

Today

I. Last Time

II. A Brief Tour of Other Phase Transitions

III. Exploring the Van Der Waals Equation of State and Phase Transitions in Detail

I. Yan told us about the graphite-diamond phase transition:

Shift of focus towards 'phase diagrams', which plot P vs. T .

We saw that the correct potential to focus on was the Gibbs free energy: $G = G(P, T, N) = \mu(P, T)N$.

We've also been exploring the fact that the material is in equilibrium (or stable, or has max entropy) when the Gibbs free energy is minimized.

II. A few more phase transitions:

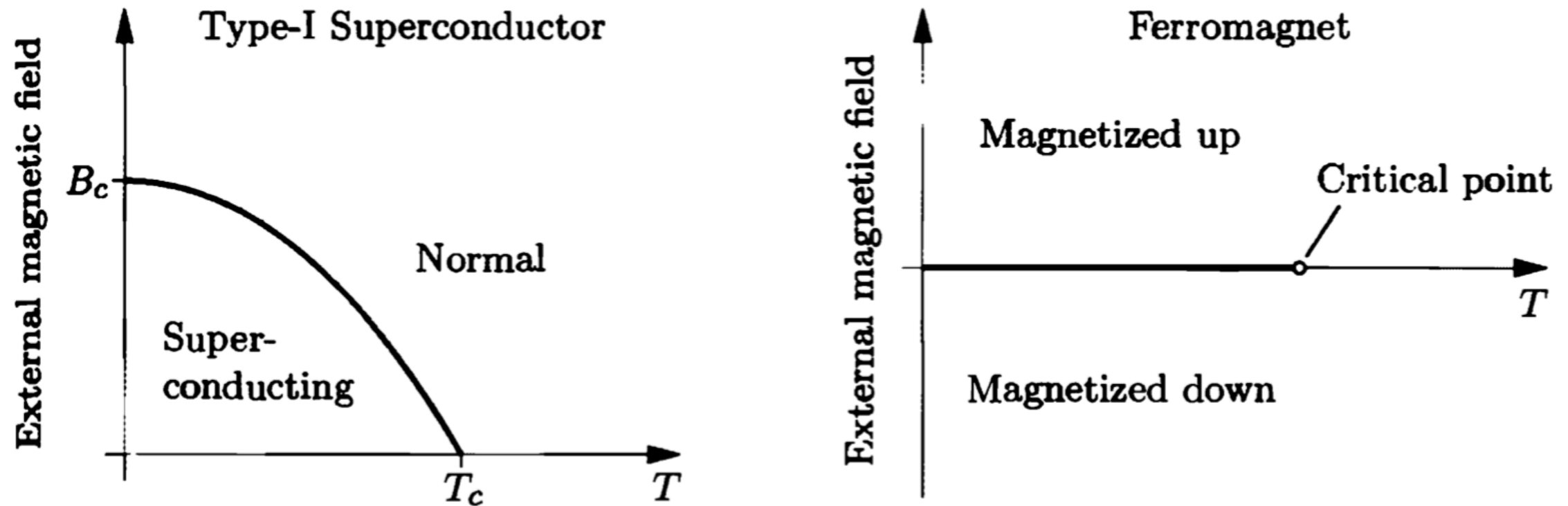


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.

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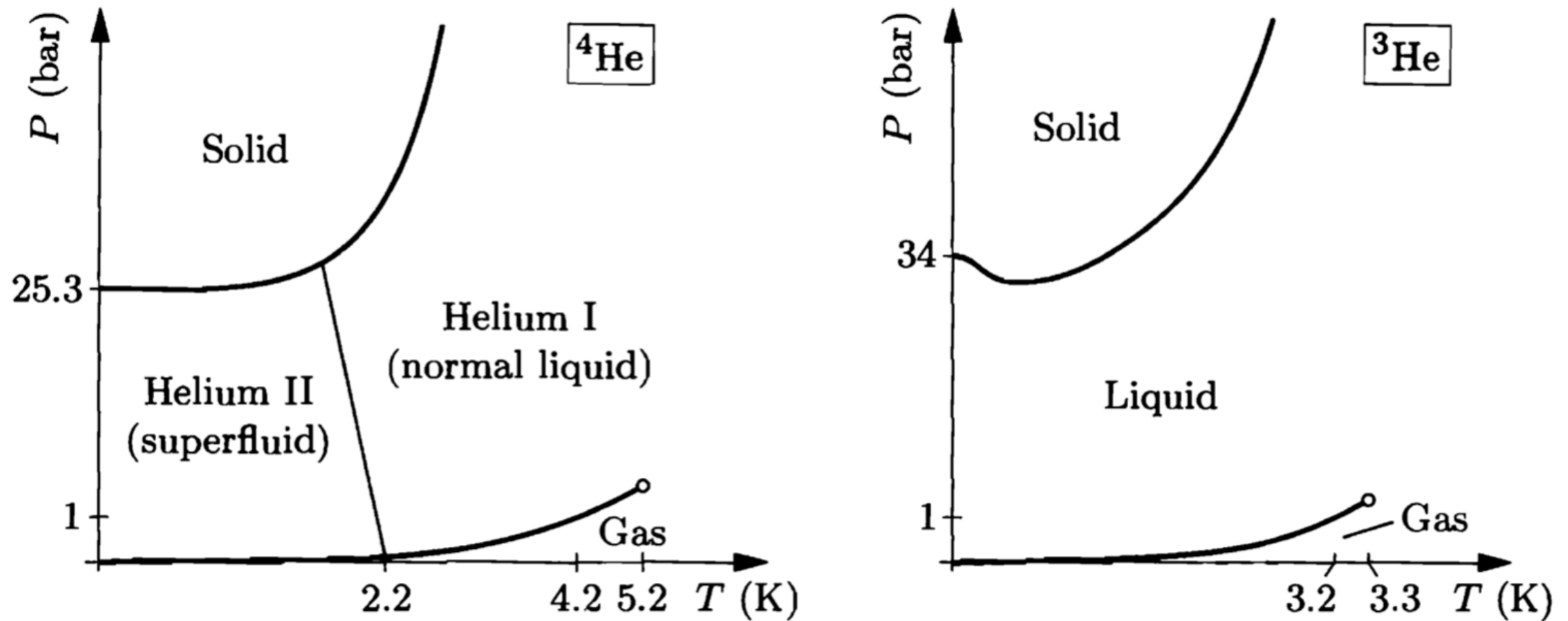


Figure 5.13. Phase diagrams of ${}^4\text{He}$ (left) and ${}^3\text{He}$ (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ${}^3\text{He}$ below 3 mK.

III. Let's explore the van der Waals equation of state as a detailed model of phase transition.

Why this one? This is one of the simplest non-trivial models.

Another reason is that it's great for doing numerical simulations.

These things said, the van der Waals equation of state is approximate. So, its predictions are not necessarily quantitatively accurate.

The equation of state is:

$$\left(P + \frac{aN^2}{V^2} \right) (V - bN) = NkT.$$

The modification of the volume comes from taking the volume of the molecular constituents into account. What about the a term?

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How does potential energy scale with density? The potential energy of the gas should scale linearly with the density, and we have N particles, so

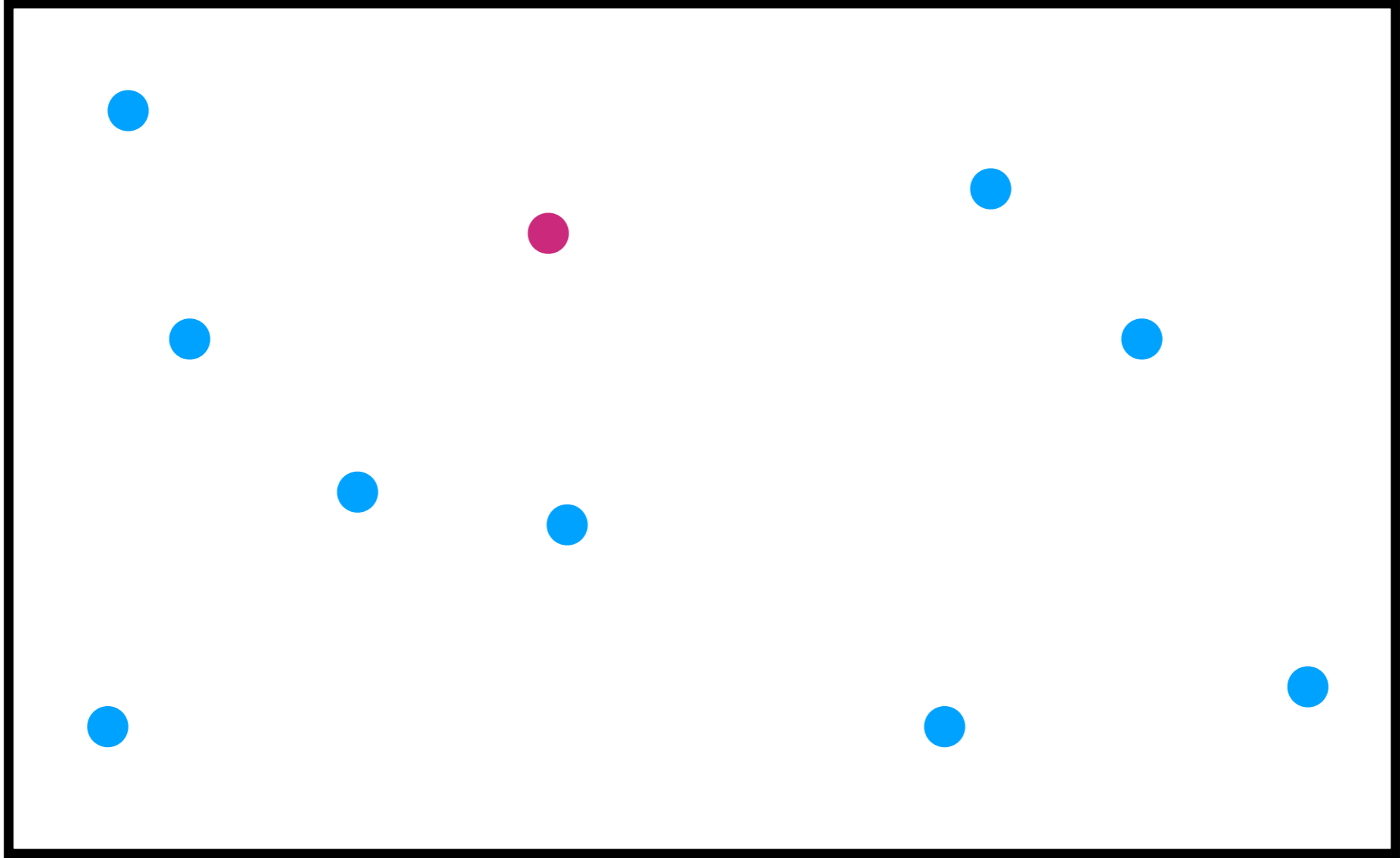
$$\text{total P.E.} = -aN \frac{N}{V} = -\frac{aN^2}{V}.$$

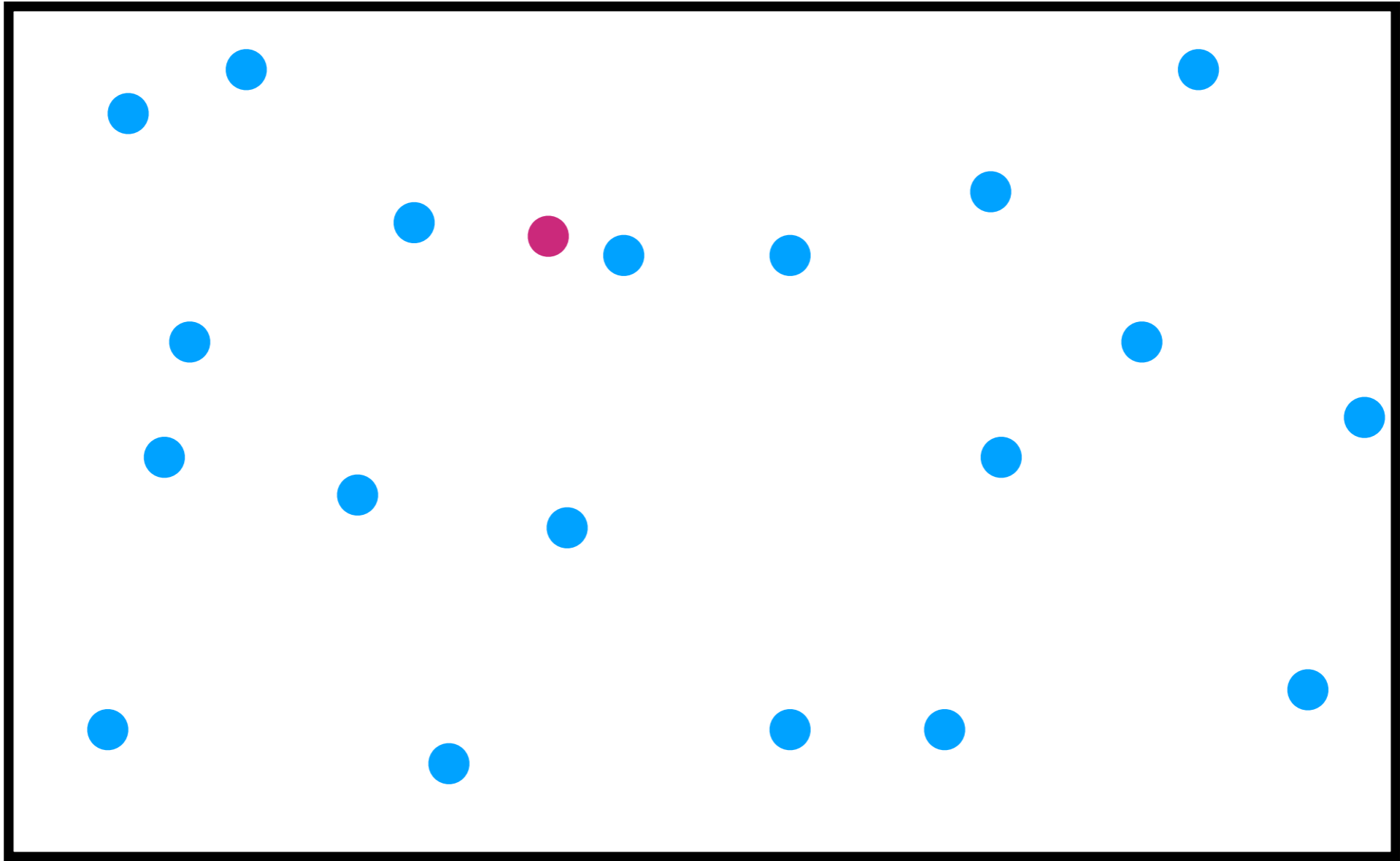
The Thermo identity states:

$$dU = TdS - PdV + \mu dN,$$

or for a fixed amount of stuff (N), and a fixed entropy we have

$$dU = -PdV \quad \text{and} \quad P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}.$$





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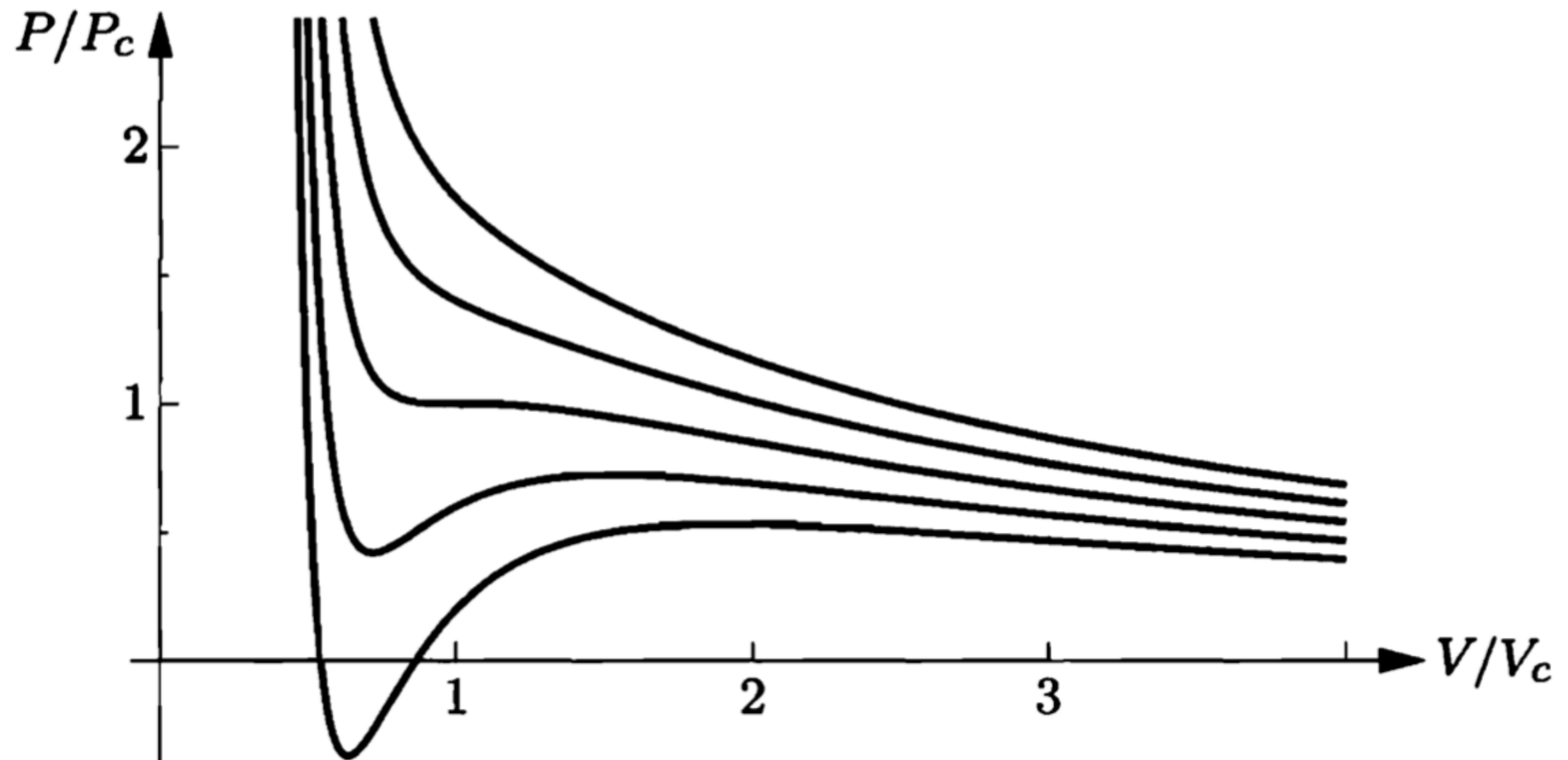
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This gives $P_{\text{due to P.E.}} = -aN^2/V^2$:

$$P = \frac{NkT}{(V - bN)} - \frac{aN^2}{V^2}.$$

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The key to understanding what happens with our substance is Yan's insight that we should look for the phase that has the lowest Gibbs free energy.

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We have

$$dG = -SdT + VdP + \mu dN,$$

Again we fix the amount of material (N) and the temperature:

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V \left(\frac{\partial P}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V - Nb)^2} + \frac{2aN^2}{V^2}.$$

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$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$$