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Übungen zur Theoretischen Physik Fa WS 17/18

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Blatt 2
Lösungsvorschlag

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1. Anwendung des Funktionaldeterminantenkalküls:

(a) Maxwell relation

We prove the Maxwell relation by examining the differential of the free energy F. We know that

$$dU = dQ - pdV = TdS - pdV \tag{1}$$

where U is the internal energy, S is the entropy. The free energy is given by $F = U - TS$. From this it follows that

$$dF = dU - TdS - SdT \tag{2}$$

Then substituting Eq (1) into Eq (2), we get that

$$dF = -SdT - pdV \tag{3}$$

On the other hand one can write

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \tag{4}$$

Comparing Eqns (3) and (4) one concludes that

$$\begin{aligned} -S &= \left(\frac{\partial F}{\partial T}\right)_V \\ -p &= \left(\frac{\partial S}{\partial V}\right)_T \end{aligned} \tag{5}$$

Then, if we use the commutativity of the second derivatives of F, and (5) one can write

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V \tag{6}$$

Now, if one substitutes (5) into (6), one obtains that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{7}$$

We can rewrite (7) this in the form of a Jacoby determinant

$$\frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(p,V)}{\partial(T,V)} \tag{8}$$

From this it follows that

$$\frac{\frac{\partial(S,T)}{\partial(V,T)}}{\frac{\partial(p,V)}{\partial(T,V)}} = 1 \tag{9}$$

then using the identity from the first problem sheet, one arrives at the result

$$\frac{\partial(T,S)}{\partial(p,V)} = 1 \tag{10}$$

where we also used that $\frac{\partial(T,S)}{\partial(p,V)} = -\frac{\partial(S,T)}{\partial(p,V)}$ from the first problem sheet.

(b) $c_p - c_V$ relation.

First, at constant volume $dQ = TdS = c_V dT$, and from this it follows that

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} \tag{11}$$

Similarly,

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{12}$$

We begin by inspecting c_V:

$$\begin{aligned}
c_V &= T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} \\
&= \frac{\frac{\partial(S,V)}{\partial(T,p)}}{\frac{\partial(T,V)}{\partial(T,p)}} \\
&=^{\text{(written out explicitly)}} T\frac{\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} \\
&=^{(12)} c_p - T\frac{\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}
\end{aligned} \tag{13}$$

Next using the identity that $\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T$, and above we get that

$$c_V - c_p = -T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p \tag{14}$$

We then use the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ (derived in part (a) of this question). Then it follows that

$$c_V - c_p = -T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p \tag{15}$$

Next we use identity from Problem sheet 1, to write $\left(\frac{\partial V}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial p}{\partial V}\right)_T}$. Putting this into (15) we get the desired result:

$$c_p - c_V = -T\frac{\left(\frac{\partial p}{\partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T} \tag{16}$$

(c) Gas in a container

(i) show that the enthalpy does not change in this process.

Let a certain quantity of gas V_1 at pressure p_1 pass from left into right and acquire volume V_2. The change in energy is then $\Delta E = E_2 - E_2 = p_1V_1 - p_2V_2$, where p_1V_1 is the work done to remove the gas from volume V_1, and p_2V_2 work done by the gas to occupy the volume V_2. Rewriting this we get that $p_1V_1 + E_1 = p_2V_2 + E_2$, which means that the enthalpy $H = E + pV$ does not change during this process.

(ii) change in temperature

We are interested in change of temperature with pressure, while enthalpy H is held constant because of (i). We calculate

$$\begin{aligned}
\left(\frac{\partial T}{\partial p}\right)_H &= \frac{\partial(T,H)}{\partial(p,H)} = \frac{\frac{\partial(T,H)}{\partial(p,T)}}{\frac{\partial(p,H)}{\partial(p,T)}} \\
&= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \\
&= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{c_p}
\end{aligned} \tag{17}$$

where in the last line we have replaced $c_p = \left(\frac{\partial H}{\partial T}\right)_p$. This statement can be deduced by looking at $dH = dE + pdV + Vdp = dQ + Vdp = c_pdT + Vdp$, from where it follows that $c_p = \left(\frac{\partial H}{\partial T}\right)_p$. From (17), we see that we need to calculate $\left(\frac{\partial H}{\partial p}\right)_T$. In order to do so we consider:

$$\begin{aligned}
dH &= TdS + Vdp \\
dH &= T\left(\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp\right) + Vdp
\end{aligned} \tag{18}$$

Then taking the partial derivative of the above expression with respect to p at constant T, one obtains

$$\begin{aligned}
\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V \\
&= T\frac{\partial(S,T)}{\partial(p,T)} + V \\
&= -T\frac{\partial(p,V)}{\partial(p,T)} + V
\end{aligned} \tag{19}$$

where in the last line we have used the result of part (i) – the Maxwell relation. We then get that

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(-\frac{\partial V}{\partial T}\right)_p + V \tag{20}$$

Combining (20) and (17) one gets that

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{1}{c_p}\left(-T\left(\frac{\partial V}{\partial T}\right)_p + V\right) \tag{21}$$

(iii) entropy in this process.

Since $dH = TdS + Vdp$, we get that $dS = \frac{dH}{T} - \frac{V}{T}dp$, from which it follows that

$$\left(\frac{\partial S}{\partial p}\right)_H = -\frac{V}{T} \tag{22}$$

and this quantity is always negative, since the process of a gas expanding into the area of lower pressure is irreversible and there is an increase in entropy.

2. Erzeugende Funktionen und Zentraler Grenzwertsatz:

(a) show that the characteristic function generates moments.

We start from

$$\phi_X(k) = \int dx P(x) e^{ikx} \tag{23}$$

Then

$$\begin{aligned}\frac{d^n}{dk^n}\phi_X(k) = \frac{d^n}{dk^n}\int dx P(x) e^{ikx} \\ = i^n \int dx P(x) x^n e^{ikx}\end{aligned} \tag{24}$$

From this it follows that

$$\frac{d^n}{dk^n}\phi_X(k)|_{k=0} = i^n \langle x^n \rangle \tag{25}$$

(b) cumulants.

We start from the definition of the cummulant

$$\phi_X(k) := \exp\left(\sum_n C_n(X)\frac{(ik)^n}{n!}\right). \tag{26}$$

From this it follows that

$$\ln\phi_X(k) = \left(\sum_n C_n(X)\frac{(ik)^n}{n!}\right). \tag{27}$$

The mth cummulant can then be obtained from

$$C_m(X) = \frac{1}{i^m}\frac{d^m \ln\phi_X(k)}{dk^m}|_{k=0} \tag{28}$$

Then it follows that

$$\begin{aligned} C_1(X) &= \frac{1}{i}\frac{d\ln\phi_X(k)}{dk}|_{k=0} \\ &= \frac{1}{i}\frac{d}{dk}\ln\left\{\int P_X(x)e^{ikx}dx\right\}|_{k=0} \\ &= \frac{\int P_X(x)xdx}{\int P_X(x)dx} = \langle X\rangle \end{aligned} \tag{29}$$

Similarly, the second cummulant is given by

$$\begin{aligned} C_2(X) &= \frac{1}{i^2}\frac{d^2\ln\phi_X(k)}{dk^2}|_{k=0} \\ &= \frac{1}{i}\frac{d}{dk}\frac{\int P_X(x)e^{ikx}xdx}{\int P_X(x)e^{ikx}dx}|_{k=0} \\ &= \frac{\int P_X(x)x^2dx}{\int P_X(x)dx} - \left(\frac{\int P_X(x)xdx}{\int P_X(x)dx}\right)^2 \\ &= \langle X^2\rangle - (\langle X\rangle)^2 \end{aligned} \tag{30}$$

(c) independent variables.

We know $\phi_{X_1}(k)$ and $\phi_{X_2}(k)$. Then

$$\begin{aligned} \phi_{X_1+X_2}(k) &= \int dx_1\int dx_2 P(X_1,X_2)e^{ik(x_1+x_2)} \\ &= \int dx_1\int dx_2 P(X_1)P(X_2)e^{ik(x_1+x_2)} \\ &= \phi_{X_1}(k)\phi_{X_2}(k). \end{aligned} \tag{31}$$

Here $P(X_1, X2)$ is the joint probability distribution for the variables X_1 and X_2. Iin the second line we have used that $P(X_1,X_2) = P(X_1)P(X_2)$ since X_1 and X_2 are independent.

(d) proof of the central limit theorem.

The $S_N = \frac{\sum_{i=1}^{N} X_i}{N}$ As suggested, first we prove the identity between the cummulants of the two distributions. We write

$$\phi_{S_N}(k) = \langle e^{ikS_N}\rangle = \langle e^{ik\frac{\sum_{i=1}^{N} X_i}{N}}\rangle = \prod_{i=1}^{N}\langle e^{ik\frac{X_i}{N}}\rangle = \left[\phi_X\left(\frac{k}{N}\right)\right]^N \tag{32}$$

We then write

$$\begin{aligned}\left[\phi_X\left(\frac{k}{N}\right)\right]^N &= \left[\exp\left(\sum_m C_m(X)\frac{(i\frac{k}{n})^m}{m!}\right)\right]^N \\ &= \phi_{S_N}(k) = \exp\left(\sum_m C_m(S_N)\frac{(ik)^m}{m!}\right)\end{aligned} \tag{33}$$

where in the second line we used equality (32). If we compare the first and the second line of (33), we conclude that $C_m(S_N) = \frac{N}{N^m}C_m(X)$. This suggests that for large N, only $C_1(S_N)$ and $C_2(S_N)$ are significant, and that the distribution of S_N is Gaussian. Taking into account only the first two cummulants

$$\begin{aligned}\phi_{S_N}(k) &\approx \exp\left(ikC_1(S_N) - \frac{k^2}{2}C_2(S_N)\right) \\ &= \exp\left(ikC_1(S_N) - \frac{k^2}{2}C_2(S_N)\right) \\ &= \exp\left(ik\langle X\rangle - \frac{k^2}{2}C_2(X)/N\right)\end{aligned} \tag{34}$$

where we used the relation $C_m(S_N) = \frac{N}{N^m}C_m(X)$. By applying the inverse Furrier transform we get

$$\begin{aligned}P_{S_N}(s) &= \frac{1}{2\pi}\int e^{-iks}\phi_{S_N}(k)dk \\ &= \frac{1}{2\pi}\int dk\exp\left(-iks + ik\langle X\rangle - \frac{k^2}{2N}\sigma_X^2\right)\end{aligned} \tag{35}$$

where we also used that $C_2(X) = \sigma_X^2$ (which was proved in part (b) of this question). Next, after completing the square, we get

$$P_{S_N}(s) = \sqrt{\frac{N}{2\pi\sigma_X^2}}\exp\left(-\frac{N(s-\langle X\rangle)^2}{2\sigma_X^2}\right), \tag{36}$$

which is a Gaussian with a mean value (centered at) $\langle X\rangle$, and variance $\sigma_S^2 = \frac{\sigma_X^2}{N}$.

3. Gaußverteilung für mehrere Variablen:

Wir betrachten die charakteristische Funktion

$$\phi(\lambda_1, \dots, \lambda_M) = \langle e^{i \sum_{j=1}^M \lambda_j \xi_j} \rangle$$

Es ergibt sich

$$\phi(\lambda_1, \dots, \lambda_M) = \frac{\sqrt{\det A}}{(2\pi)^{M/2}} \int_{-\infty}^{\infty} d^M \xi \; e^{-\frac{1}{2} \sum_{i,j=1}^M \xi_i A_{ij} \xi_j + i \sum_{j=1}^M \lambda_j \xi_j}$$

Zur Berechnung des Integrals wird der Exponent mittels quadratischer Ergänzung (mehrdimensional !) umgeschrieben:

$$-\frac{1}{2} \sum_{i,j=1}^M \xi_i A_{ij} \xi_j + i \sum_{j=1}^M \lambda_j \xi_j + \frac{1}{2} \sum_{i,j=1}^M \lambda_i G_{ij} \lambda_j - \frac{1}{2} \sum_{i,j=1}^M \lambda_i G_{ij} \lambda_j$$

mit $G_{ij} = [A^{-1}]_{ij}$.
Es gilt

$$A_{ij} = A_{ji} \quad \Rightarrow \quad G_{ij} = G_{ji}, \quad \sum_{j=1}^M A_{ij} G_{jk} = \delta_{ik}, \quad \sum_{j=1}^M G_{ij} A_{jk} = \delta_{ik}.$$

Die ersten drei Summanden können zusammengefasst werden zu

$$-\frac{1}{2} \sum_{i,j=1}^M \left(\xi_i - i \sum_k \lambda_k G_{ki} \right) A_{ij} \left(\xi_j - i \sum_k G_{jk} \lambda_k \right) = -\frac{1}{2} \sum_{i,j=1}^M y_i A_{ij} y_j$$

mit $y_j = \xi_j - i \sum_k G_{jk} \lambda_k = \xi_j - i \sum_k \lambda_k G_{kj}$.
Wir erhalten somit schließlich

$$\phi(\lambda_1, \dots, \lambda_M) = \underbrace{\frac{\sqrt{\det A}}{(2\pi)^{M/2}} \int_{-\infty}^{\infty} d^M y \; e^{-\frac{1}{2} \sum_{i,j=1}^M y_i A_{ij} y_j}}_{=1 \qquad \text{(Normierung)}} e^{-\frac{1}{2} \sum_{i,j=1}^M \lambda_i G_{ij} \lambda_j}$$

$$\phi(\lambda_1, \dots, \lambda_M) = e^{-\frac{1}{2} \sum_{i,j=1}^M \lambda_i G_{ij} \lambda_j}$$

Daraus ergibt sich

(a)

$$\langle \xi_i \rangle = \frac{1}{i} \frac{d}{d\lambda_i} \phi(\lambda_1, \dots, \lambda_M) \Big|_{\lambda_1 = \ldots = \lambda_M = 0} = -\frac{1}{i} \sum_{j=1}^M G_{ij} \lambda_j \Bigg|_{\lambda_j = 0} = 0$$

(b)

$$\langle \xi_i^2 \rangle - \langle \xi_i \rangle^2 = -\frac{d^2}{d\lambda_i^2} \phi(\lambda_1, \dots, \lambda_M) \Big|_{\lambda_1 = \ldots = \lambda_M = 0} = G_{ii}$$

(c)

$$\langle e^{i\beta\sum_{k=1}^M \xi_k}\rangle = \phi(\beta, \beta\ \ldots, \beta) = e^{-\frac{\beta^2}{2}\sum_{i,j=1}^M\langle\xi_i\xi_j\rangle}.$$

Hier setzen wir $\lambda_1 = \lambda_2 = \cdots = \lambda_M = \beta$ und substituieren $\langle\xi_i\xi_j\rangle$ für G_{ij}.

(d)

$$\langle\xi_i\xi_j\rangle = -\frac{d^2}{d\lambda_i d\lambda_j}\phi(\lambda_1, \ldots, \lambda_M)\Big|_{\lambda_1=\ldots=\lambda_M=0} = G_{ij}$$

(e) Wir definieren $t_i = i\Delta t$, $\Delta t = \frac{\tau}{M}$, $i = 1, \ldots, M$ (wir können t_i auch um $\frac{\Delta t}{2}$ verschieben, das gibt dasselbe). Genau betrachtet erhalten wir damit das Intervall $[\Delta t, \tau]$ und nicht $[0, \tau]$, aber für große M verschwindet diese Diskrepanz. Integale diskretisieren wir folgendermaßen

$$\int_0^\tau dt f(t) \quad \rightarrow \quad \sum_i \Delta t \cdot f(t_i)\ .$$

Damit wird

$$\rho\left(\{\xi(t)\}\right) \sim e^{-\frac{1}{2}\sum_{ij=1}^M \xi(t_i)(\Delta t)^2 g^{-1}(t_i-t_j)\xi(t_j)}$$

Um die Verbindung zur diskreten Verteilungsfunktion aus Aufgabe 1 herzustellen, setzen wir

$$\xi_i = \xi(t_i), \qquad A_{ij} = (\Delta t)^2 g^{-1}(t_i - t_j).$$

(f) Wir führen die Bezeichnungsweisen $\langle A\rangle_c$ für die Mittelung mit der kontinuierliche Verteilungsfunktion, und $\langle A\rangle_d$ für die Mittelung mit der diskreten Verteilungsfunktion ein. Wir diskretisieren $\langle\exp\left[i\int_0^\tau dt\xi(t)\right]\rangle_c$, und erhalten $\langle\exp\left[i\Delta t\sum_{k=1}^M \xi_k\right]\rangle_d$. Aus Aufgabe 1 wissen wir jedoch, dass

$$\left\langle \exp\left[i\Delta t\sum_{k=1}^M \xi_k\right]\right\rangle_d = \exp\left[-\frac{(\Delta t)^2}{2}\sum_{ij=1}^M\langle\xi_i\xi_j\rangle_d\right].$$

Damit ergibt sich, nachdem wir auf der rechten Seite die Doppelsumme im Exponenten wieder durch ein Doppelintegral ersetzen, die gesuchte Beziehung:

$$\left\langle \exp\left[i\int_0^\tau dt\xi(t)\right]\right\rangle_c = \exp\left[-\frac{1}{2}\int_0^\tau dt\int_0^\tau dt'\langle\xi(t)\xi(t')\rangle_c\right].$$

(g) Wir finden t_i am nächsten zu t und t_j am nächsten zu t'.
Da $\langle\xi_i\xi_j\rangle_d = G_{ij} = \left[A^{-1}\right]_{ij}$, benötigen wir A^{-1}.
Ein kurzer Ausflug in die Theorie der (linearen) Integralgleichungen:
Die Gleichung $x = Ky$ sei wie folgt zu verstehen:

$$x(r) = \int K(r, r')y(r')dr'\ , \tag{37}$$

wobei $K(r, r')$ der Integralkern ist. Die Lösung dieser Gleichung ist dann

$$y(r) = \int \bar{K}(r, r')x(r')dr'\ . \tag{38}$$

Mit $\bar{K} \equiv K^{-1}$ erhalten wir $y = K^{-1}x$. Also K^{-1} ist einfach das Inverse des Integralkerns.

Nun betrachten wir als definierende Gleichung für $g(t-t')$ folgenden Ausdruck (Beachte, dass $g^{-1}(t-t')$ nicht die Umkehrfunktion ist, wie man sie in Analysis I oder HM I kennenlernt...):

$$\int_0^\tau dt''\; g^{-1}(t-t'')g(t''-t') = \delta(t-t').$$

Diskretisiert lautet diese Gleichung

$$\Delta t \sum_{j=1}^{M} g^{-1}(t_i-t_j)g(t_j-t_k) = \underbrace{\frac{\delta_{ik}}{\Delta t}}_{\text{(diskretisierte Deltafunktion)}}$$

Warum? Die diskretisierte Form der Deltafunktion, $\delta_D(t_i-t_j)$, erhält man aus der Normierung für die Deltafunktion:

$$\int_0^\tau dt\; \delta(t-t') = 1 \qquad \Rightarrow \qquad \Delta t \sum_{j=1}^{M} \underbrace{\delta_D(t_i-t_j)}_{\delta_{ij}/\Delta t} = 1.$$

Also folgt $\sum_{j=1}^{M} \left[g^{-1}\right]_{ij} g_{jk} = \delta_{ik}/(\Delta t)^2$. Da aber andrerseits $(\Delta t)^2 \left[g^{-1}\right]_{ij} = A_{ij} \Rightarrow \sum_{j=1}^{M} A_{ij}g_{jk} = \delta_{ik}$ ist, folgt $\left[A^{-1}\right]_{ij} = g_{ij} = g(t_i-t_j)$.

Damit erhalten wir die gesuchte Beziehung:

$$\underbrace{\langle \xi(t)\xi(t')\rangle_c}_{\text{“Korrelationsfunktion”}} \quad = \quad \underbrace{g(t-t')}_{\text{(Maß für Korrelationen)}} \quad .$$

Näherung gut, wenn Δt klein gegenüber der Reichwerte der Korrelationen ist, d.h. $g(\Delta t) \approx g(0)$.

4. Stationäre Lösung der Liouville-Gleichung:

Die klassische Liouville Gleichung (vergleiche QM: von Neumann Gleichung) lautet

$$i\frac{\partial \rho}{\partial t} = -i\big\{H\,,\,\rho\big\}. \tag{39}$$

Hierbei bezeichnet $\{\cdot,\cdot\}$ die klassiche Poisson-Gleichung und nicht etwa den Antikommutator. Die Poissonklammer ist folgendermaßen definiert:

$$\big\{A\,,\,B\big\} = \sum_{j=1}^{3N}\left(\frac{\partial A}{\partial p_j}\frac{\partial B}{\partial q_j} - \frac{\partial A}{\partial q_j}\frac{\partial B}{\partial p_j}\right) \tag{40}$$

Es bleibt also zu zeigen, dass $\{H(\boldsymbol{x}), \rho(H(\boldsymbol{x}))\} = 0$ ist ($\boldsymbol{x} = (\boldsymbol{q}, \boldsymbol{p})$).

$$\big\{H(\boldsymbol{x}), \rho(H(\boldsymbol{x}))\big\} = \sum_{j=1}^{3N}\left(\frac{\partial H}{\partial p_j}\frac{\partial \rho}{\partial H}\frac{\partial H}{\partial q_j} - \frac{\partial H}{\partial q_j}\frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p_j}\right) = 0\ , \tag{41}$$

da alle (klassischen) Größen miteinander vertauschen.