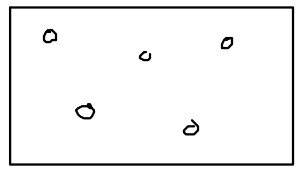
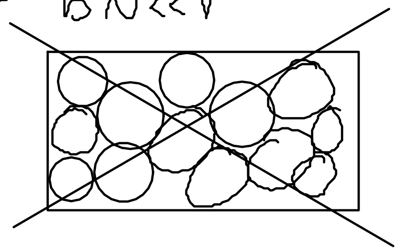
Van der Waals-Gas

für $bn \ll 1$: Gas verdünnt ← $bN \ll V$





Thermodynamische Störungstheorie (für kanonische Gesamtheit)

$H = H_0 + gV$ Dichtematrix (Zustandsoperator) $W = \frac{1}{Z} e^{-\beta H}$, $Z = \mathrm{Tr}(e^{-\beta H})$

Ziel: $W = W_0 + g W_1 + g^2 W_2$ $\quad F = -k_B T \ln Z$

$$Z = Z_0 + g Z_1 + g^2 Z_2$$

$$F = F_0 + g F_1 + g^2 F_2$$

0) $W_0 = \frac{1}{Z_0} e^{-\beta H_0}$ $\quad Z_0 = \mathrm{Tr}(e^{-\beta H_0})$ $\quad F_0 = -k_B \ln Z_0$

Problem: $[V, H_0] \neq 0$ $\quad e^{-\beta H} \neq e^{-\beta H_0} e^{-\beta g V}$

$$e^{\beta H_0} e^{-\beta H} = S(\beta) \neq e^{-\beta g V} \qquad \beta = \frac{1}{k_B T} \text{ festes } T$$

$$e^{\tau H_0} e^{-\tau H} = S(\tau) \qquad \tau \mathrel{\hat{=}} \text{variable Zeit}$$

QM Entwicklungsoperator: e^{-iHt} $\quad \tau = it$

(Statistik $\hat{=}$ QM in imaginärer Zeit)

$$\frac{\partial S}{\partial \tau} = H_0 e^{\tau H_0} e^{-\tau H} - e^{\tau H_0} H e^{-\tau H}$$

$$= e^{\tau H_0} (H_0 - H) e^{-\tau H}$$

$$= -e^{\tau H_0} g V e^{-\tau H}$$

$$= -g\, e^{\tau H_0} V \underbrace{e^{-\tau H_0} e^{\tau H_0}}_{1} e^{-\tau H}$$

$$\boxed{\frac{\partial S}{\partial \tau} = -g \tilde{V} S}$$

$$\boxed{e^{\tau A} = \sum_{n=0}^{\infty} \frac{A^n}{n!} \tau^n}$$

$$\boxed{\frac{\partial}{\partial \tau} e^{\tau A} = A e^{\tau A}}$$

$$\boxed{1 = e^{-\tau H_0} e^{\tau H_0}}$$

$$\boxed{\tilde{V}(\tau) = e^{\tau H_0} V e^{-\tau H_0}}$$

↑ in WW Darstellung

$S(\tau = 0) = 1$ $\quad$ ($\hat{=} \infty$ Temperatur)

$$S(\tau) = \int_0^{\tau} d\tau' \left(-g \tilde{V}(\tau')\right) S(\tau') + 1$$

$$S = S_0 + g S_1 + g^2 S_2 \ldots$$

0) $S_0(\tau) = 1$

1) $S_1(\tau) = -g \int_0^\tau d\tau_1 \, \tilde V(\tau_1) \overbrace{S_0(\tau_1)}^{=1} = -g \int_0^\tau d\tau_1 \, \tilde V(\tau_1)$

2) $S_2(\tau) = (-g)^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \; \tilde V(\tau_1) \tilde V(\tau_2)$

$$S = 1 - g \int_0^\tau d\tau_1 \, \tilde V(\tau_1) + (-g)^2 \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \, \tilde V(\tau_1) \tilde V(\tau_2) + \dots$$

$$(-g)^n \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \dots \int_0^{\tau_{n-1}} d\tau_n \; \tilde V(\tau_1) \dots \tilde V(\tau_n) + \dots$$

$[V(\tau_1), V(\tau_2)] \neq 0$ $\qquad \tau_n < \tau_{n-1} < \dots < \tau_1 < \tau$

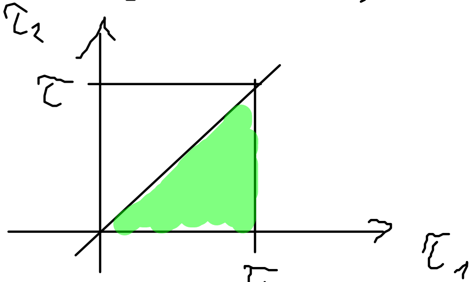
Zeitordnungs-Operator

$T \, \tilde V(\tau_1) \tilde V(\tau_2) = \tilde V(\tau_1) \tilde V(\tau_2)$ für $\tau_1 > \tau_2$

$T \, \tilde V(\tau_1) \tilde V(\tau_2) = \tilde V(\tau_2) \tilde V(\tau_1)$ für $\tau_1 < \tau_2$

$\int_0^\tau d\tau_1 \dots d\tau_n \neq \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \dots$

(ganze Fläche) (Teilfläche)



$$S = 1 - g \int_0^\tau d\tau_1 \, \tilde V(\tau_1) + \frac{(-g)^2}{n!} \int_0^\tau d\tau_1 \, d\tau_2 \; T(\tilde V(\tau_1) \tilde V(\tau_2)) + \dots \frac{(-g)^n}{n!} \int \dots$$

$$\boxed{S = T \exp\left[-g \int_0^\tau d\tau_1 \, \tilde V(\tau_1)\right]}$$ Zeitgeordneter exponent

$e^{-\tau H} = e^{-\tau H_0} S(\tau)$ $\qquad$ für $\tau = \beta$

0) $Z = \mathrm{Tr}\left(e^{-\tau H}\right)$ $\qquad Z_0 = \mathrm{Tr}\left(e^{-\tau H_0}\right)$

1) $Z = Z_0 + g Z_1 = \mathrm{Tr}\left(e^{-\tau H_0}\right) + \mathrm{Tr}\left(e^{-\tau H_0} (-g) \int_0^\tau d\tau_1 \, \tilde V(\tau_1)\right)$

$Z_1 = -\mathrm{Tr}\left(g \, e^{-\tau H_0} \int_0^\tau d\tau_1 \; e^{\tau_1 H_0} V e^{-\tau_1 H_0}\right)$

$= -\int_0^\tau d\tau_1 \; \mathrm{Tr}\left(e^{(\tau_1 - \tau) H_0} V e^{-\tau_1 H_0}\right)$

gerade Permutationen

$\boxed{\mathrm{Tr}(ABC) = \mathrm{Tr}(CAB)}$

$Z_1(\beta) = -\int_0^\beta d\tau_1 \; \mathrm{Tr}\left(e^{-\beta H_0} e^{\tau_1 H_0} V e^{-\tau_1 H_0}\right)$

$= -\int_0^\beta d\tau_1 \; \mathrm{Tr}\left(e^{-\beta H_0} V\right) = -\beta \, \mathrm{Tr}\left(e^{-\beta H_0} V\right)$

mit $W_0 = \frac{1}{Z_0} e^{-\beta H_0}$

$$\boxed{\langle V \rangle = -\frac{1}{Z_0} \mathrm{Tr}\left(e^{-\beta H_0} V \right)}$$

$$\boxed{Z_1 = -\beta Z_0 \langle V \rangle_0}$$

$$\boxed{\langle A \rangle = \mathrm{Tr}(W A)}$$