Course 565/665 Lecturer Prof. Cavagnero
Day 3.5.04 Date 9:55 am
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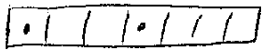
$F = F(N.V.T)$

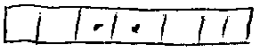
↳ natural variables : when constant, the corresponding direction follows a new extremum principle; at equilibrium. $F(N.V.T)$ is minimized, so $dF \leq 0$ (at const. $N.V.T$)

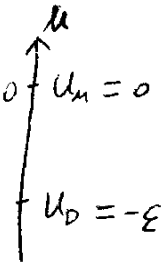
Review for criteria for equilibrium {same for Mech. and thermodynamic sys.? put together?}

1. net "S" acting on system is zero.
2. Potential energy of system is minimized
3. multiplicity maximized → S maximized
   (for universe, or isolated system)
   •?
4. new criteria

(ex) · dimerization


monomer


dimer



V. N. const. v : # of lattice sites.

$$W_p = \frac{(v-1)!}{1!\,(v-2)!} = v-1$$

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$$F_D = U_D - TS_D = -\varepsilon - kT\ln(V-1)$$

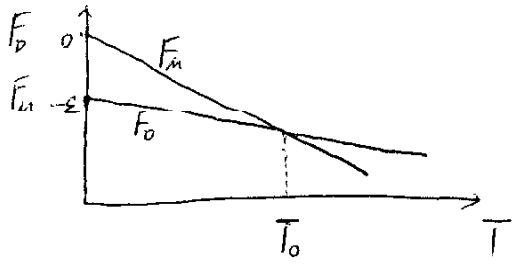
Monomer:

$$W_M = W_{TOT} - W_D = \frac{V!}{2!(V-2)!} - (V-1) = \left(\frac{V}{2}-1\right)(V-1)$$

$$F_M = U_M - TS_M = -kT\ln\left[\left(\frac{V}{2}-1\right)(V-1)\right]$$

$T < T_0$, more dimer

$T > T_0$, more monomer.



at T_0, $F_D = F_M \Rightarrow$ $T_0 = \dfrac{\varepsilon}{k\ln\left(\frac{V}{2}-1\right)}$

at low T: U dominates.

high: $-TS$ term dominates.