5. Offene Systeme

5.1 Teilchenzahl-Operator

Neben $\mathcal{H}$ tritt der Teilchenzahl-Operator $\mathcal{N}$, der mit $\mathcal{H}$ vertauscht

$$[\mathcal{H}, \mathcal{N}] = 0 \quad , [\mathcal{H}^{\square}, \mathcal{N}^{\square}] = 0$$

→ gemeinsames System von Eigenfunktionen

aus 4.1

$$\mathcal{H} |\psi_{jk}\rangle = E_j |\psi_{jk}\rangle = E |\psi_{jk}\rangle$$
$$\mathcal{N} |\psi_{jk}\rangle = N_k |\psi_{jk}\rangle = N |\psi_{jk}\rangle$$

E-N-Schale

$$\mathcal{H}^{\square} |\psi^{\square}_{\alpha\beta}\rangle = E^{\square}_{\alpha} |\psi^{\square}_{\alpha\beta}\rangle = E^{\square} |\psi^{\square}_{\alpha\beta}\rangle$$
$$\mathcal{N}^{\square} |\psi^{\square}_{\alpha\beta}\rangle = N^{\square}_{\alpha} |\psi^{\square}_{\alpha\beta}\rangle = N^{\square} |\psi^{\square}_{\alpha\beta}\rangle$$

Teilchenzahlen additiv wie von den Energien vorausgesetzt. Alles analog wie in 4.1 und 4.7.

5.2 Großkanonischer Dichteoperator

$$\rho^{gkan} = \frac{1}{Z} e^{-\beta \mathcal{H} - \alpha N} \qquad Z = Sp(e^{-\beta\mathcal{H} - \alpha N})$$

α ist wie β ein Kontaktparameter, hier für den Teilchenaustausch

$$g^{\square}(E^{\square}, N^{\square}) = g^{\square}(E^{ges} - E_n, N^{ges} - N_K)$$

aus 4.7

$$\beta^{\square}(E^{ges}, N^{ges}) = \frac{\partial}{\partial E^{ges}} \ln g^{\square}(E^{ges}, N^{ges})$$

und analog

$$\alpha^{\square}(E^{ges}, N^{ges}) = \frac{\partial}{\partial N^{ges}} \ln g^{\square}(E^{ges}, N^{ges})$$

Mit der Reservoireigenschaft von $g^{\square}$ und mit den Gleichgewichtsbedingungen

$$\beta^{\square}(E^{ges}, N^{ges}) = \beta(E, N) = \beta = const$$

$$\alpha^{\square}(E^{ges}, N^{ges}) = \alpha(E, N) = \alpha = const$$

folgt ρ^{gkan}.

$$\hat{\mu} := -\frac{\alpha}{\beta}$$

$$\boxed{\rho^{gkan} = \frac{1}{Z} e^{-\beta(\mathcal{H} - \hat{\mu} N)}}$$

Zustandssumme:

$$Z = Sp\, e^{-\beta(\mathcal{H} - \mu N)} = Sp\, e^{-\beta\mathcal{H} - \alpha N} =$$

$$= Z(\beta, \alpha)$$

$$Z(\alpha, \beta) = \sum_{JK} \langle \psi_{JK} | e^{-\beta\mathcal{H} - \alpha N} \psi_{JK} \rangle$$

$$Z(\alpha, \beta) = \sum_{JK} e^{-\beta E_J - \alpha N_K}$$

$$P_{JK}^{gkan} := \langle \psi_{JK} | \varrho^{gkan} \psi_{JK} \rangle =$$

$$= \frac{1}{Z} e^{-\beta E_J - \alpha N_K}$$

$$\curvearrowright \sum_{JK} P_{JK}^{gkan} = 1$$

5.3 Zustandssumme als Rechenhilfe

□ Beh.: Für die großkanonische Gesamtheit gilt:

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\bar{N} = -\frac{1}{Z} \frac{\partial Z}{\partial \alpha} = -\frac{\partial \ln Z}{\partial \alpha}$$

$$\frac{\partial \ln Z}{\partial E_J} = -\beta\, P_{JK}^{gkan}$$

und mit der mittleren quadratischen Abweichung

$$\overline{(\Delta x)^2} := \overline{(x - \overline{x})^2} = \overline{x^2} - \overline{x}^2$$

$$\overline{(\Delta E)^2} = - \frac{\partial \overline{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\overline{(\Delta N)^2} = - \frac{\partial \overline{N}}{\partial \alpha} = \frac{\partial^2 \ln Z}{\partial \alpha^2}$$

□

* Bew.:

$$\rho_{JK}^{\text{gkan.}} = \frac{1}{Z} e^{-\beta E_J - \alpha N_K}, \quad Z = \sum_{JK} e^{-\beta E_J - \alpha N_K}$$

$$\overline{E} = \frac{1}{Z} \sum_{JK} E_J e^{-\beta E_J - \alpha N_K} =$$

$$= \frac{1}{Z} \sum_{JK} - \frac{\partial}{\partial \beta} e^{-\beta E_J - \alpha N_K} = - \frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\overline{E} = - \frac{\partial \ln Z}{\partial \beta}$$

$$\overline{(\Delta E)^2} = \overline{(E - \overline{E})^2} = \overline{E^2 - 2E\overline{E} + \overline{E}^2} =$$

$$= \overline{E^2} - 2\overline{E}^2 + \overline{E}^2 = \overline{E^2} - \overline{E}^2$$

$$\overline{E^2} = \frac{1}{Z} \sum_{jk} E_j^2 \, e^{-\beta E_j - \alpha N_k} =$$

$$= \frac{1}{Z} \sum_{jk} - E_j \frac{\partial}{\partial \beta} e^{-\beta E_j - \alpha N_k} =$$

$$= \frac{1}{Z} \sum_{jk} \frac{\partial^2}{\partial \beta^2} e^{-\beta E_j - \alpha N_k}$$

$$\overline{E^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \underbrace{\frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)}_{-\bar{E}} \underbrace{- \frac{\partial}{\partial \beta} \frac{1}{Z} \frac{\partial Z}{\partial \beta}}_{+\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2}$$

$$\overline{E^2} = - \frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

$$\curvearrowright \quad \overline{E^2} - \bar{E}^2 = \overline{(\Delta E)^2} = - \frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

ebenso:

$$\overline{(\Delta N)^2} = - \frac{\partial \bar{N}}{\partial \alpha} = \frac{\partial^2 \ln Z}{\partial \alpha^2}$$

$$\frac{\partial \ln Z}{\partial E_j} = \frac{1}{Z} \frac{\partial Z}{\partial E_j} = \frac{1}{Z} \frac{\partial}{\partial E_j} \sum_{jk} e^{-\beta E_j - \alpha N_k} =$$

$$= - \beta \frac{1}{Z} e^{-\beta E_j - \alpha N_k} = - \beta P_{jk}^{gkan}$$

$*$