Thermodynamics Question 1

One form of the Gibbs-Thompson Equation (GTE) describes the shift in melting point for nano-crystals as a function of their size and can be adapted to describe the shift in melting point for confined fluids such as at an AFM tip as a function of a fluid filled gap's height, *h*, Fig. 2 below. Scalfi L, Coasne B, Rotenberg B, *On the Gibbs-Thomson equation for the crystallization of confined fluids.* J. Chem. Phys. **154** 114711 (2021) present a new derivation of the GTE for confined fluids and use the derivation to simulate crystallization in confined pores and gaps using a Monte Carlo method.

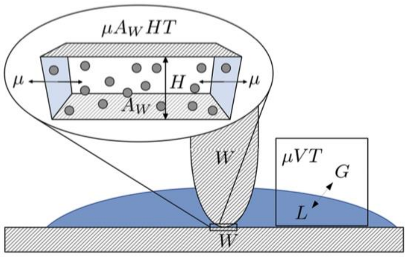


FIG. 2. Illustration of a system confined between the tip of an atomic force microscope and a substrate, as in the experiments of Ref. 5. From the thermodynamic point of view, it forms an open system confined in a slit pore with lateral area A_W and distance between walls H at a fixed temperature T and chemical potential μ set by the liquid–gas equilibrium in the reservoir.

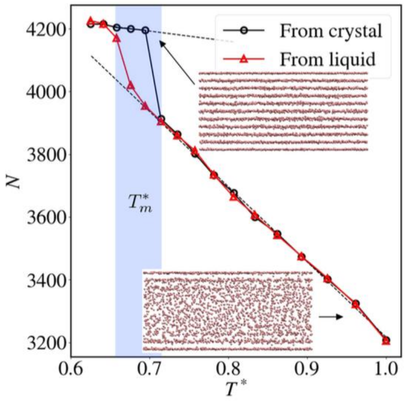


FIG. 9. Average number of atoms N in each HPT-GCMC replica as a function of the replica's temperature T^* for a pore size H^* = 11.6. The two sets of data are obtained starting either from crystal (black circles) or liquid (red triangles) configurations in all replicas. Black dashed lines are linear fits to the low and high temperature regions, which are used to locate the melting temperature T_m (blue shaded area indicating the confidence interval). The snapshots illustrate typical crystal (top right) and liquid (bottom) configurations.

a) **The normal derivation of the GTE involves simply writing an expression for the Gibbs free energy that includes volumetric and surface terms, considering equilibrium for small particles (spheres) and solving for the particle size. Derive the GTE in this way for a planar crystal with infinite width and height *H* (Scalfi uses "*h*" for the enthalpy per particle). Scalfi's GTE includes two surface energies, that of the liquid and that of the solid. How do you accommodate this in your derivation?**

$$\frac{T_m - T_m^b}{T_m^b} = \frac{2(\gamma_{LW} - \gamma_{SW})}{H\rho\Delta_m h}, \qquad (1)$$

GT equation .

-5

a.) $\mu_l(T_m') = \mu_s(T_m, P_2)$

$d\mu = -\bar{s}dT + \bar{v}dp$

$$\cancel{\mu_l(T_m)} + \int_{T_m}^{T_m'} -\bar{s}_l dT = \cancel{\mu_s(T_m)} + \int_{T_m}^{T_m'} -\bar{s}_s dT + \int_{p^0}^{P_2} \bar{v}\, dp$$

$$-\int(\bar{s}_l - \bar{s}_s)dT = \int_{p^0}^{p^2} \bar{v}_s\, dp$$

$$-\int_{T_m}^{T_m'} \Delta_{fw} s\, dT = \bar{V}_s \int_{P_2^0}^{P_2} dp$$

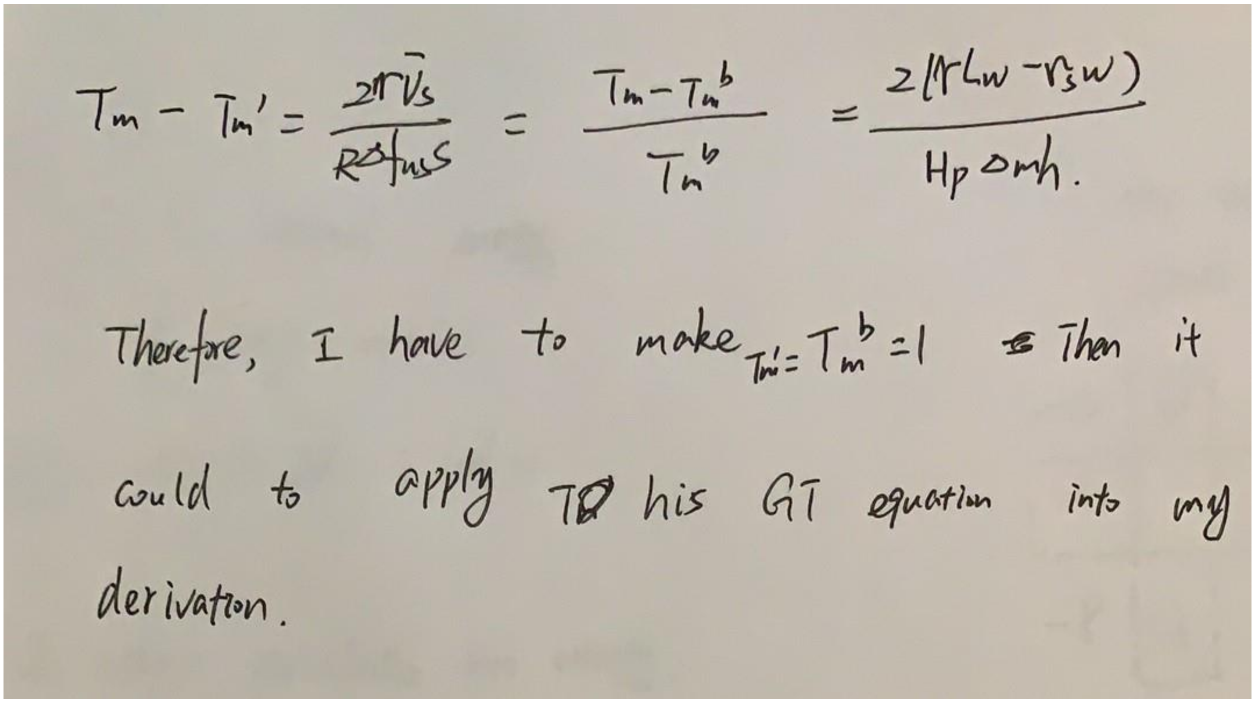
$$-\Delta_{fus} S(T_m' - T_m) = \bar{V}_s \Delta P$$

$$\Delta_{fus} S(T_m' - T_m) = \frac{-\bar{V}_s 2\gamma}{R}$$

spherical

$$\Rightarrow T_m' = T_m - \frac{2\gamma\bar{V}_s}{R\Delta_{fus}S}$$

Combine withe the paper equation (1)



$$T_m - T_m' = \frac{2\pi \bar{V}_s}{R\Delta_{fus}S} = \frac{T_m - T_m^b}{T_m^b} = \frac{2(\gamma_{Lw} - \gamma_{Sw})}{H\rho\Delta_m h}.$$

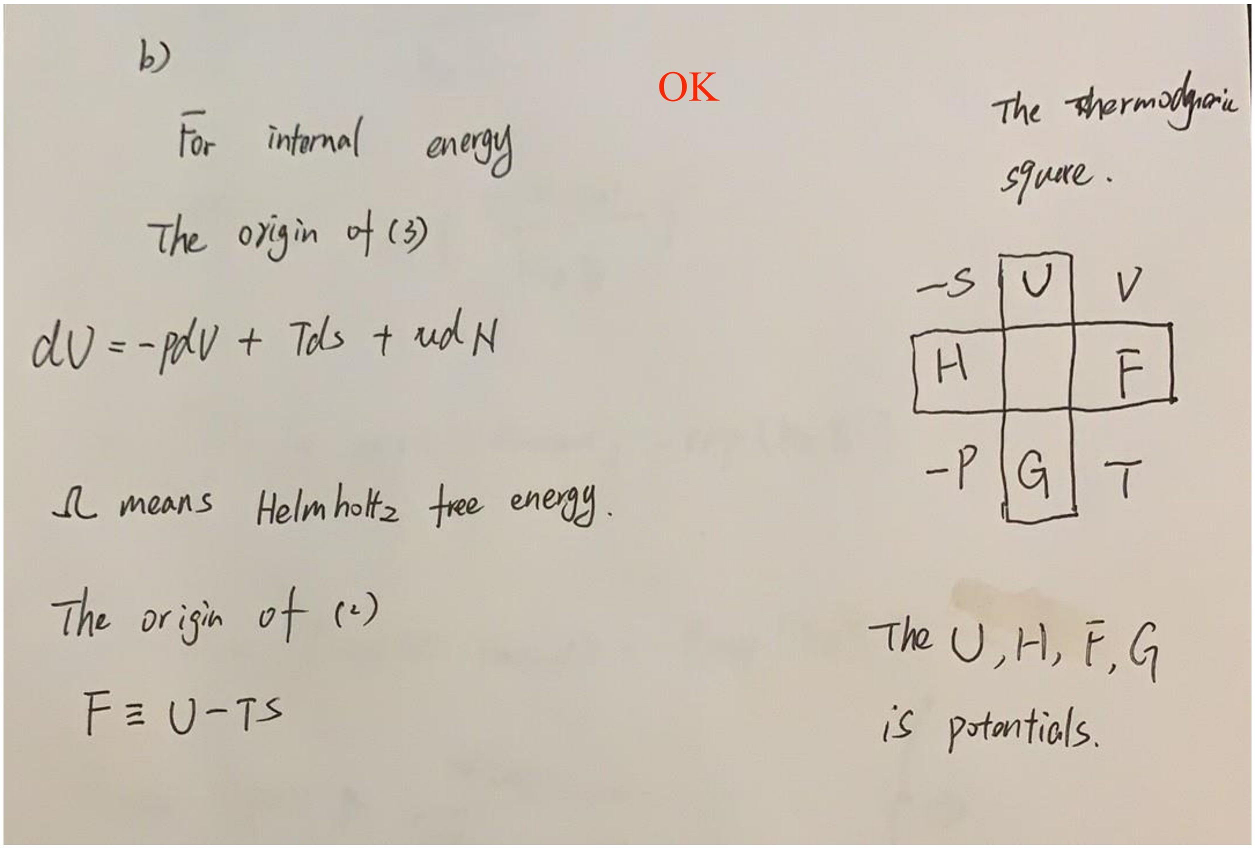
Therefore, I have to make $T_m' = T_m^b = 1$ Then it could to apply T~~o~~ his GT equation into my derivation.

b) **Scalfi gives the following thermodynamic potential (2) and internal energy (3) for the fluid/solid between the gap,**

$$\Omega = U - TS - \mu N = -PA_W H + 2\gamma A_W, \qquad (2)$$

$$U = TS - PA_W H + 2\gamma A_W + \mu N, \qquad (3)$$

Use the thermodynamic square or other means to explain the origin of these two expressions. What kind of free energy is Ω?



b)

OK

For internal energy

The origin of (3)

$dU = -pdV + Tds + \mu dN$

Ω means Helmholtz free energy.

The origin of (2)

$F \equiv U - TS$

The thermodynamic square.

-S	U	V
H		F
-P	G	T

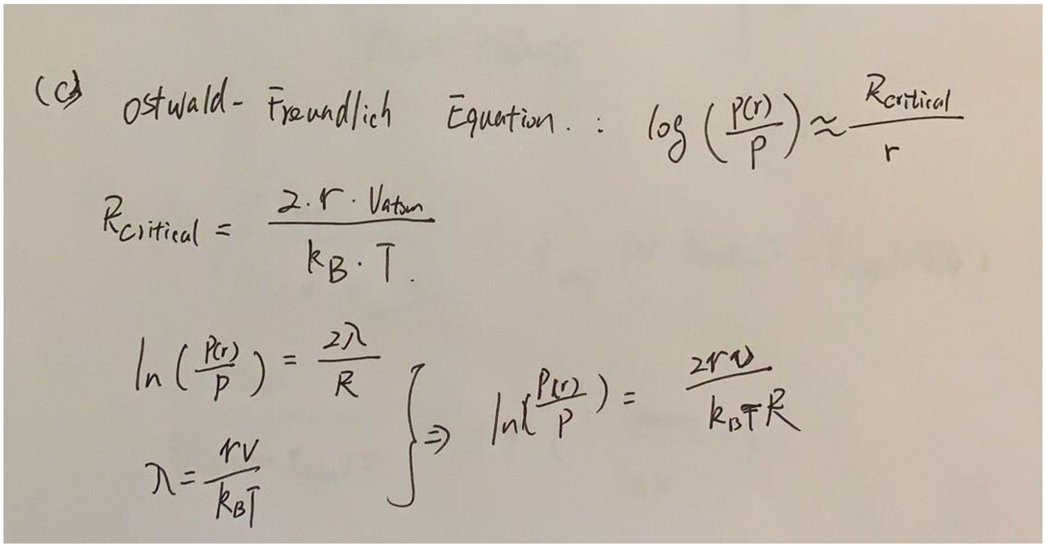
The U, H, F, G is potentials.

c) The son of Herman von Helmholtz (Robert von Helmholz) derived the Gibbs-Thompson equation from the Oswald-Freundlich Equation (OFE) using the integrated Clausius-Clapeyron Equation (CCE) for his PhD dissertation in 1885 (things were simpler then).

$$\ln\left(\frac{p(r)}{P}\right) = \frac{2\gamma V_{\text{molecule}}}{k_B T r}$$ **OFE**

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{PL}{T^2 R}$$ **CCE**

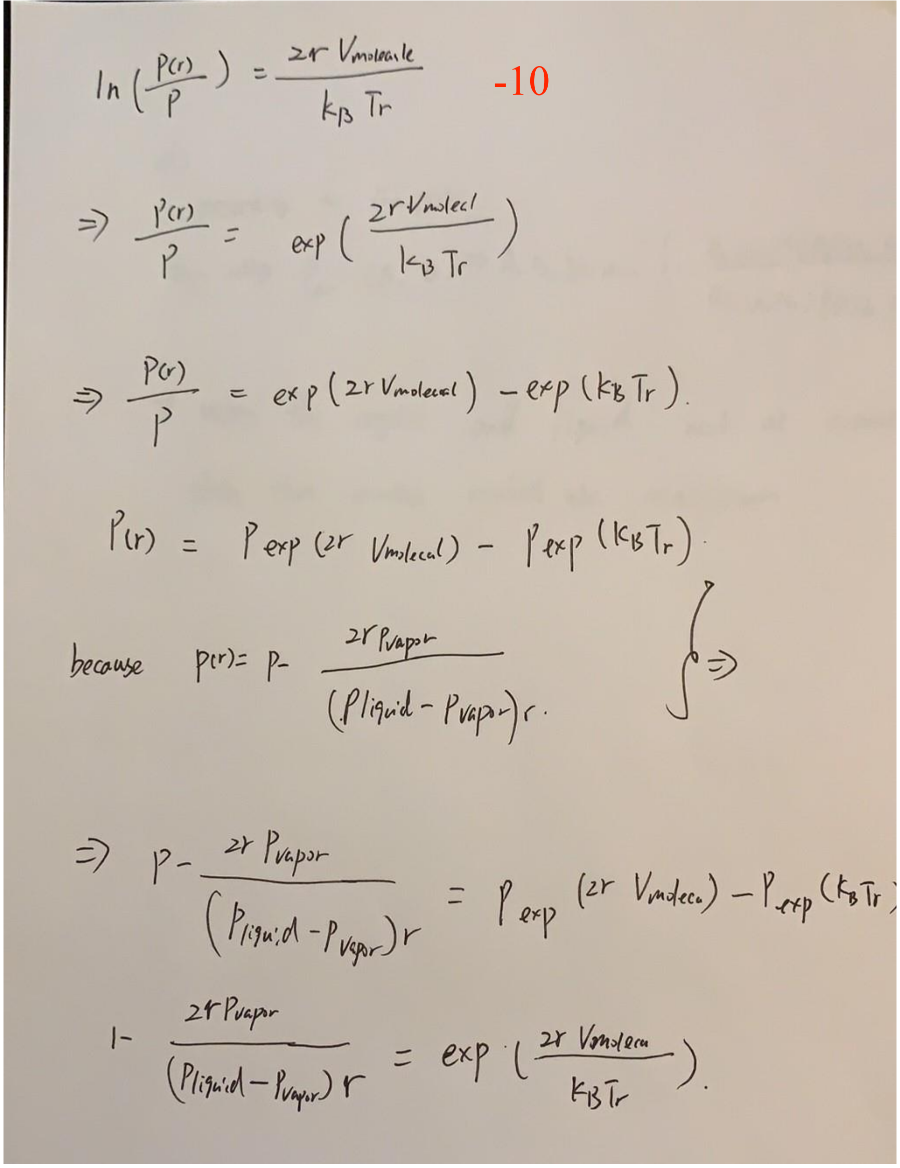
For this reason, the OFE or Kelvin Equation is sometimes referred to as the GTE. Obtain the GTE from the OFE using the integrated CCE. Also, give (don't derive) the Ostwald-Freundlich Equation which describes the relationship between the supersaturated mole fraction, *x*, and nanoparticle size, *r*, for crystallization from solution.



(c) Ostwald- Freundlich Equation. : $\log\left(\frac{P(r)}{P}\right) \approx \frac{R_{critical}}{r}$

$$R_{critical} = \frac{2 \cdot r \cdot V_{atom}}{k_B \cdot T}.$$

$$\left.\begin{aligned} \ln\left(\frac{P(r)}{P}\right) &= \frac{2\lambda}{R} \\ \lambda &= \frac{rV}{k_B T} \end{aligned}\right\} \Rightarrow \ln\left(\frac{P(r)}{P}\right) = \frac{2rv}{k_B T R}$$



$$\ln\left(\frac{P(r)}{P}\right) = \frac{2r\, V_{molecule}}{k_B\, Tr}$$

-10

$$\Rightarrow \frac{P(r)}{P} = \exp\left(\frac{2r V_{molecl}}{k_B\, Tr}\right)$$

$$\Rightarrow \frac{P(r)}{P} = \exp\left(2r V_{molecul}\right) - \exp\left(k_B\, Tr\right).$$

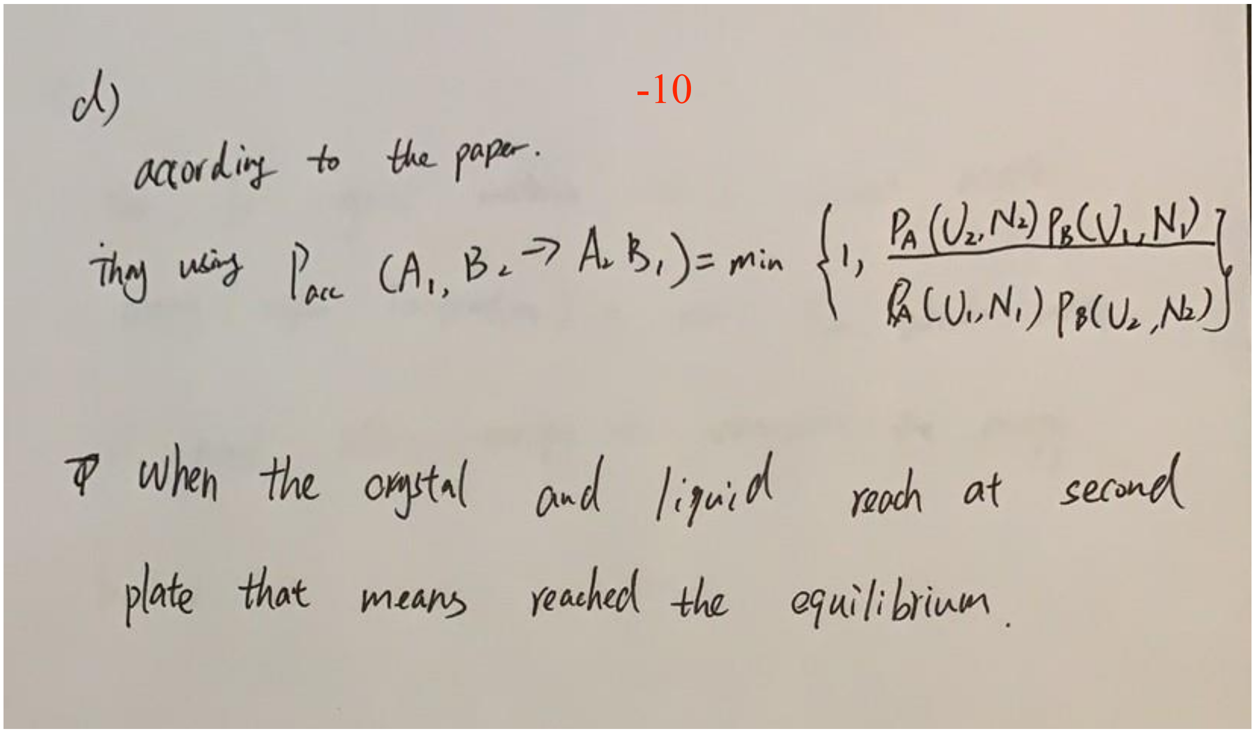
$$P(r) = P \exp\left(2r\ V_{molecul}\right) - P \exp\left(k_B T_r\right).$$

$$\left.\text{because}\quad p(r) = p - \frac{2r P_{vapor}}{(P_{liquid} - P_{vapor})r}.\right\} \Rightarrow$$

$$\Rightarrow p - \frac{2r\, P_{vapor}}{(P_{liquid} - P_{vapor})r} = P_{exp}\left(2r\ V_{molecu}\right) - P_{exp}\left(k_B Tr\right)$$

$$1 - \frac{2r P_{vapor}}{(P_{liquid} - P_{vapor})\, r} = \exp\left(\frac{2r\ V_{molecu}}{k_B Tr}\right).$$

d) Scalfi used Monte Carlo Simulations with the Metropolis method to determine the melting point, Figure 9 where N is the density and T^* is a reduced temperature. He used a 6-12 potential with a cutoff of 2.5 σ where σ is the atomic size. Monte Carlo steps involved translation, deletion or insertion. The starting state could be liquid or crystal structures and resulted in the densities shown in Figure 9. Give an algorithm for a typical Metropolis simulation of this type. How would you determine if the simulation had reached equilibrium?



d)

-10

according to the paper.

They using $P_{acc}(A_1, B_2 \to A_2 B_1) = \min\left\{1, \frac{P_A(U_2,N_2)\,P_B(U_1,N_1)}{P_A(U_1,N_1)\,P_B(U_2,N_2)}\right\}$

When the crystal and liquid reach at second plate that means reached the equilibrium.

e) In Figure 9 Scalfi shows that the crystalline structure exists at the interface with the AFM tip and the stage (which is the same material in the simulation) even in the (bulk) amorphous state (lower structure). Derive expressions comparing the free energy barrier, ΔG^*, and phase size, r^*, for surface (heterogeneous) and bulk (homogeneous nucleation). Can this explain the observed behavior?

Yes, for crystal materials, it is require more energy(higher temperature) to reach Tm which means it need more energy to overcome the energy barrier.

-10

Thermodynamics Question 2

Seede R, Ye J, Whitt A, Trehern W, Elwany A, Arroyave R, Karaman I, *Effect of composition and phase diagram features on printability and microstructure in laser powder bed fusion: Development and comparison of processing maps across alloy systems* Add. Man. **47** 102258 (2021) consider four nickel super alloys that are used for laser powder-bed-fusion (LPBF) additive manufacturing (AM) (3d printing). In this process a layer of metal powder is deposited followed by melting of a structural layer using a laser to form a solid metal layer. The process is repeated for successive layers. After many layers are deposited the excess metal powder is removed and a 3d part has been created. Control of the crystalline phases and their structure during the AM process is important to the final properties. Seede considers four super alloys Ni-20% Cu, Ni-5% Al, Ni-5% Zr, and Ni-8.8% Zr. Figure 1 shows the phase diagrams for these four alloys.

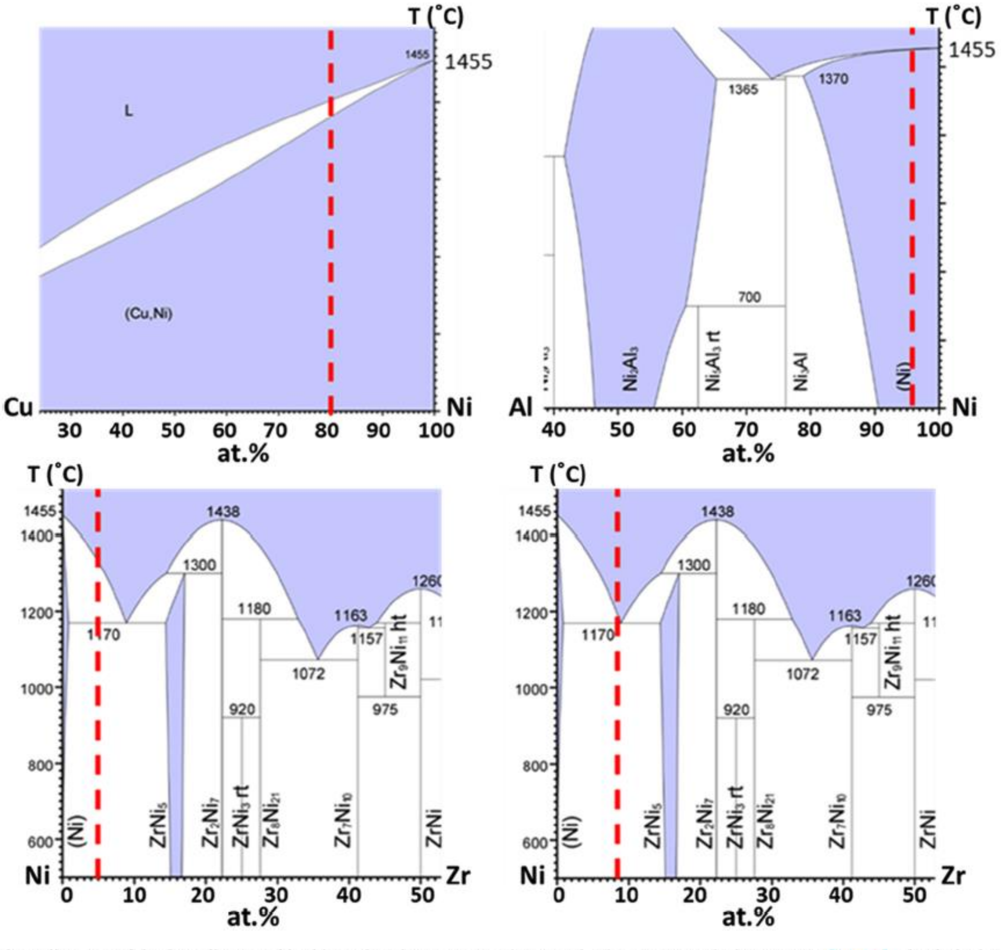


Fig. 1. Binary phase diagrams of the four alloys used in this study: Ni-20 at% Cu, Ni-5 at% Al, Ni-5 at% Zr, and Ni-8.8 at% Zr [44–46]. The dashed red lines indicate the alloy composition within each of the phase diagrams. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

a) For Ni-20% Cu **what type of system** is this? How would you determine the **composition and amounts** of the phases present if the temperature and composition were in the white region of the phase diagram? For such a system if you observed spherical domains in a matrix phase, **what is the state and composition of the spherical domains and of the matrix phase**?

b) For Ni 8.8% Zr **what type of phase region** is this? **What is the triple point called**? **Write the reaction** that occurs at this point and **write the Gibbs phase rule** that shows that this condition only occurs at a point on the phase diagram. If the sample were quenched from the liquid to the melt sketch a cartoon of the structure that would result including which parts would be Ni rich and which would be Zr rich.

c) For Ni 5% Zr consider two thermal regimes, a slow cool to the bottom of the phase diagram and a quench to the bottom. Sketch a cartoon showing the resulting structure including accurate phase amount and labeled compositions of the phases.

d) There are several intermetallic phases that exist in these phase diagrams. Explain what an intermetallic is and why it forms. List the location of all of the intermetallic phases in these phase diagrams.

e) Seede presents the following processing maps for LPBF AM. In these maps keyholing is the presence of voids between previous powder grains that remain in a solid part. Balling indicates beading of the powder. Both are defects that are detrimental to the product. Explain **why the boundary between the orange and white regions are linear** in these plots **why the linearity fails** and **why balling and keyholing are observed**. **Why is the phase diagram important** to an analysis of these processes?

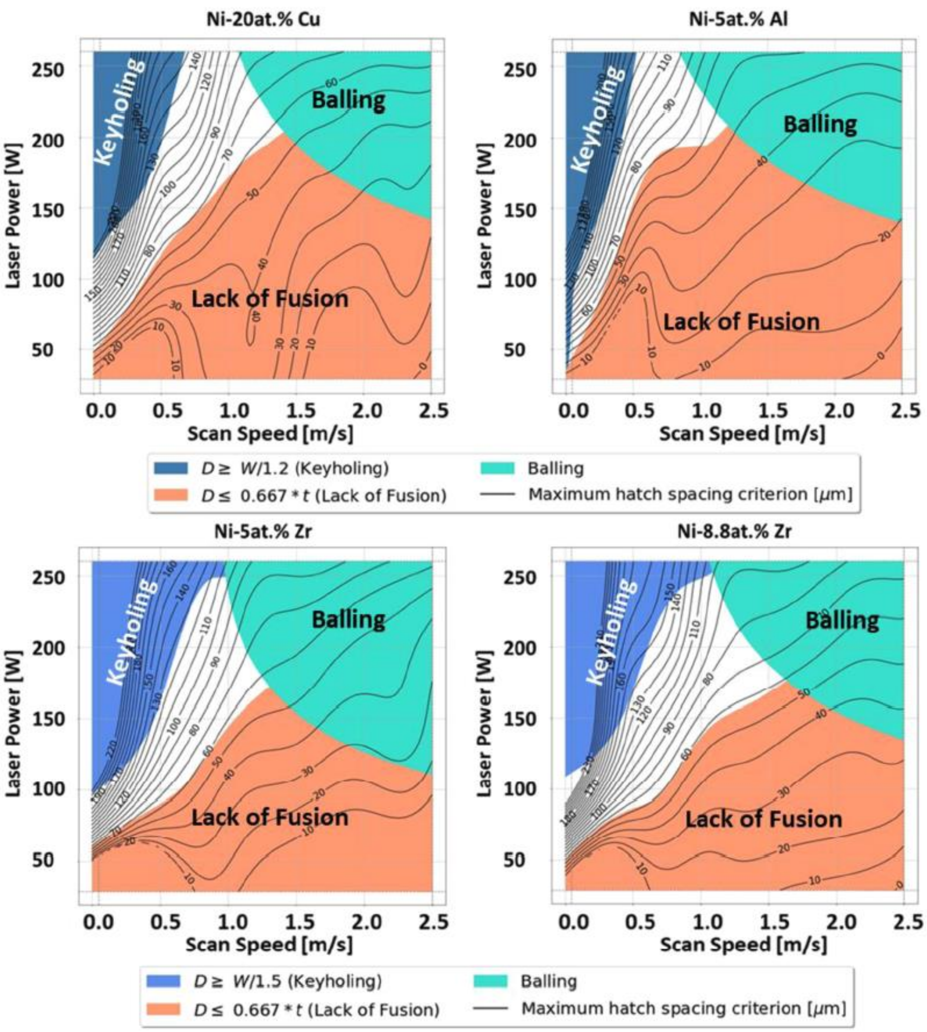
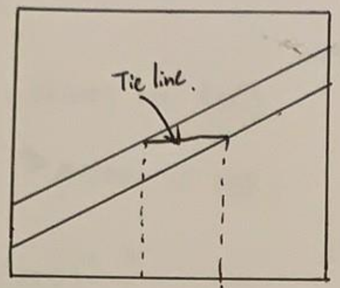


Fig. 3. L-PBF process parameter maps with finalized selections of keyholing criteria and maximum hatch spacing contours. The keyholing criterion selected for Ni-20 at % Cu and Ni-5 at% Al is $W/D \le 1.2$, and $W/D \le 1.5$ for Ni-5 at% Zr and Ni-8.8 at% Zr. Lack of fusion criteria is kept at $D \le 0.667t$ for all maps, and the balling region was fit to single track experimental data using a Support Vector Machine (SVM) classifier. *D*: Melt Pool Depth, *W*: Melt Pool Width, *t*: Powder Layer Thickness, h_{max}: Maximum Hatch Spacing.

a) It is Binary isomorphous system.

OK



phase composition.

phase amount: $W_L = \frac{S}{R+S}$ $W_{(Cu,Ni)} = \frac{R}{R+S}$.

[redacted]

spherical domain: solid state Matrix: liquid state

b)

Sketch cartoon -2.

For T higher 1170°C (the up blue area) is liquid phase.

T = 1170°C, it is liquid + solid Ni + solid $ZrNi_5$.

T < 1170 it's solid Ni + Solid $ZrNi_5$

Triple point is Eutectic point.

Reaction : $L \underset{\Delta}{\overset{\text{cooling}}{\rightleftharpoons}} Ni + ZrNi_5$.

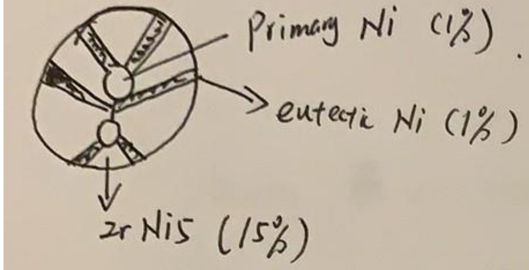
Gibbs phase rule.

$P + F = C + N \Rightarrow F = C + N - P$

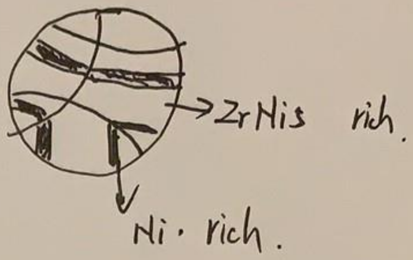
$= 2 + 1 - 3 = 0$.

c) For Ni 5% Zr. -5

slow cool.



quench



phase amount.

$$W_{ZrNi_5} = \frac{5-1}{15-1} = 0.29 \qquad W_{Ni} = \frac{15-5}{15-1} = 0.71$$

eutectic $W_{e(Ni)} = \left(\frac{5-1}{8.8-1}\right) W_{Ni} = 0.51 \cdot 0.71 = 0.362.$

primary $W_{Ni}' = \left(\frac{8.8-5}{8.8-1}\right) \cdot W_{Ni} = 0.49 \cdot 0.71 = 0.348$

d) An intermetallic is alloy that forms an orderd solid-state compound.

list.

Na_2Al_3. at 44at.%Ni.

Ni_5Al_3rt at ~~63%~~ 63at.% Ni.

Ni_3Al at 76at% Ni

ZrNi5 at 14at% Zr

ZrNi7 at 17at% Zr

$ZrNi_3$ at 25% Zr.

Zr_8Ni21 at 27.5% at Zr

Zr_7Ni10 at 41at% Zr.

-15

e) -15

This is related to phase diagram .and it will tell us how the compostion and Temerature effect the physic property of materials