

Today

I. Last Time

II. Yan's Guest Lecture on Phase Transitions in Graphite, Diamond, and Beyond

III. A Brief Tour of Other Phase Transitions

IV. Exploring the Van Der Waals Equation of State and Phase Transitions

I. We studied how we can use extensivity as a tool to find thermodynamic potentials:

$$\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N) \quad \Longrightarrow \quad U = TS - PV + \mu N.$$

We then could say what the other potentials were too:

$$F = U - TS = -PV + \mu N, \quad G = U - TS + PV = \mu N.$$

There are still plenty of subtleties, e.g. $G = G(P, T, N)$, so it must be that

$$G = \mu(P, T)N.$$

I. We also studied equilibrium in the context of constant temperature. The environment acts as a constant temperature reservoir and fixes that property of the system: we are able to conclude that the system is in equilibrium when the Helmholtz free energy was minimized.

Yet another role for the thermodynamic potentials is to help us in identifying equilibrium.

III. Why is the Gibbs free energy a good tool for studying phase transitions?

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Our mathematical derivation showed that $G = \mu N$. We can also think about this from the perspective Yan was presenting

$$\mu(P, T) = \left(\frac{\partial G}{\partial N} \right)_{P, T} \approx \frac{\Delta G}{\Delta N}, \text{ then we can also say } \Delta G = \mu \Delta N.$$

If I choose to add just one particle the change in G is just

$$\Delta G = \mu(\Delta N = 1) = \mu.$$

Then adding particles one by one we get $G = \sum_{n=1}^N \mu = \mu N$. This

argument only works because we hold P and T fixed while adding the particles.

III. Why doesn't this work for F ?

$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T}$, since μ depends the pressure and that changes while I

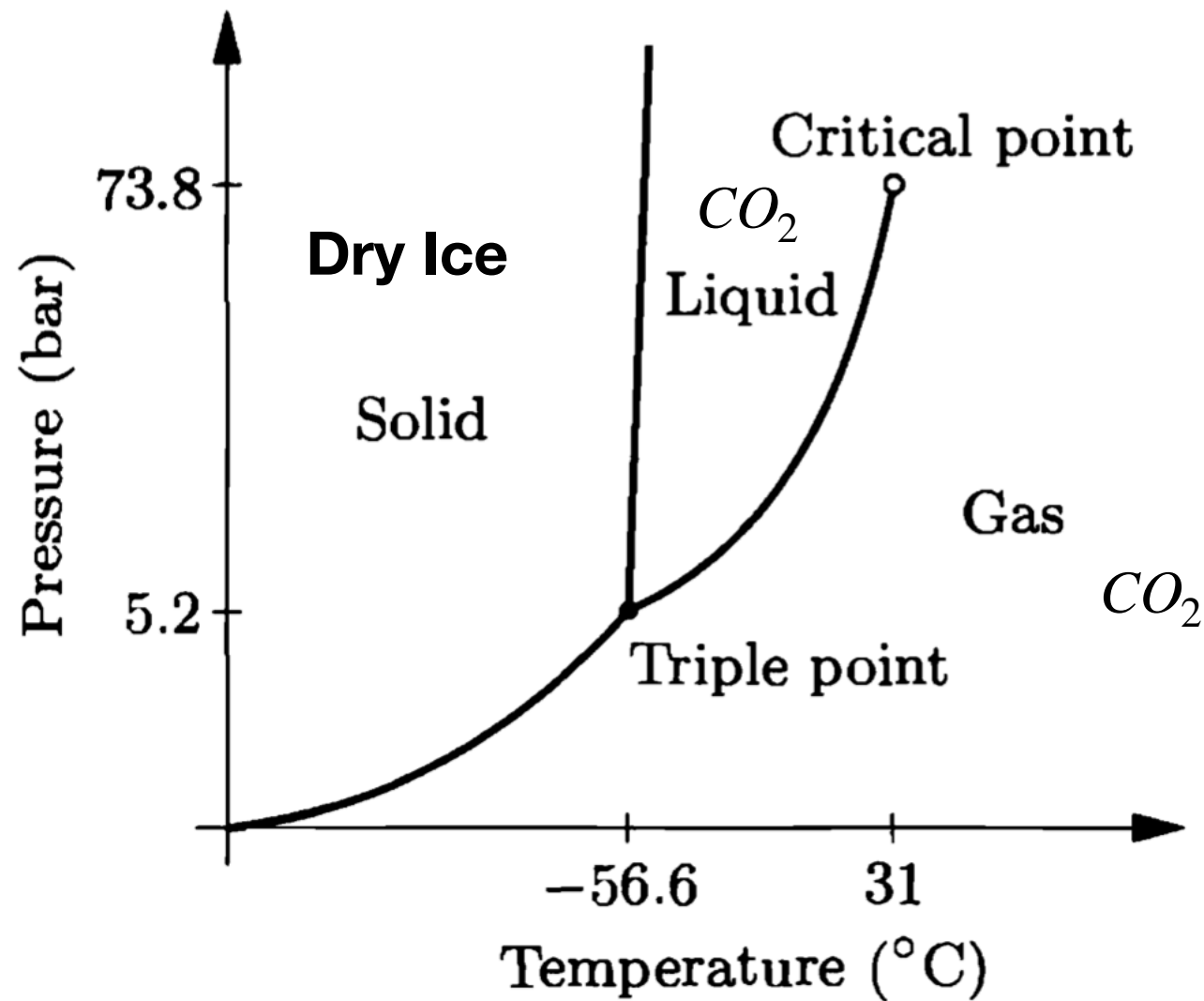
add particles in this setup, we have $F \neq \mu N$. Instead

$$F = U - TS = -PV + \mu N.$$

We've just learned that G is the potential most sensitive to changes in numbers of particle. This is one way of understanding why G is the best potential for characterizing phase transitions.

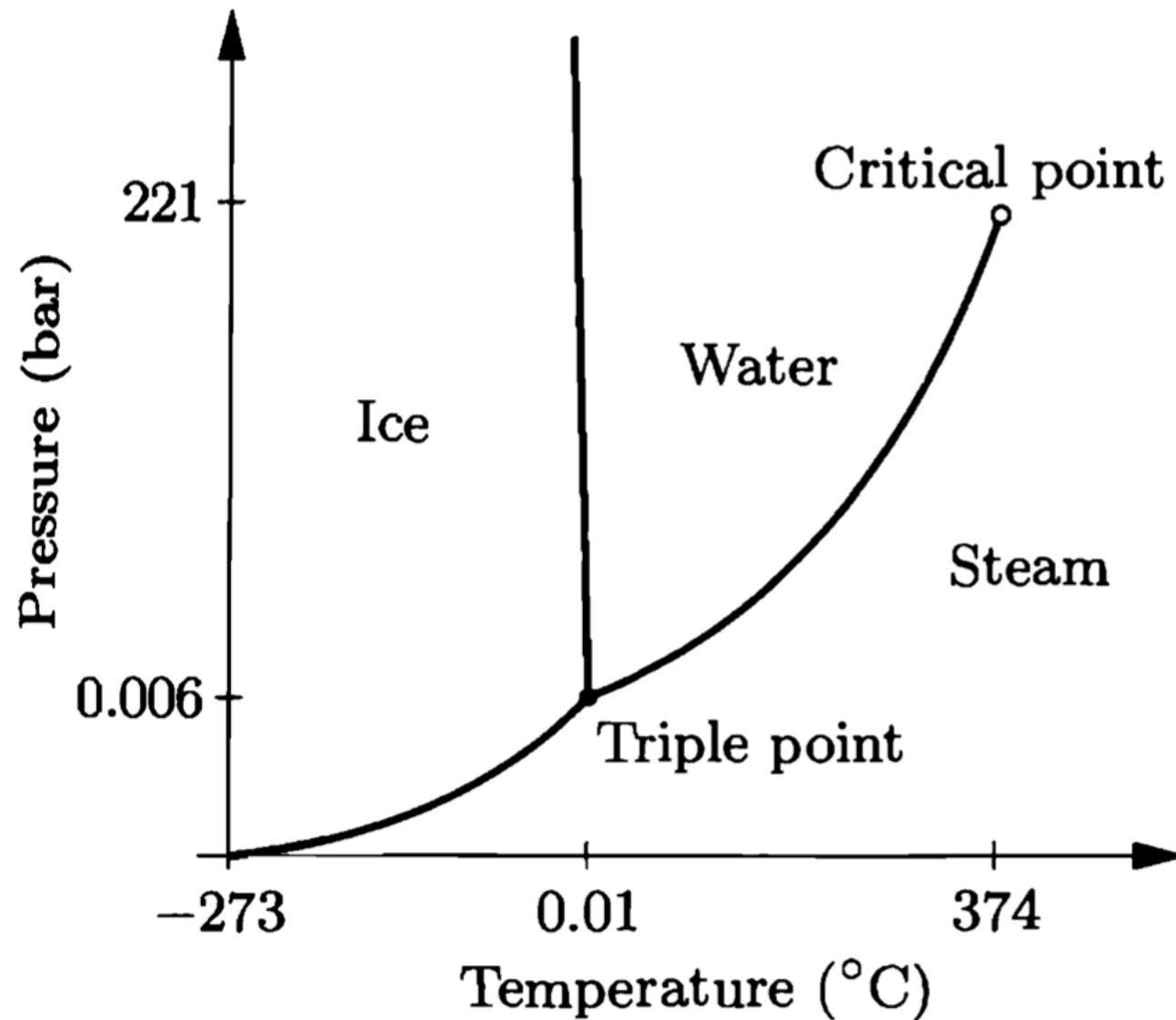
Let's do a tour of a few phase transitions.

III. The phase diagram for carbon dioxide. 1 bar is 0.987 atm.



T (°C)	P_v (bar)
-120	0.0124
-100	0.135
-80	0.889
-78.6	1.000
-60	4.11
-56.6	5.18
-40	10.07
-20	19.72
0	34.85
20	57.2
31	73.8

III. The phase diagram for water. 1 bar is 0.987 atm.



T (°C)	P_v (bar)	L (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Appendix: In Ch. 1 Schroeder defined the latent heat of

transformation $L = \frac{Q}{m}$.