Review up to this point

Use
  Summary
  Key words
  The reader should be able to do
and
  Index
to review the elementary portion of Stat Thermod.

Problems (including representative qual problems) with solutions posted.
http://www.yoono.org/Y_OONO_official_site/Problems.html

according to my experience of these 30 years:
Qual never asks conceptual questions, and questions about thermodynamics and phase transition.
Lecture 20 Phase and Phase Transition

What is a phase? — not so simple 31.1. clear definition only after defining phase transitions

What is a phase transition?
\textbf{singularity} of a thermodynamic potential

Why is the study of phase transitions important? 32.9

Phase diagram: the ordinary PT diagram is incomplete. 31.2

Recall

A

B

C
Complete description: in terms of thermodynamic coordinates

\((E, V)\) [instead of \((P, T)\)] 31.2

Coexisting line \(\rightarrow\) a band

Triple point \(\rightarrow\) a triangle.

Triple point water cell for calibrating \(K\)

http://www.youtube.com/watch?v=EkFmrWsszgA
How about $E = E(S, V)$?

A **convex $C^1$ function** for ‘normal’ intermolecular interactions.

$-G \sup_{S,V}[ST - PV - E]$ : Legendre transformation

$-G$ is convex. 31.6
Gibbs phase rule: $f = c + 2 - \phi$ 31.3-5.
no statistical mechanical proof

Classification of phase transitions 31.7
First vs Second order

Second-order phase transition
Ising model (Who was Ising?) 31.9

Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} s_i s_j$$

with a magnetic field $h$:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i$$

Strictly speaking, this is NOT the system Hamiltonian.

http://physics.weber.edu/schroeder/software/demos/IsingModel.html
The ‘canonical ensemble approach’

\[ Z = \sum \exp \left( \beta J \sum_{\langle i,j \rangle} s_i s_j \right) \]

This is NOT really the canonical partition function, since \( M \) is NOT fixed.

Generalized canonical partition function (31.11):

\[ \tilde{Z} = \sum \exp \left( \beta J \sum_{\langle i,j \rangle} s_i s_j + \beta h \sum_i s_i \right) \]

\[ \tilde{A} = -k_B T \log \tilde{Z} : \text{corresponding to the Gibbs free energy} \]

\[-\tilde{A} = \sup_M [hM - E] \]

Therefore, \( d\tilde{A} = -SdT - Mdh \). cf \( dG = -SdT + VdP \)
Phase transition = singularity

\[ \tilde{Z} \text{ is a finite sum of } e^{-\beta E + \beta h M} \rightarrow \text{no singularity as a function of } T \]

It is even \( C^\omega .31.11 \)

**Necessity of thermodynamic limit**

\( H \) not well defined!

**Basic questions of statistical mechanics:**

Is the limit well-defined?

Thermodynamically, partition/rejoining invariance guarantees this.

Is there any phase transition?

later....
Gibbs measure 31.12: $|V| \rightarrow \infty$ limit of

$$\mu_{V,B} = \frac{1}{Z_{V,B}} e^{-\beta H_V(B)}$$

(1) Existence:
(2) Convexity.

Pure state/Mixed state

Translationally symmetric pure state = thermodynamic pure phases.

Cluster property: for $|x| \rightarrow \infty$

$$\langle A(x)B(0) \rangle \rightarrow \langle A \rangle \langle B \rangle.$$ 

Existence:

States are distinguished only through observables.

(1) Pedestrian way: choose countably many observables \( \{Q_i\} \)

\[ \text{actually } \simeq (2) \]

(2) Compactness argument

In weak topology the totality of \( \mu_{V,B} \) is compact.

An accumulation point exists.

Wrt \(^*\)-weak topology \( \{\mu\} \) is compact, because the space of observables is separable.

The space of observables is a vector space, which is separable:

\[ \exists \text{ dense countable subset.} \]

Then, the space of linear functional on it is compact (or any infinite subset has an accumulation point.

cf Bolzano-Weierstrass is not easy if the space is not finite dimensional.

BUT basically what we observe is essentially a finite dimensional space.
Convexity:

Obviously, if \( \nu_A \to \mu_A \) and if \( \nu_B \to \mu_B \), then
\[
(1 - \alpha)\nu_A + \alpha\nu_B \to (1 - \alpha)\mu_A + \alpha\mu_B.
\]
\[\Rightarrow\] the totality of the Gibbs measure is convex (and compact).

Pure state = vertex states
why the phase rule is hard statistical-mechanically
Translationally symmetric pure state = thermodynamic

pure phases.
Pure states have Cluster Property

(1) Cluster property $\iff$ states determined by distant event is constant state

constant $=$ macroobservables are constant.

$\mathcal{B}_\mu$: states determined by the conditions far away: (called algebra at infinity)

If this is almost constant, we say $\mathcal{B}_\mu$ is simple.

$\mathcal{B}_\infty$ is simple $\iff$ for $A$ determined on a finite $M$

$$|\mu(AB_\infty) - \mu(A)\mu(B_\infty)| \leq ||B_\infty||^*.$$  

If $\ast$, then $B_\infty$ is constant. (Scale $A$ with large $\lambda$.)

If the inequality is not true, then

$$|\mu(AB_\infty) - \mu(A)\mu(B_\infty)| \geq 1,$$

so $B_\infty$ cannot be constant.
(2) Pure state $\equiv$ states determined by distant event is constant state.