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Chapter 1 (Conceptual)

Q1) You are reading an article where the authors minimize the Gibb's free energy to solve for an order parameter. Which quantities can you assume were fixed in the calculation? (Circle all that apply)

a) Pressure
b) Volume
c) Temperature
d) Particle number
e) Density
f) Chemical potential
g) Energy density

Solution:

The Gibb's free energy is

$$G \equiv \mu Q = E + PV - TS$$

This will be minimized when dG is 0 for a change in the order parameter dx.

$$dG = d(E + PV - TS) = dE + PdV + VdP - TdS - SdT = 0$$

Using the fundamental thermodynamic relationship, $TdS = PdV + dE - \mu dQ$, we get

$$dG = \mu dQ + VdP - SdT = 0$$

Thus, the particle number, pressure, and temperature must be fixed (a,c,d) to minimize the Gibb's free energy.

Note: A quick way to get to this solution is to look at $dG = d(E + PV - TS)$ and notice that you will remove the $dE,\ PdV,$ and $\ TdS$ terms and introduce the μdQ from the fundamental thermodynamic relationship. Then, the only terms that will remain are $\mu dQ,\ VdP,$ and $\ SdT$. Hence, $Q,\ P,$ and T must be held constant.

Q2) You are reading an article where the authors minimize the Helmholtz free energy to solve for an order parameter. Which quantities can you assume were fixed in the calculation? (Circle all that apply)

a) Pressure
b) Volume
c) Temperature
d) Particle number
e) Density
f) Chemical potential
g) Energy density

Solution:

The Helmholtz free energy is

$$F = E - TS$$

Using the fundamental thermodynamic relationship, it is easy to see that the volume, particle number, and temperature must be fixed (b,c,d).