (10) the reasoning is general leading to the expression

$$I = \frac{C_{g*} n_0 \exp\left[-\Delta G/\tilde{k}T_G\right]}{(2\pi\tilde{k}\ T_G/Z)^{\frac{1}{2}}} \qquad \dots (38)$$

where

$$Z = -\left(\frac{\partial^2 \Delta G}{\partial g^2}\right)_{g=g^*}$$

The only terms affected by the virial coefficient in the further development of the analysis are Z and C_{g*}. To avoid the introduction of the virial coefficient it is best to work in terms of density. The value of Z can be found from equations 25 as;

$$\grave{Z} = \frac{2}{9}\left[\frac{36\pi m^2}{\rho L^2}\right]^{1/3} \frac{\sigma}{G^{*4/3}}$$

and

$$C_{g*} = \frac{q\, 4\pi r^{*2}}{m} \rho G \sqrt{\frac{RT_G}{2\pi}}$$

$$I = q\sqrt{\frac{2\sigma}{\pi m^3}}\ \frac{\rho G^2}{\rho L}\ \exp\left[-\Delta G^*/\tilde{k}\ T_G\right] \qquad \dots (39)$$

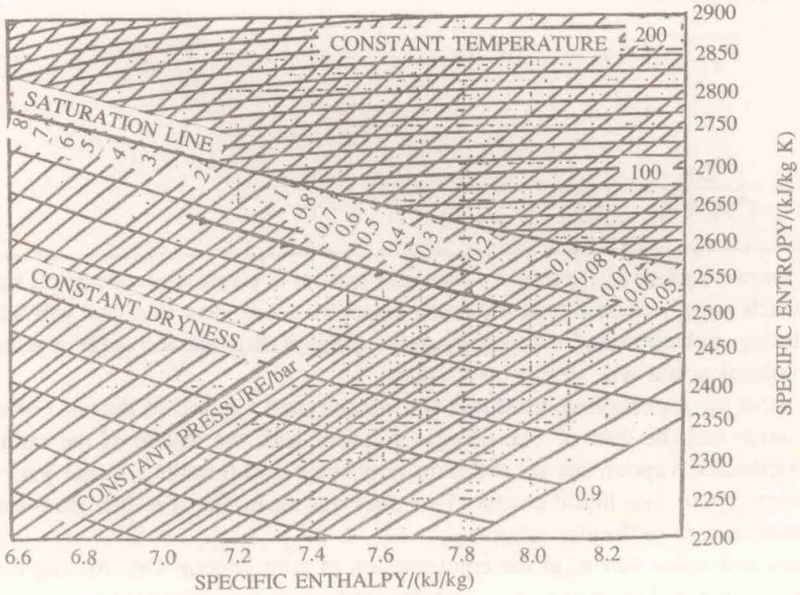

Figure 7: Wilson Line at $\dot{P}$ = 1000