

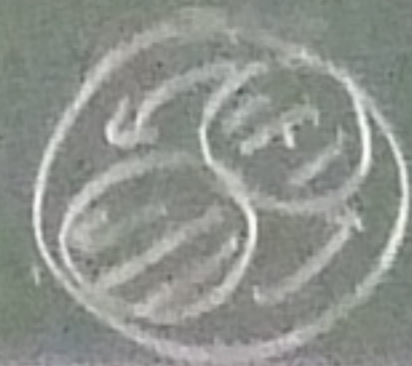
Die Zustandsgleichung realer Gase

Die atomistische Betrachtungsweise zeigt, in welcher Richtung die Zustandsgleichung idealer Gase verbessert werden kann. (insbes. gasf. \rightarrow flüssig)

1. Eigene Raumbedarf der Moleküle

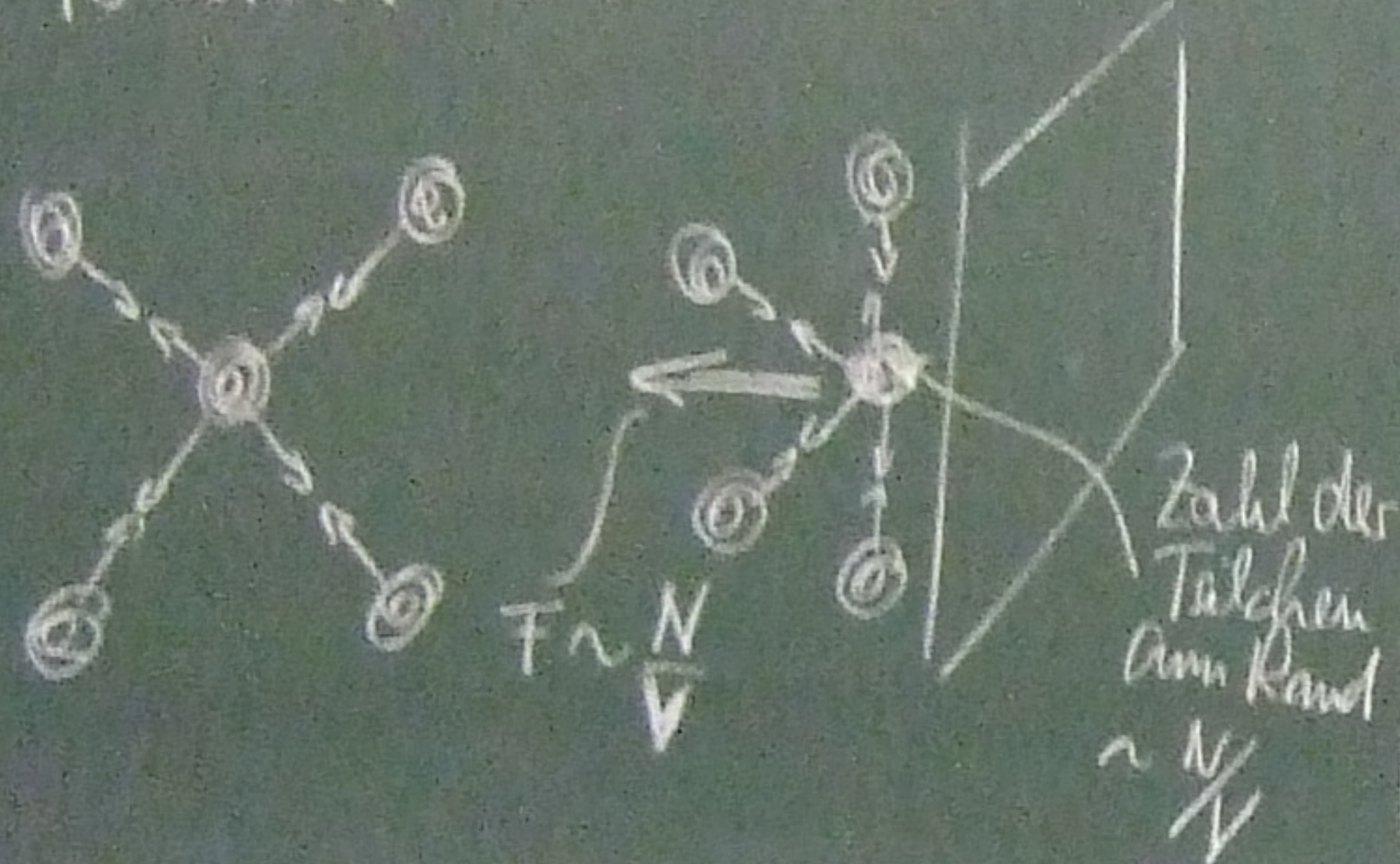
$$V_{id} \rightarrow V - Nb$$

Typischerweise mit b das 4-fache Eigenvolumen



2. Anziehende Wechselwirkung (WV) zwischen den Molekülen hebt sich zwar im Inneren auf (allseitige Richtung), zieht jedoch ein in Wandnähe befindliches

Molekül ins Innere zurück



$$p_{idial} \rightarrow p + a \frac{N^2}{V^2}$$

Damit ergibt sich in 1. Näherung für reale Gase

$$(p + a \frac{N^2}{V^2}) \cdot (V - Nb) = NkT$$

(Van der Waals Gleichung)

Bem. genauere Herleitung für den Druck

(Thermal Physics S. 180)

- Zahl der Nachbarn $\sim \frac{N}{V}$
- Gesamtenergie der WV in Summe über alle N Moleküle $\sim \frac{aN^2}{V}$

Bei konstanter Entropie

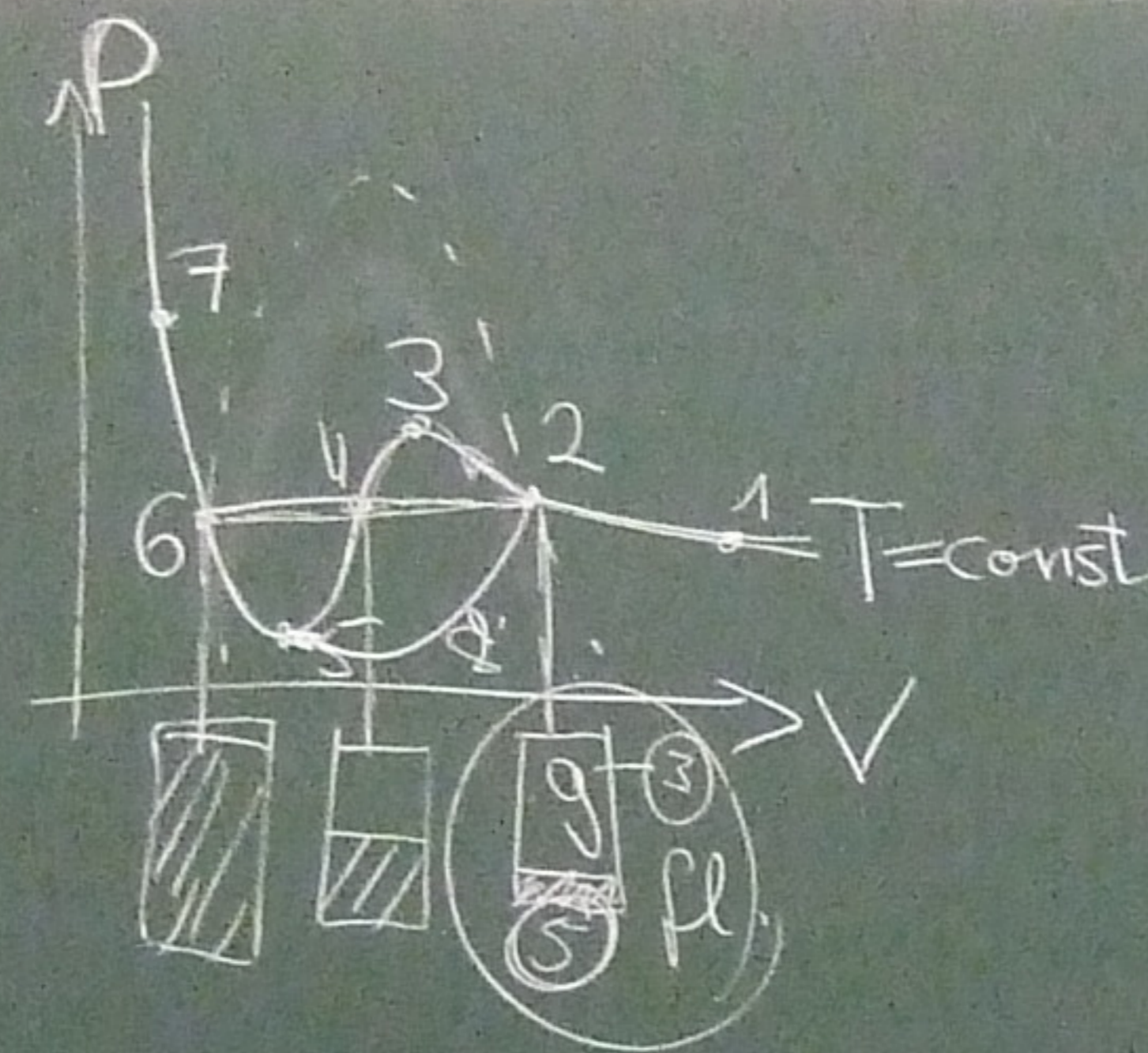
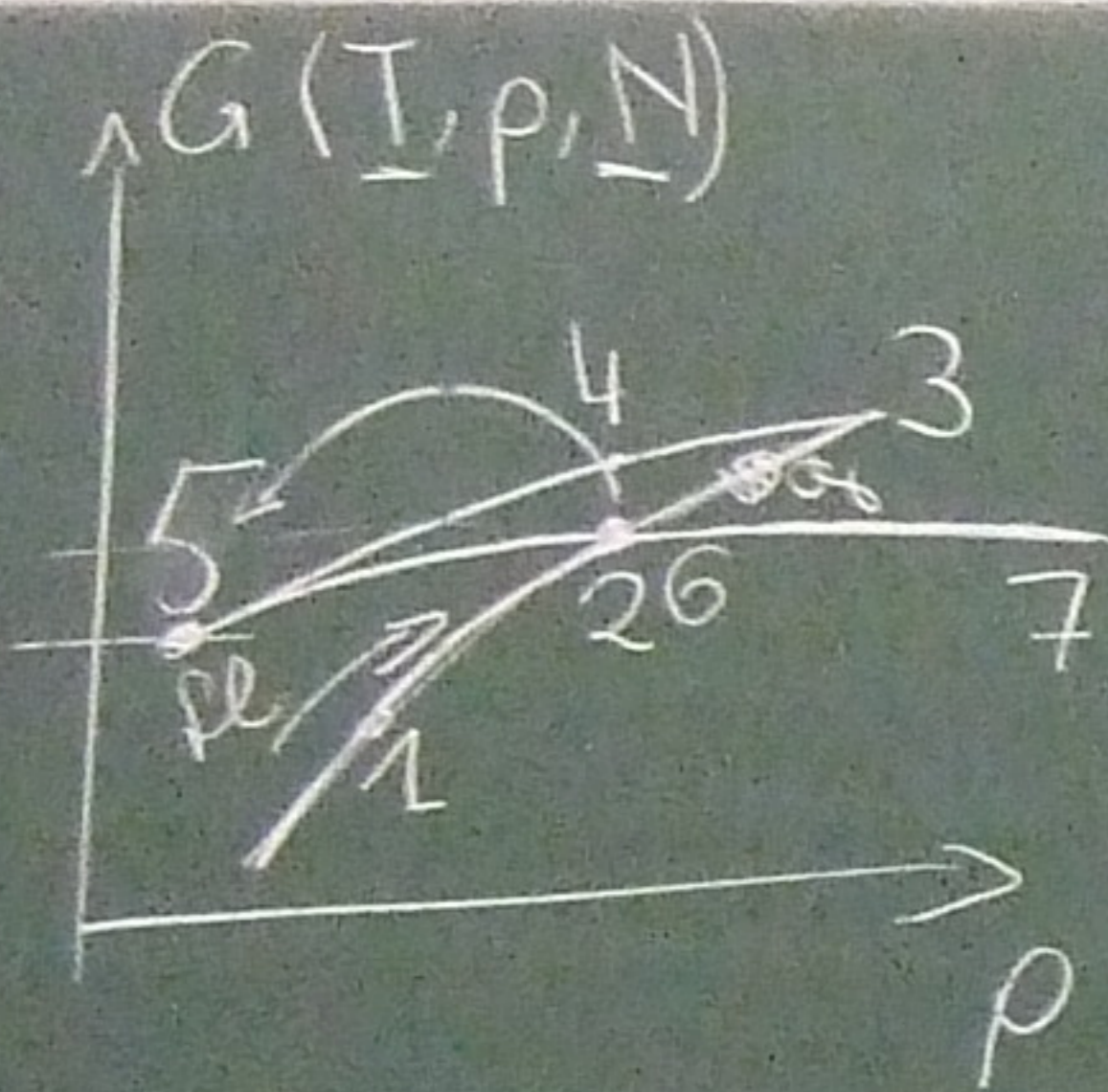
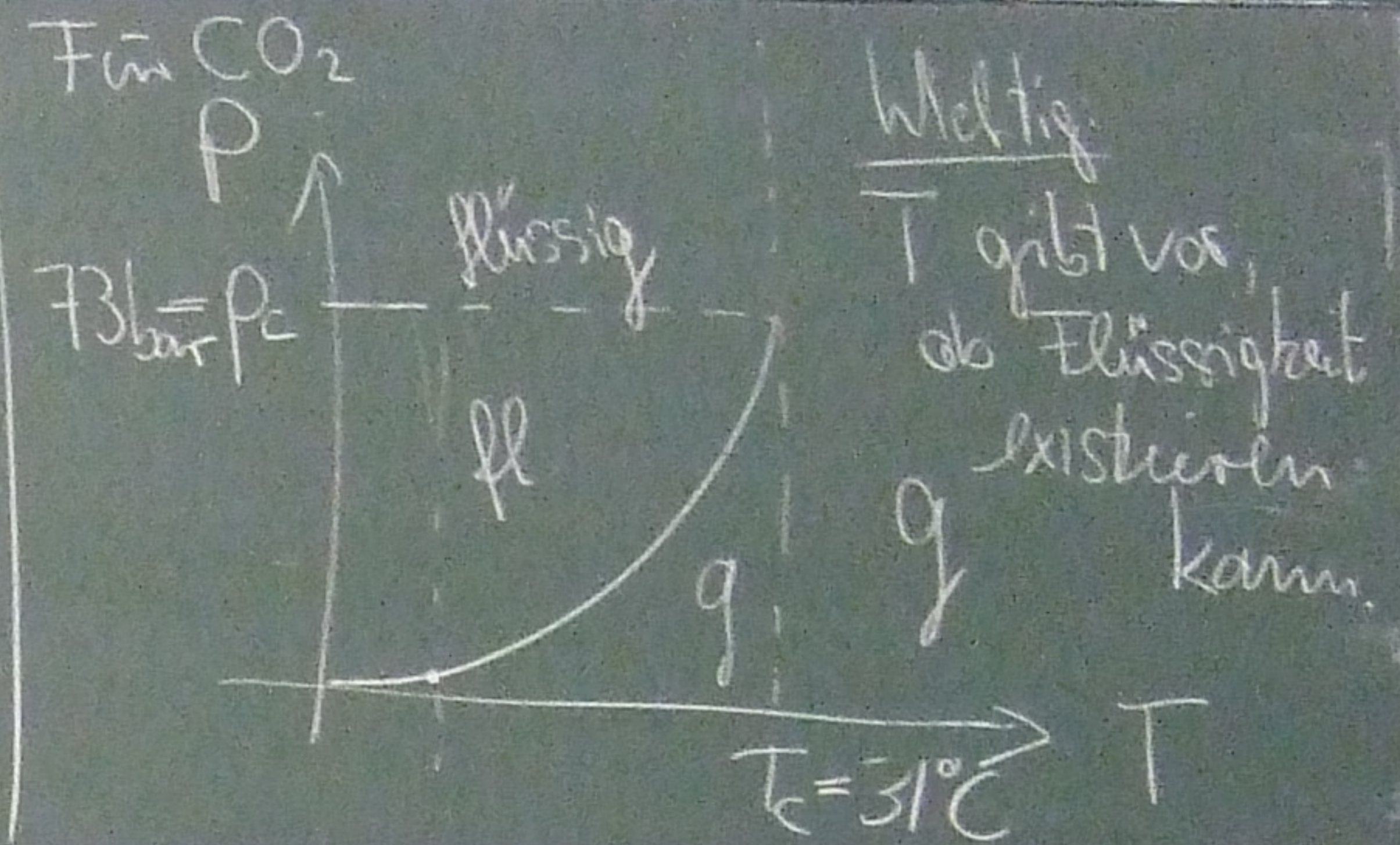
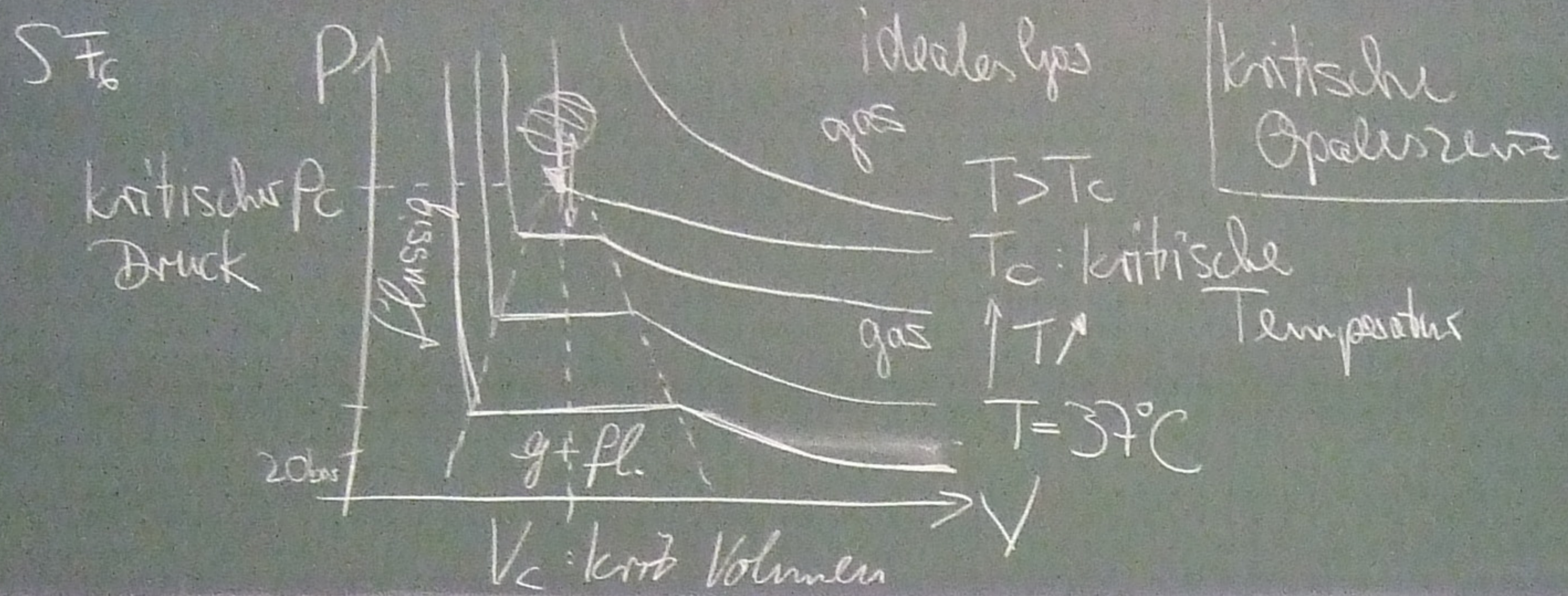
$$U(S, V, N)$$

$$dU = -pdV \rightarrow p = - \frac{\partial U}{\partial V} \Big|_S$$

$$p_{WV} = - \frac{\partial}{\partial V} \left(-a \frac{N^2}{V} \right) = - \frac{\partial U_{WV}}{\partial V} = -a \frac{N^2}{V^2}$$

$$p = p_{id} + p_{WV}$$

$$\sim p_{id} = p + a \frac{N^2}{V^2}$$



Verhalten im Koexistenzgebiet

$$dG = -SdT + Vdp + \mu dN$$

$$= Vdp \quad (T = \text{const}, N = \text{const})$$

Teilen durch dV :

$$\left. \frac{\partial G}{\partial V} \right|_{N,T} = V \cdot \left. \frac{\partial p}{\partial V} \right|_{N,T} \stackrel{vdW}{=} - \frac{NkT}{(V-Nb)^3} + \frac{2aN^2}{V^2}$$

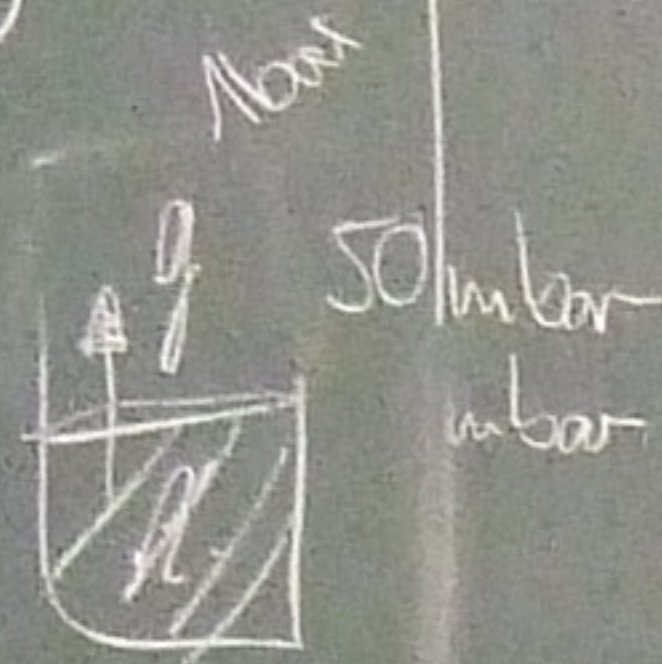
Integration über V

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

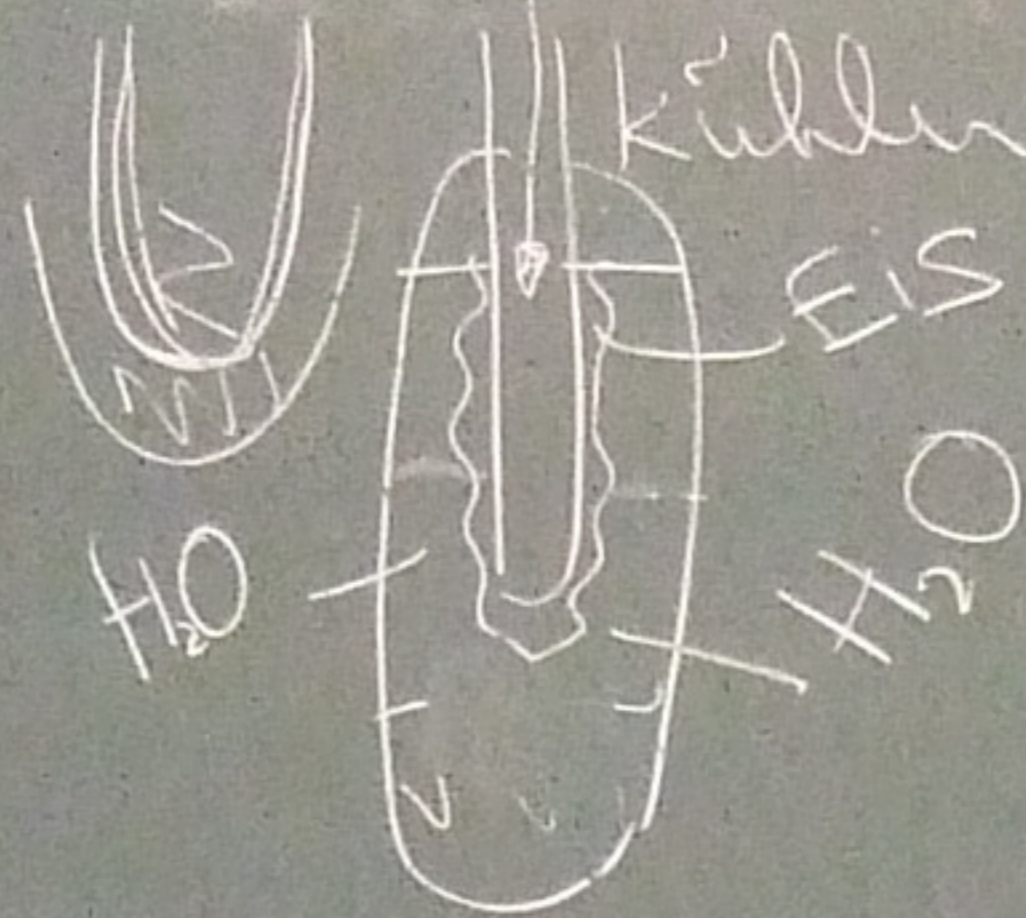
$$f(V) \rightarrow f(p)$$

$$\left. \frac{\partial G}{\partial V} \right|_{N,T} = - \frac{NkTV}{(V-Nb)} \quad (2)$$

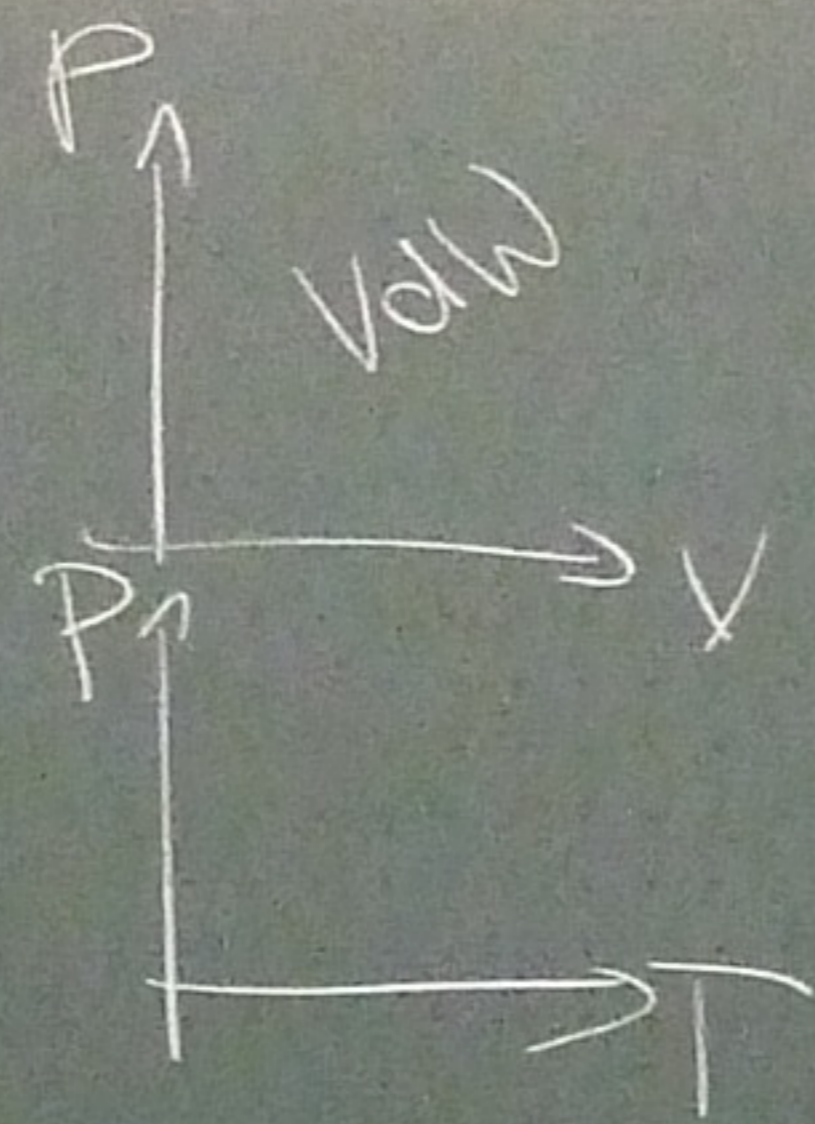
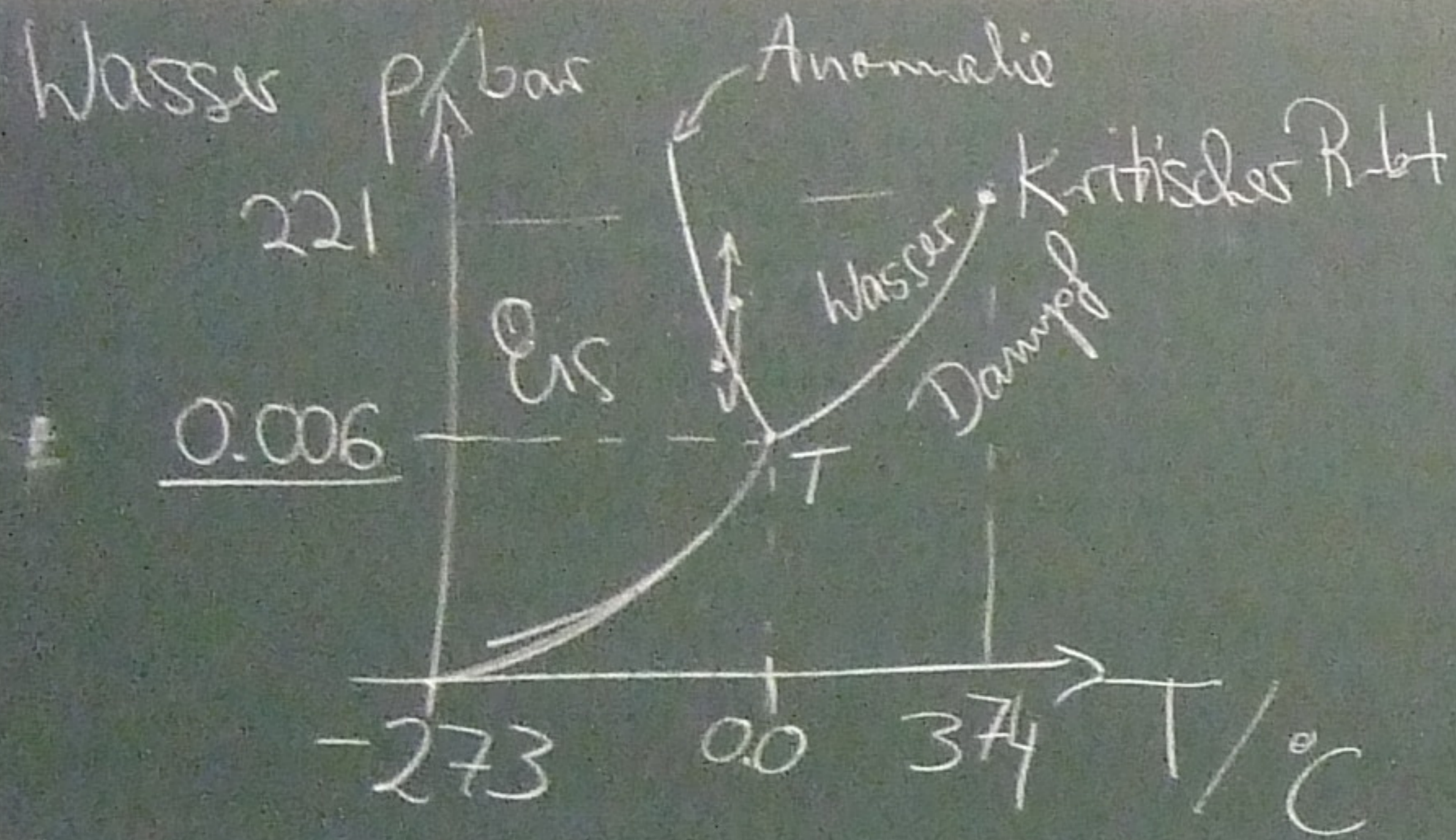
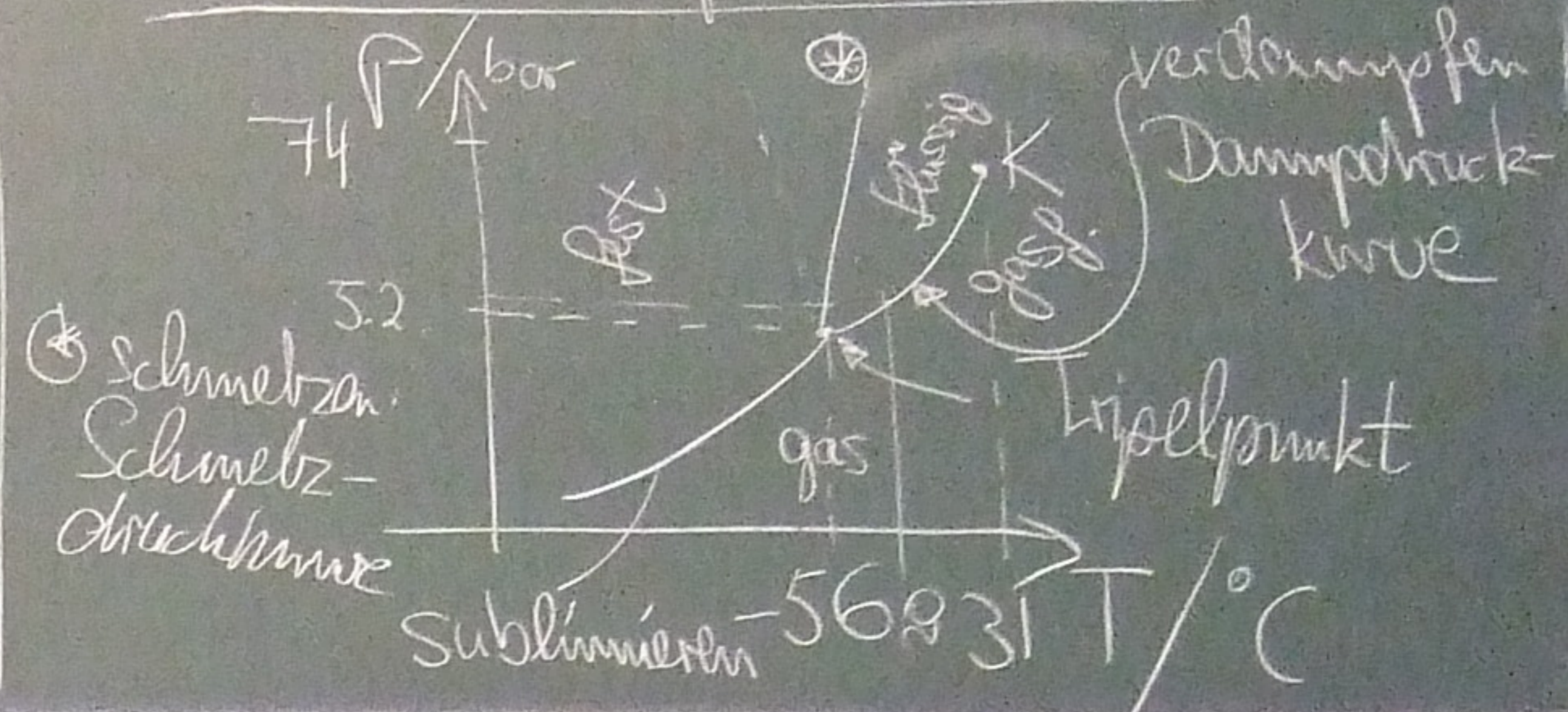
$p_0 = \text{Dampfdruck}$



$$p_{H_2O} < p_{Alk} < p_{Äther}$$



Zustandsdiagramm CO₂



Die Zustandsgleichung einer Mischung idealer Gase

Jedes Gas j hat einen sog. Partialdruck p_j mit $p = \sum p_j$

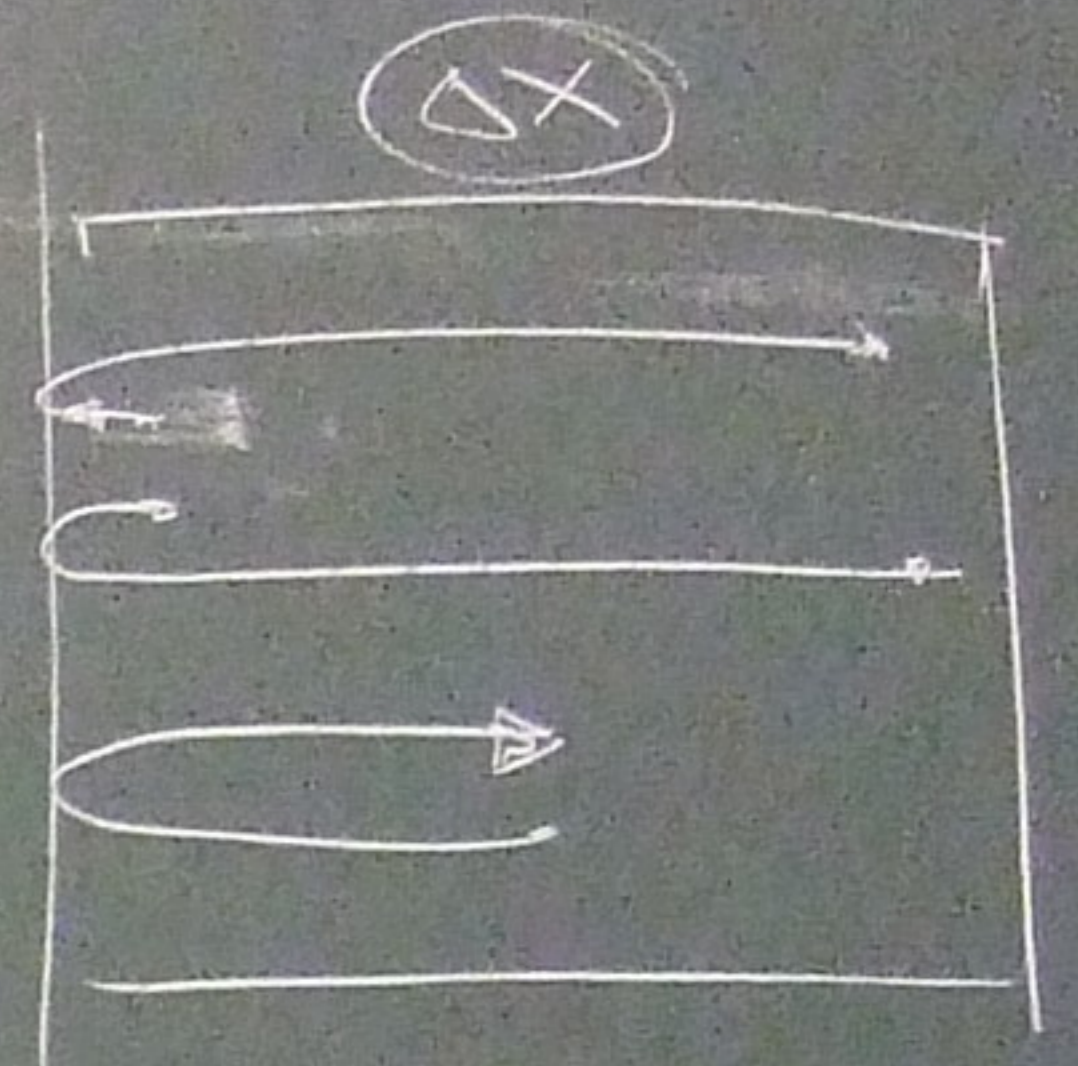
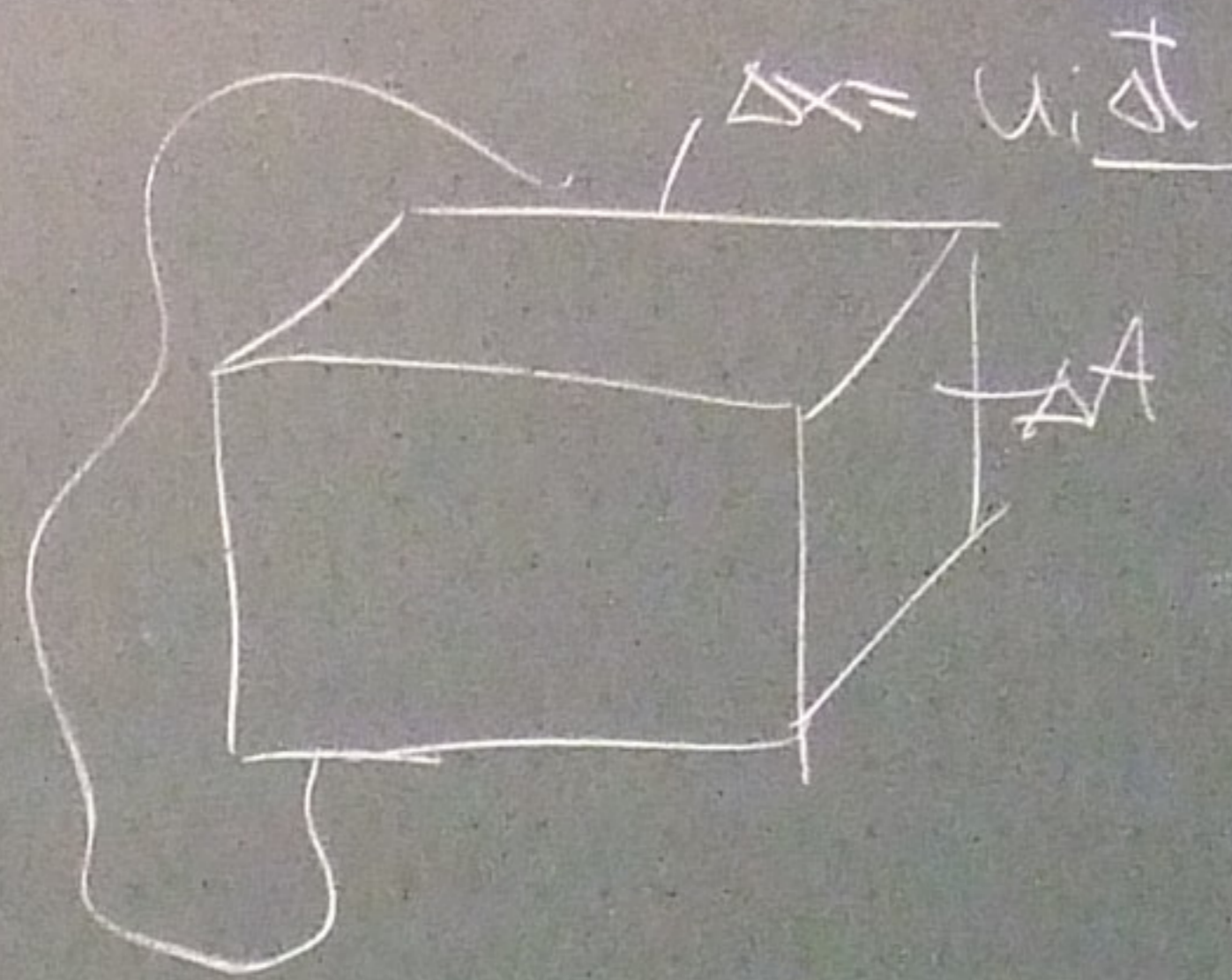
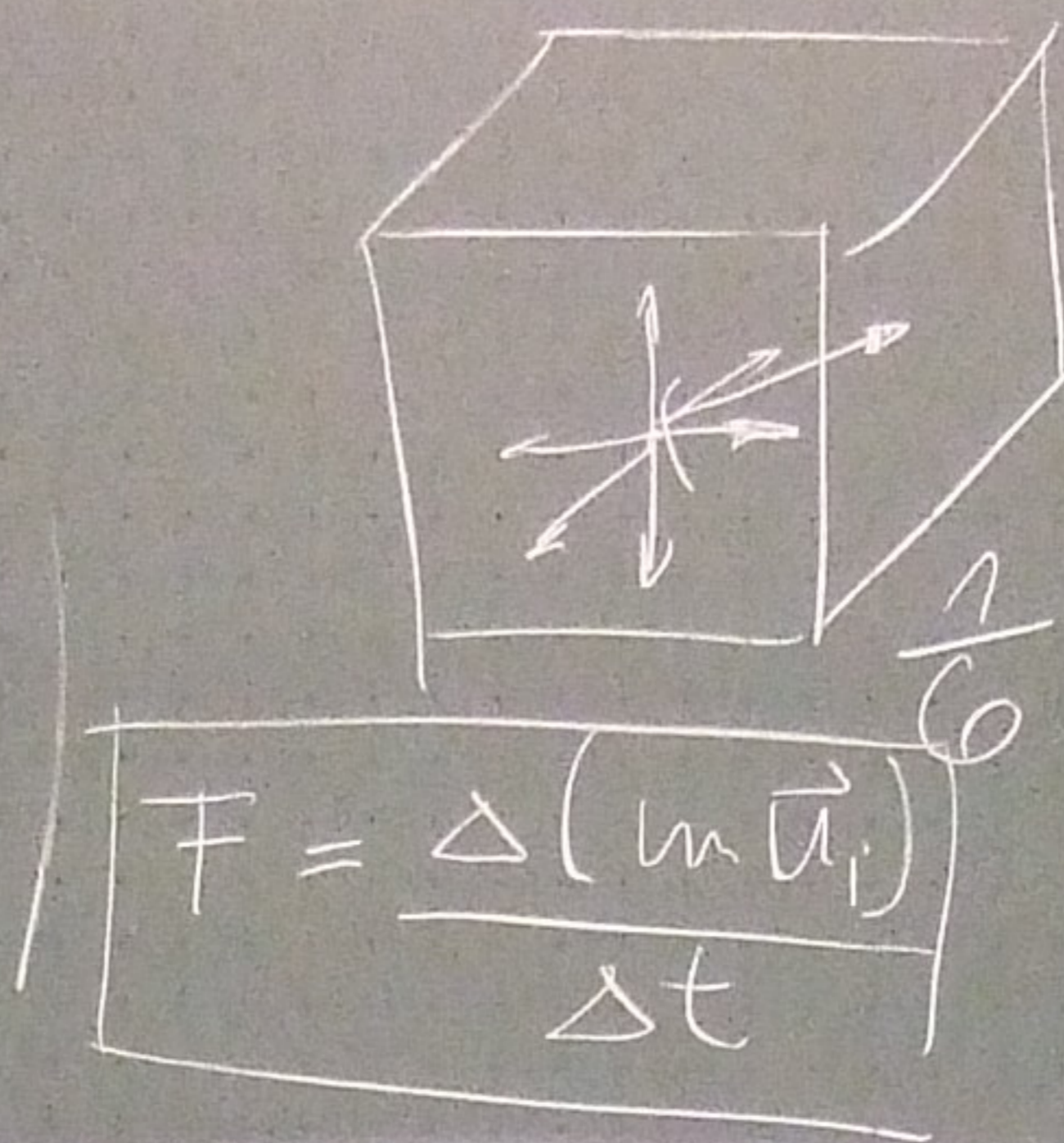
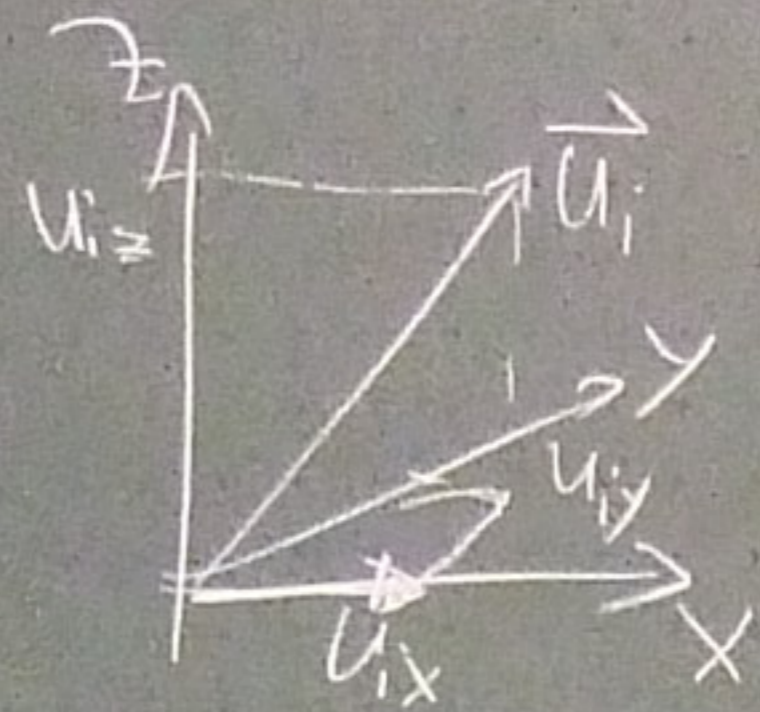
Teilchenzahl N_j jeder Gasart:

$$p_j V = N_j k T$$

für den Gesamtdruck $p = \sum p_j$

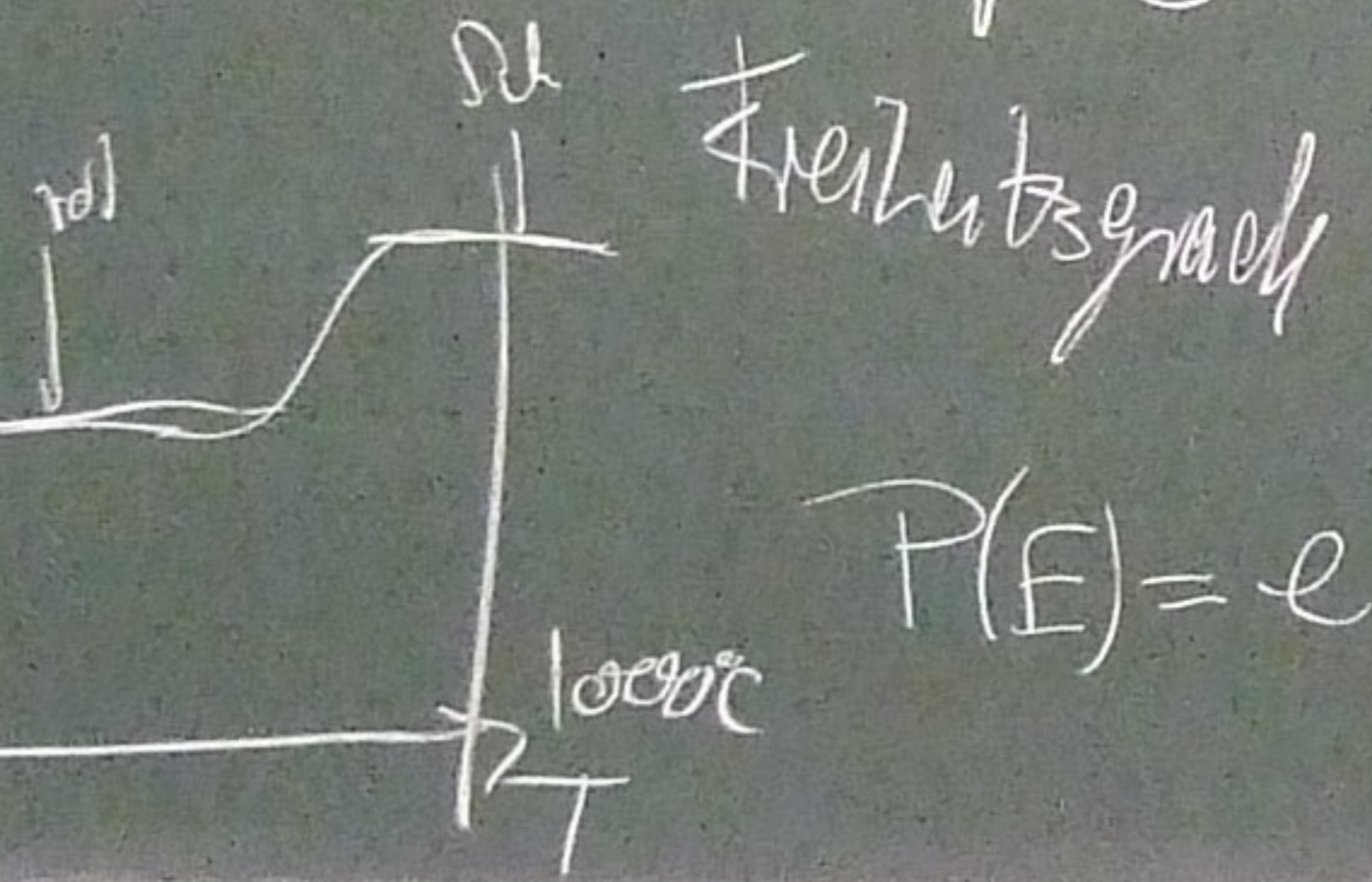
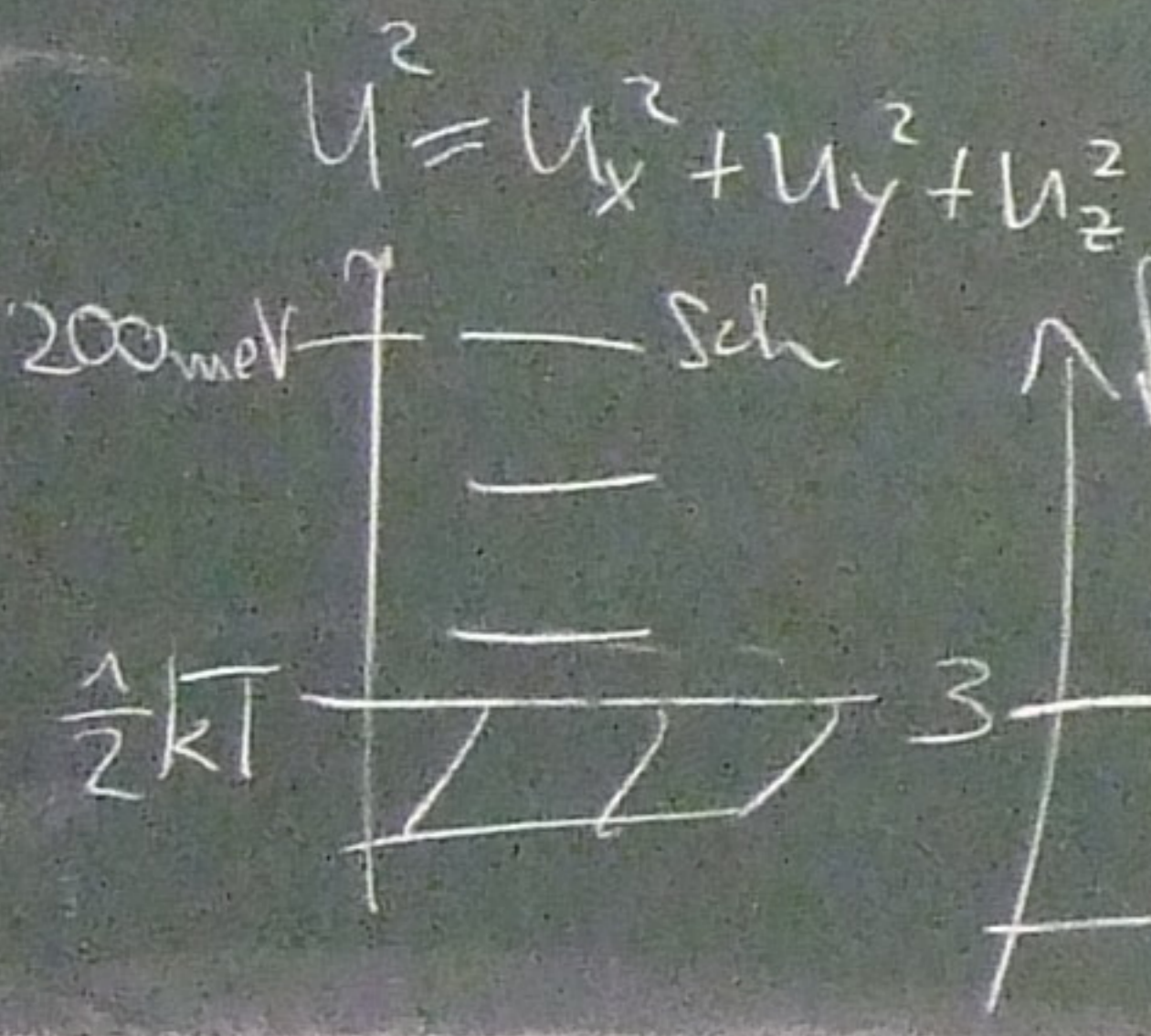
gilt mit $N = \sum N_j$
 $pV = NkT$

Herleitung mikroskop. Bild ideales Gas

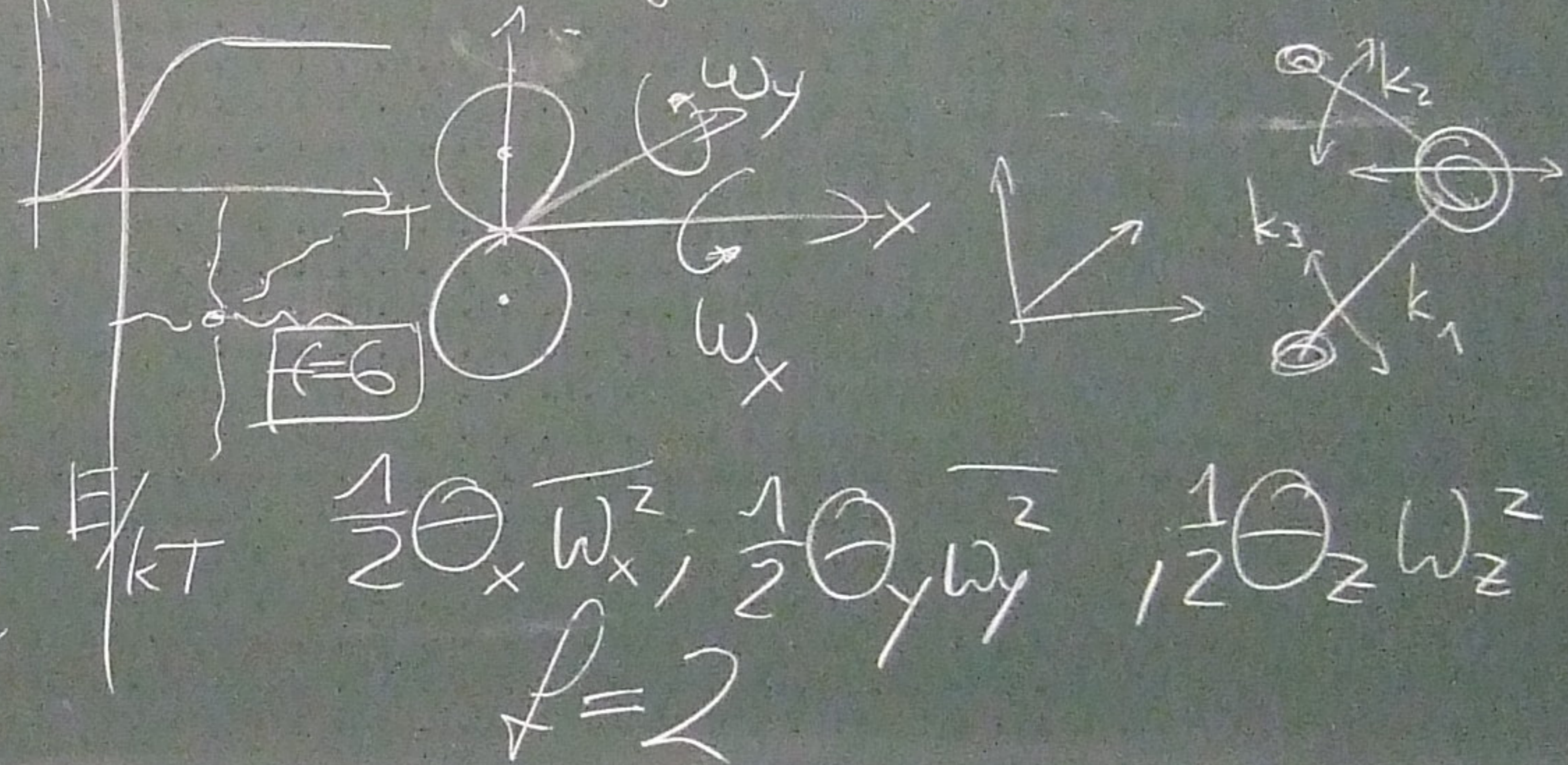


$$\frac{1}{2} m \overline{u^2} = \frac{1}{2} m (\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2})$$

3 Terme $\rightarrow f=3$

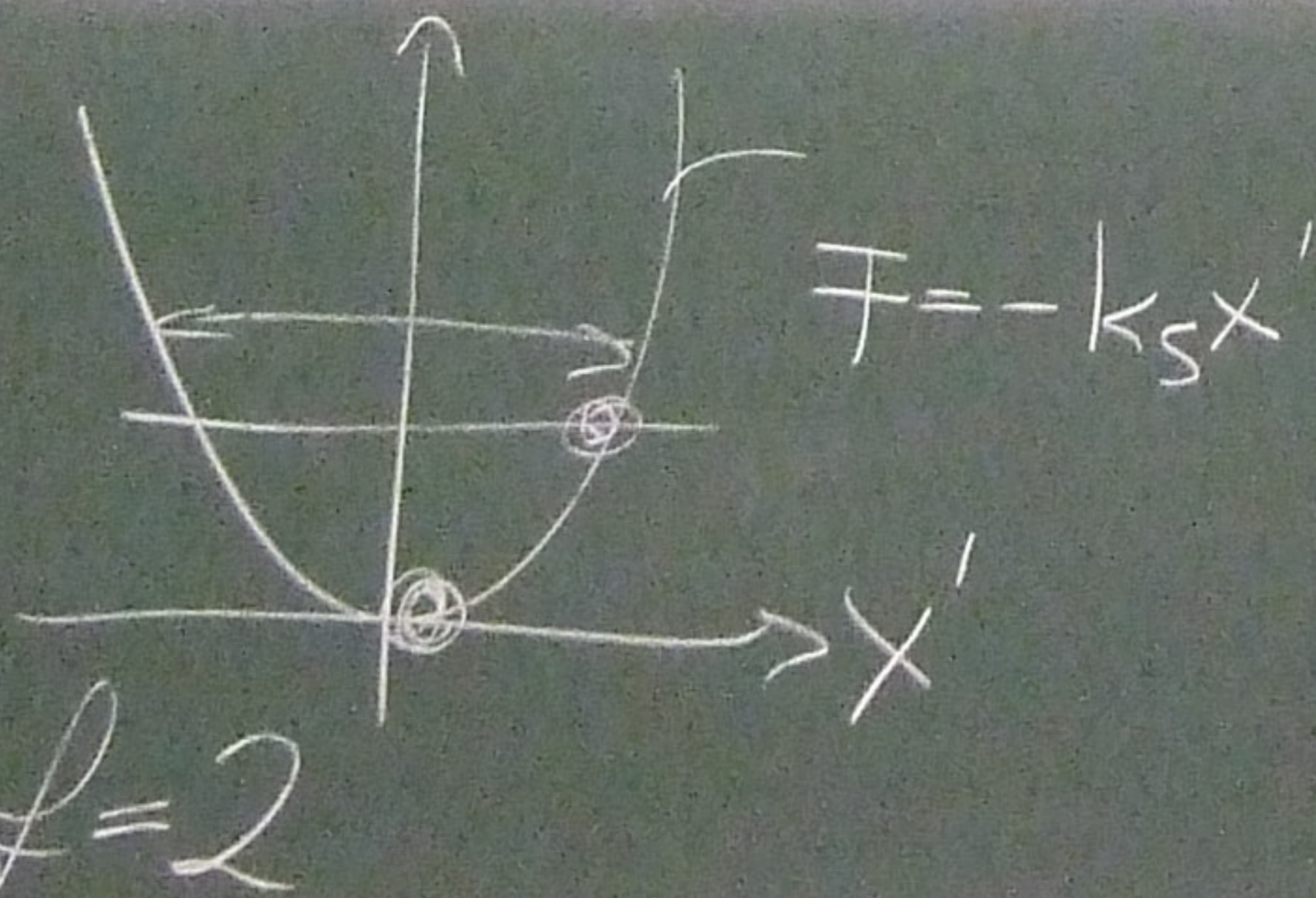


- 2 atomiges Molekül

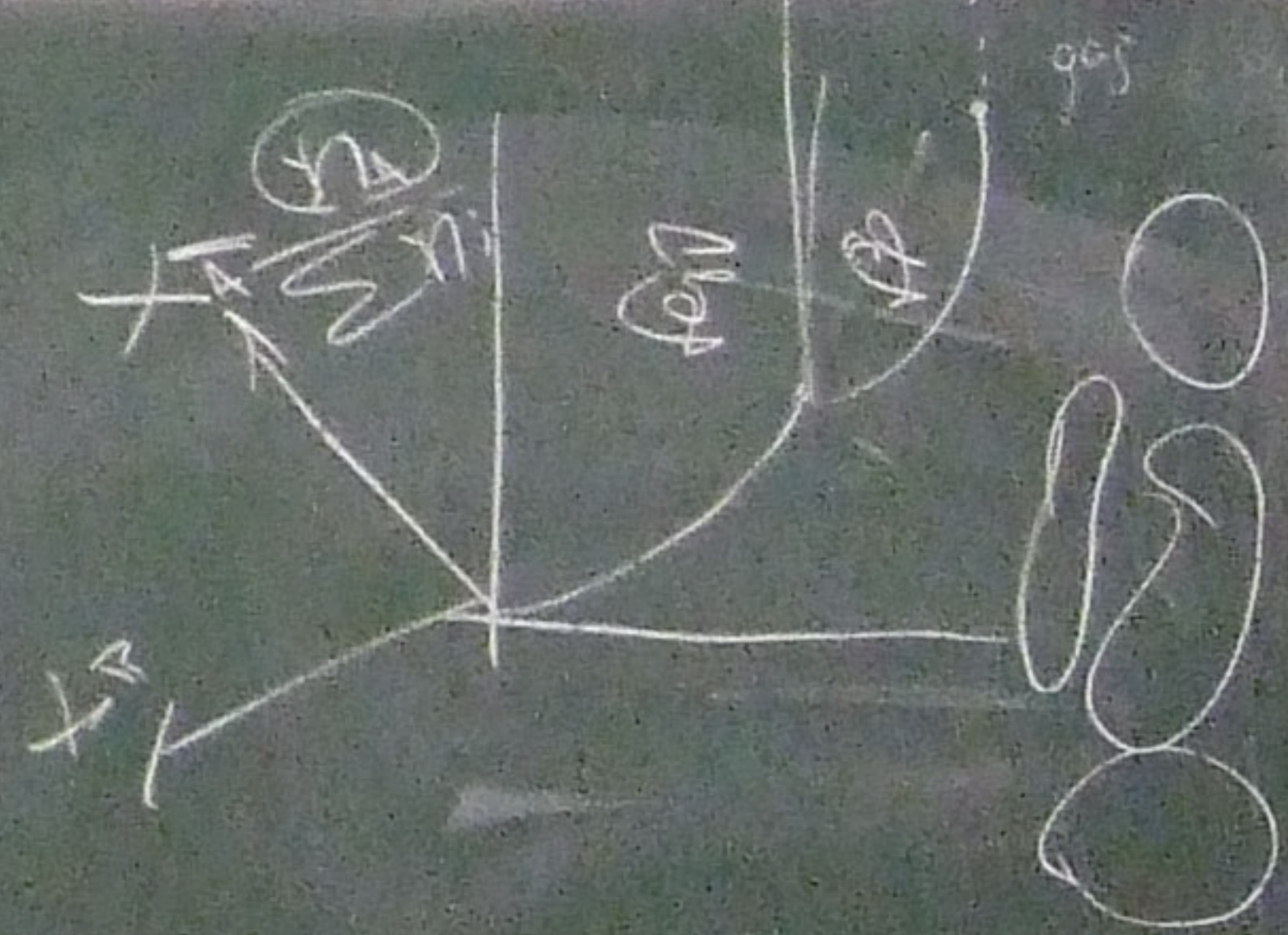


$$\frac{1}{2} \Theta_x \overline{\omega_x^2}, \frac{1}{2} \Theta_y \overline{\omega_y^2}, \frac{1}{2} \Theta_z \overline{\omega_z^2} \quad f=3$$

Schwingung



$$U = \frac{f}{2} N k T$$



$$\frac{1}{2} k T = \frac{1}{2} k_s x'^2 + \frac{1}{2} m \dot{x}'^2$$

f=2