PHYS4031 STATISTICAL MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 2 EXERCISE CLASSES
(12, 14 September 2016)

You may want to think about (work out) them before attending exercise class.
Concepts and techniques covered:
SQ3 - Proving Stirling's formula for $n!$ and $\ln n!$ (using Gamma function introduced in Problem 1.5 in Problem Set 1)
SQ4 - Euler equation and Gibbs-Duhem relation in thermodynamics. Using scaling argument.
SQ5 - Getting the Gibbs free energy $G(T, p, N)$ by Legendre transformation of $E(S, V, N)$.

SQ3 Stirling's Formula follows from Γ-function representation of $n!$

This is a by-product of Problem 1.5 in Problem Set 1 in which we introduced the Γ-functions. Starting from Eq. (13) in Problem Set 1, show that

$$n! = \Gamma(n+1) = \int_0^\infty x^n e^{-x} dx = ...? \tag{1}$$

and hence

$$n! \approx \sqrt{2\pi n}\ \ n^n e^{-n}\ . \tag{2}$$

Hence, illustrate that the Stirling's formula for $\ln n!$ follows. In our course, we usually use $\ln N! \approx N \ln N - N$.

SQ4 A bit more Thermodynamics: Fundamental Relation, Euler's equation and Gibbs-Duhem relation, and a scaling argument.

"The first and second laws of thermodynamics combined" gives the fundamental relation

$$\boxed{dE = TdS - pdV + \mu dN} \tag{3}$$

This is important. It says if we know $E(S, V, N)$, i.e. in terms of the natural variables of E, we can work out T, p, μ and everything about the thermodynamics of a system by taking simple partial derivatives. Turning it into an equation for dS, then if we know $S(E, V, N)$, then T, p, μ follow by easy derivatives. Nice! And the first formalism in Stat. Mech. aims at getting $S(E, V, N)$.

It is, however, **not-at-all obvious from Eq.(3)** that we have

$$\boxed{E = TS - pV + \mu N}\ , \tag{4}$$

which is called the **Euler's equation** in thermodynamics.

TA: Starting with scaling up the system by a factor λ and that E is an **extensive** quantity, i.e.,

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)\ ,$$

and considering $\lambda = 1 + \epsilon$ with $\epsilon \ll 1$ (i.e., scaling the system up only by a tiny amount), show that the Euler's equation Eq.(4) follows. [**Pay attention to the argument. You will need it in a future problem set.**] The origin of this formula comes from the *Euler's theorem* for homogeneous functions, usually discussed under Partial Derivatives in math books.

Here is a by-product. By taking dE from the Euler's equation and comparing with the fundamental relation (Eq. (3)), show that

$$\boxed{SdT - Vdp + Nd\mu = 0}\ , \tag{5}$$

which is called the **Gibbs-Duhem relation** in thermodynamics. It is very useful for finding the boundary different different phases.

SQ5 Getting other thermodynamics potentials from $E(S, V, N)$.

In Chapter II, we reviewed the Helmholtz free energy $F \equiv E - TS$. If we know $F(T, V, N)$, then we know everything about the thermodynamics of the system. Obviously, F is the "energy" to study a system of a fixed number N of particles confined in a fixed volume V in thermal equilibrium with a heat bath at a temperature T. (See the difference - for E, it is $E(S, V, N)$.) Mathematically, we have carried out a Legendre transform in going from $E(S, V, N)$ to $F(T, V, N)$ – where we “traded” the variable S in $E(S, V, N)$ into T in $F(T, V, N)$. A graphical interpretation of the Legendre Transform is given as an Appendix in class notes.

Chemists often like to carry out experiments under constant pressure instead of a constant volume condition.

TA: Start with $E(S, V, N)$, go to $G(T, p, N)$, which is called the Gibbs free energy. **Find an expression for** dG and **give the formulas** that would give the conjugate variables S, V and μ if $G(T, p, N)$ is known.

Finally, noting that N is the only extensive variable in G, make a scaling argument and show that an interpretation of the chemical potential μ is the Gibbs free energy per particle. [**Students: Pay attention to the argument. We will use it later.**]