

**Homework 2 Advanced Thermodynamics**  
**Due Tuesday September 7, 2020**

- a) By performing a Legendre transformation show that  $-(\partial S/\partial P)_T = (\partial V/\partial T)_P$ . Start by obtaining an expression for dG from the definition of the Gibbs free energy,  $G = H - ST$ ; obtaining an expression for dH from the definition of H,  $H = U + PV$ , and an expression for dU from  $dU = dq + dw_{ec}$ . Perform a Legendre transform with the expression for dG to obtain the desired Maxwell relationship.
- b) Show how you can obtain the expressions for G, H, U; dG, dH, dU, and the final Maxwell expression from the thermodynamic square.
- c) Han Guangze and Meng Jianjia, *Extension of Gibbs–Duhem equation including influences of external field* Continuum Mech. Thermodyn. (2018) **30** 817–823, wrote an expression extending the Gibbs-Duhem equation to include the influence of an external field such as gravity or an electric field,  $SdT - Vdp + \sum n_i d\mu_i + \sum Y_j dX_j = 0$ , where X is an intensive property and Y is the corresponding extensive property. The energy postulate states that the differential of a form of energy is the intensive property, X, times the differential of the extensive property, Y. for instance for gravity (gh)dm; for surfaces  $\gamma dA$ ; for and electric potential field  $\phi dq$ , for polarization  $EdP'$  (see the Guangze/Jianjia paper for definition of the terms). Ma, Gao, Qian and Su, *Size-dependent Electrochemical Properties of Binary Solid Solution Nanoparticles*, J. Elec. Soc. (2020) **167** 041501, proposed the following expression for the impact of particle size on electrical potential in nanoparticles,

$$\bar{\mu}^B = \mu^B + RT \ln(1 - x_s^s) + 2|\sigma_s| \underline{V}_s^B / 3 + ZF\phi$$

$$\bar{\mu}^A = \mu^A + RT \ln x_s^s + 2|\sigma_s| \underline{V}_s^A / 3 + ZF\phi$$

Where F is the Faraday constant (charge per mole of electrons), Z is the moles of transferred electrons,  $\phi$  is electric potential. Does this expression agree with the proposed expression of Guangze and Jianjia? What is the origin of the  $\ln()$  terms? What is the origin of the surface energy terms? How does the final term for electric potential relate to Guangze and Jianjia's expression?

- d) We obtained in class that  $C_V = T(\partial S/\partial T)_V$ . Show the origin of this expression, then use this expression to obtain an expression for  $(\partial C_V/\partial V)_T$ . You will need to change the order of differentiation and use a Maxwell relation. Provide an answer in T, P, V, and the tabulated derivatives  $\alpha$ ,  $\kappa_T$ ,  $C_p$ ,  $C_V$ ,  $\mu_{JT}$ .
- e) Find a value for  $(\partial C_V/\partial T)_V$  for an ideal gas,  $PV = RT$  where V is the molar volume, and for the van der Waals equation,  $P = RT/(V - b) - a/V$  (or  $Z = PV/RT = (1/(1-b/V)) - a/(VRT)$ ). What does this tell you about an ideal gas, and about a van der Waals gas? You will need to define heat capacity in your explanation.

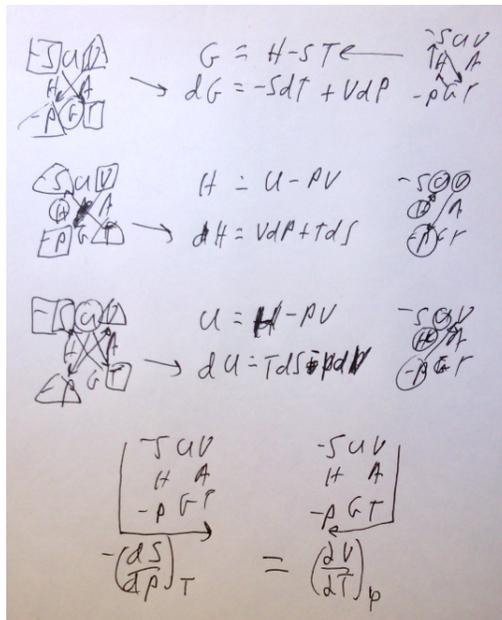
**Answers: Homework 2 Advanced Thermodynamics**  
**Due Tuesday September 7, 2020**

- a) By performing a Legendre transformation show that  $-(\partial S/\partial P)_T = (\partial V/\partial T)_P$ . Start by obtaining an expression for  $dG$  from the definition of the Gibbs free energy,  $G = H - ST$ ; obtaining an expression for  $dH$  from the definition of  $H$ ,  $H = U + PV$ , and an expression for  $dU$  from  $dU = dq + dw_{ec}$ . Perform a Legendre transform with the expression for  $dG$  to obtain the desired Maxwell relationship.

$$\begin{aligned} dG &= dH - SdT - TdS \\ dH &= dU + pdV + Vdp \\ dq &= TdS; dw_{ec} = -pdV \\ \text{so} \\ dU &= TdS - pdV \end{aligned}$$

$$\begin{aligned} dG &= dU + pdV + Vdp - SdT - TdS \\ dG &= Vdp - SdT \\ d^2G/(dpdT) &= (d/dp(dG/dT))_T = -(d/dT(dG/dp))_T = d^2G/(dTdp) \\ -(\partial S/\partial p)_T &= (\partial V/\partial T)_p \end{aligned}$$

- b) Show how you can obtain the expressions for  $G$ ,  $H$ ,  $U$ ;  $dG$ ,  $dH$ ,  $dU$ , and the final Maxwell expression from the thermodynamic square.



- c) Han Guangze and Meng Jianjia, *Extension of Gibbs–Duhem equation including influences of external field Continuum Mech. Thermodyn. (2018) 30 817–823*, wrote an expression extending the Gibbs–Duhem equation to include the influence of an external field such as gravity or an electric field,  $SdT - Vdp + \sum n_i d\mu_i + \sum Y_j dX_j =$

0, where X is an intensive property and Y is the corresponding extensive property. The energy postulate states that the differential of a form of energy is the intensive property, X, times the differential of the extensive property, Y. for instance for gravity (gh)dm; for surfaces  $\gamma dA$ ; for and electric potential field  $\phi dq$ , for polarization  $EdP'$  (see the Guangze/Jianjia paper for definition of the terms). Ma, Gao, Qian and Su, Size-dependent Electrochemical Properties of Binary Solid Solution Nanoparticles, J. Elec. Soc. (2020) **167** 041501, proposed the following expression for the impact of particle size on electrical potential in nanoparticles,

$$\bar{\mu}^B = \mu^B + RT \ln(1 - x_s^s) + 2|\sigma_s| \underline{V}_s^B / 3 + ZF\phi$$

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Where F is the Faraday constant (charge per mole of electrons), Z is the moles of transferred electrons,  $\phi$  is electric potential. Does this expression agree with the proposed expression of Guangze and Jianjia? What is the origin of the ln() terms? What is the origin of the surface energy terms? How does the final term for electric potential relate to Guangze and Jianjia's expression?

The Ma et al. expression includes the electric potential which is sometimes written V. This term should be the electric field so that it is a derivative term,  $dV/dr$ .

The ln() terms are the entropy of mixing for the two components A and B. This is from the ideal mixing law.

The surface energy term arises from the Gibbs-Duhem equation.  $SdT - Vdp + \sum n_i d\mu_i = 0$  for constant temperature the first term is 0. The pressure is in units of F/A which is the same as stress. So the internal pressure for a material can be thought of as a pressure. The chemical potential is V times this excess stress due to the nanosized of the particles. There is a surface stress associated with molecules at the surface,  $\sigma_s$ . The prefactor is associated with the geometry at the surface of the particle and in the core.

The final term is similar to that of Guangze and Jianjia as mentioned above.

d) We obtained in class that  $C_V = T(\delta S/\delta T)_V$ . Show the origin of this expression, then use this expression to obtain an expression for  $(\delta C_V/\delta V)_T$ . You will need to change the order of differentiation and use a Maxwell relation. Provide an answer in T, P, V, and the tabulated derivatives  $\alpha$ ,  $\kappa_T$ ,  $C_p$ ,  $C_V$ ,  $\mu_{JT}$ .

$$C_V = (dU/dT)_V$$

From the Thermodynamic Square

$$dU = TdS - pdV \text{ so } C_V = (dU/dT)_V = T (dS/dT)_V - p (dV/dT)_V$$

Second term is 0  $dV$  at constant V is 0

$$(dS/dT)_V = C_V / T$$

To obtain  $(\delta C_V/\delta V)_T$  you can use the chain rule on  $C_V = T(dS/dT)_V$ :

$$(\delta C_V/\delta V)_T = (dT/dV)_T (dS/dT)_V + T (d(dS/dT)_V/dV)_T$$

The first term is 0 since  $dT$  at constant  $T$  is 0. Changing the order of differentiation for the second term:  $(\partial C_V / \partial V)_T = T (d(dS/dT)_V / dV)_T = T (d(dS/dV)_T / dT)_V$   
 From the thermodynamic square we have  $(dS/dV)_T = (dP/dT)_V$   
 So the expression becomes  $(\partial C_V / \partial V)_T = T(d^2P/dT^2)_V$

*e) Find a value for  $(\partial C_V / \partial T)_V$  for an ideal gas,  $PV = RT$  where  $V$  is the molar volume, and for the van der Waals equation,  $P = RT/(V - b) - a/V$  (or  $Z = PV/RT = (1/(1-b/V)) - a/(VRT)$ ). What does this tell you about an ideal gas, and about a van der Waals gas? You will need to define heat capacity in your explanation.*

$(dP/dT)_V$  for an ideal gas is  $R/V$  and this doesn't change at constant  $V$  so  $(\partial C_V / \partial T)_V = 0$  for an ideal gas. For the van der Waals equation  $(dP/dT)_V = R/(V-b)$  and the second derivative is also 0.

The heat capacity has to do with how the atoms or molecules move and vibrate to store energy. At low temperatures there might be only vibrational energy that is being stored. As the temperature rises rotation and translation can store energy. So changes in the heat capacity with temperature have to do with changes in the mechanism that the atoms or molecules are storing energy and the distribution of these different energy storage mechanisms as the temperature increases and density decreases. The details depend on the detailed structure of the material and how it is impacted by temperature. The ideal gas model doesn't include changes in energy storage since the different molecules do not interact with each other, they are always at infinite dilution. So they have available all of the same energy storage mechanisms at any temperature. The van der Waals model includes excluded volume,  $b$ , two atoms cannot exist in the same space (repulsive interaction), and an enthalpy of interaction,  $a$ , which could be an attractive potential between atoms that allows for dense states. Neither of these numbers are inherently temperature dependent, so there is no change in the mechanism of energy storage with temperature.