

Übungen zur Theoretischen Physik Fa WS 17/18

Prof. Dr. A. Shnirman
PD Dr. B. NarozhnyBlatt 1
Lösungsvorschlag

1. Stirlingsformel:

We begin from

$$n! = \int_0^{\infty} x^n e^{-x} = \int_0^{\infty} \exp(n \ln x - x) \quad (1)$$

It is easy to check that the function $f(x) = n \ln x - x$ has a maximum at $x = n$, (obtained by setting $f'(x) = 0$, and checking that indeed it is a maximum by computing $f''(n) = \frac{-1}{n} < 0$). The main contribution to the integral comes from integrating around this maximum. Hence, we can expand the integration limits from $(-\infty, \infty)$ and Taylor-expand the function $f(x)$ around the maximum at $x = n$, i.e. $f(x) = f(n) + \frac{1}{2}f''(n)(x - n)^2 + \dots$

This gives

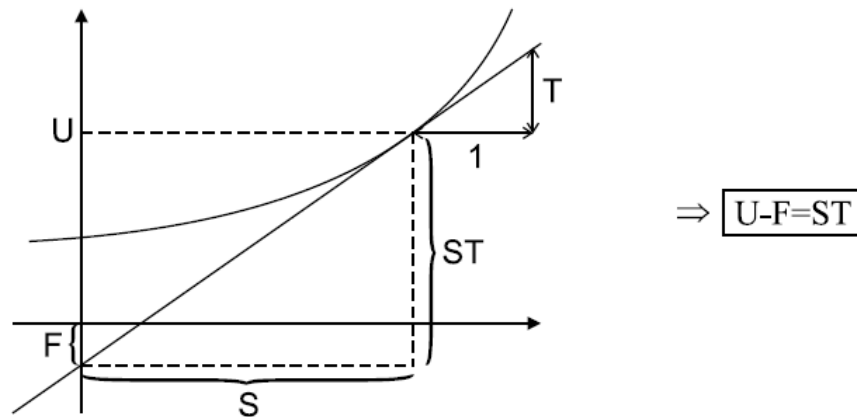
$$\begin{aligned} n! &= \int_{-\infty}^{\infty} dx \exp\left(n \ln n - n - \frac{1}{2n}(x - n)^2 + \dots\right) \\ &= \exp(n \ln n - n) \int_{-\infty}^{\infty} dy \exp\left(-\frac{y^2}{2n}\right) \\ &= \exp(n \ln n - n) \sqrt{2\pi n} \end{aligned} \quad (2)$$

After taking the log of (2), and bearing in mind that for $n \gg 1$ we have that $\ln n \ll n$ (so that we can drop it), it follows that

$$\ln n! = n \ln n - n. \quad (3)$$

2. Legendretransformation:

(a)



$$U = U(S), \text{ Steigung } T = \frac{\partial U}{\partial S} \Rightarrow S = S(T) \quad \boxed{dU(S) = \frac{\partial U}{\partial S} dS = T(S) dS}$$

$$F = F(T) = U(S(T)) - S(T)T,$$

$$dF(T) = \left[\overbrace{\frac{\partial U}{\partial S}}^T \frac{\partial S}{\partial T} - \frac{\partial S}{\partial T} T - S(T) \right] dT \Rightarrow \boxed{dF(T) = -S(T) dT}$$

(b)

$$U(S, V), \quad T = \left. \frac{\partial U(S, V)}{\partial S} \right|_V \Rightarrow S(T, V)$$

$$-P = \left. \frac{\partial U(S, V)}{\partial V} \right|_S \Rightarrow V(S, P)$$

$$dU(S, V) = T(S, V) dS - P(S, V) dV \quad \text{Innere Energie}$$

analog zu a):

$$F(T, V) = U(S(T, V), V) - S(T, V)T \quad \text{Freie Energie,}$$

$$dF(T, V) = -S(T, V) dT - P(S, (T, V), V) dV$$

$$H(S, P) = U(S, V(S, P)) + V(S, P)P \quad \text{Enthalpie,}$$

$$dH(S, P) = T(S, V(S, P)) dS + V(S, P) dP$$

3. Funktionaldeterminantenkalkül:

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial u}{\partial x} \Big|_y \frac{\partial v}{\partial y} \Big|_x - \frac{\partial u}{\partial y} \Big|_x \frac{\partial v}{\partial x} \Big|_y \quad \text{Def. der Determinante}$$

(a)

1. $v(x, y) = y \Rightarrow \frac{\partial v}{\partial y} \Big|_x = 1, \frac{\partial v}{\partial x} \Big|_y = 0 \Rightarrow \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial u}{\partial x} \Big|_y$
2. $u(x, y) = x \Rightarrow \text{analog } \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial u}{\partial y} \Big|_x$
3. folgt trivial aus Determinanteneigenschaft (Vertauschen von $u \leftrightarrow v$ oder $x \leftrightarrow y$ vertauscht Vorzeichen)
- 4.

$$\begin{aligned} \frac{\partial(u, v)}{\partial(x, y)} &= \frac{\partial(u(s(x, y), t(x, y)), v(s(x, y), t(x, y)))}{\partial(x, y)} \\ &= \left(\frac{\partial u}{\partial s} \Big|_t \frac{\partial s}{\partial x} \Big|_y + \frac{\partial u}{\partial t} \Big|_s \frac{\partial t}{\partial x} \Big|_y \right) \left(\frac{\partial v}{\partial s} \Big|_t \frac{\partial s}{\partial y} \Big|_x + \frac{\partial v}{\partial t} \Big|_s \frac{\partial t}{\partial y} \Big|_x \right) \\ &\quad - \left(\frac{\partial u}{\partial s} \Big|_t \frac{\partial s}{\partial y} \Big|_x + \frac{\partial u}{\partial t} \Big|_s \frac{\partial t}{\partial y} \Big|_x \right) \left(\frac{\partial v}{\partial s} \Big|_t \frac{\partial s}{\partial x} \Big|_y + \frac{\partial v}{\partial t} \Big|_s \frac{\partial t}{\partial x} \Big|_y \right) \\ &= \frac{\partial u}{\partial s} \Big|_t \frac{\partial v}{\partial s} \Big|_t \left(\frac{\partial s}{\partial x} \Big|_y \frac{\partial s}{\partial y} \Big|_x - \frac{\partial s}{\partial y} \Big|_x \frac{\partial s}{\partial x} \Big|_y \right) + \frac{\partial u}{\partial s} \Big|_t \frac{\partial v}{\partial t} \Big|_s \left(\frac{\partial s}{\partial x} \Big|_y \frac{\partial t}{\partial y} \Big|_x - \frac{\partial s}{\partial y} \Big|_x \frac{\partial t}{\partial x} \Big|_y \right) \\ &\quad + \frac{\partial u}{\partial t} \Big|_s \frac{\partial v}{\partial s} \Big|_t \left(\frac{\partial t}{\partial x} \Big|_y \frac{\partial s}{\partial y} \Big|_x - \frac{\partial t}{\partial y} \Big|_x \frac{\partial s}{\partial x} \Big|_y \right) + \frac{\partial u}{\partial t} \Big|_s \frac{\partial v}{\partial t} \Big|_s \left(\frac{\partial t}{\partial x} \Big|_y \frac{\partial t}{\partial y} \Big|_x - \frac{\partial t}{\partial y} \Big|_x \frac{\partial t}{\partial x} \Big|_y \right) \end{aligned}$$

1. und 4. Term sind Null. 2. und 3. Term ergeben

$$\left(\frac{\partial u}{\partial s} \Big|_t \frac{\partial v}{\partial t} \Big|_s - \frac{\partial u}{\partial t} \Big|_s \frac{\partial v}{\partial s} \Big|_t \right) \left(\frac{\partial s}{\partial x} \Big|_y \frac{\partial t}{\partial y} \Big|_x - \frac{\partial s}{\partial y} \Big|_x \frac{\partial t}{\partial x} \Big|_y \right) = \frac{\partial(u, v)}{\partial(s, t)} \frac{\partial(s, t)}{\partial(x, y)}$$

Durch Umbenennen von $x, y \rightarrow s, t$ und $s, t \rightarrow x, y$ folgt

$$\frac{\partial(u, v)}{\partial(s, t)} = \frac{\partial(u, v)}{\partial(x, y)} \frac{\partial(x, y)}{\partial(s, t)} \quad \xrightarrow{\text{auflösen}} \quad \frac{\partial(u, v)}{\partial(x, y)} = \frac{\frac{\partial(u, v)}{\partial(s, t)}}{\frac{\partial(x, y)}{\partial(s, t)}}$$

(b)

Die erste Relation spiegelt einfach den *Satz der lokalen Umkehrbarkeit* aus Analysis wieder. Z.B. so: Sei $\phi(x, y) = \text{const.}$, also $x(y)$. Dann ist das Differential $dx(y) = \frac{\partial x}{\partial y} dy$. Andererseits ist aber $dy(x) = \frac{\partial y}{\partial x} dx$. Einsetzen liefert dann $dx = \frac{\partial x}{\partial y} \frac{\partial y}{\partial x} dx$, also $1 = \frac{\partial x}{\partial y} \frac{\partial y}{\partial x}$. Und daraus folgt schließlich

$$\frac{\partial x}{\partial y} = \left(\frac{\partial y}{\partial x} \right)^{-1}.$$

Da wir ja von Anfang an $\phi = \text{const.}$ angenommen haben, dürfen wir auch noch bei beiden partiellen Ableitungen die ϕ 's dazuschreiben und erhalten das gesuchte Resultat.

$$\left. \frac{\partial y}{\partial x} \right|_{\phi} = \frac{\partial(y, \phi)}{\partial(x, \phi)} = \frac{\partial(y, \phi)}{\partial(y, x)} \frac{\partial(y, x)}{\partial(x, \phi)} = - \left. \frac{\partial \phi}{\partial x} \right|_y \frac{1}{\frac{\partial(x, \phi)}{\partial(x, y)}} = - \frac{\left. \frac{\partial \phi}{\partial x} \right|_y}{\left. \frac{\partial \phi}{\partial y} \right|_x}$$

{Hier wird $\phi = \phi(x, y) = \text{const.}$ als unabhängige Variable aufgefasst, d. h. $y = y(x, \phi)$ }.

(c)

Wir betrachten x und z als unabhängige Variable, so dass $y = y(x, z)$. Das erfolgt durch Auflösen von $F(x, y, z) = 0$ nach y . Das Differential für y ist dann

$$dy = \left. \frac{\partial y}{\partial x} \right|_z dx + \left. \frac{\partial y}{\partial z} \right|_x dz$$

Weiterhin ist $w = w(x, y)$, also

$$dw = \left. \frac{\partial w}{\partial x} \right|_y dx + \left. \frac{\partial w}{\partial y} \right|_x dy.$$

Wir substituieren $y(x, z)$ für y in $w(x, y)$, und erhalten als Differential für $w(x, z)$:

$$dw = \left. \frac{\partial w}{\partial y} \right|_x \left. \frac{\partial y}{\partial z} \right|_x dz + \left(\left. \frac{\partial w}{\partial x} \right|_y + \left. \frac{\partial w}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z \right) dx.$$

Daraus folgt

$$\left. \frac{\partial w}{\partial x} \right|_z = \left. \frac{\partial w}{\partial x} \right|_y + \left. \frac{\partial w}{\partial y} \right|_x \left. \frac{\partial y}{\partial x} \right|_z. \quad (4)$$

Analog erhalten wir aus dem Differential für $w(x(y, z), y)$:

$$\left. \frac{\partial w}{\partial y} \right|_z = \left. \frac{\partial w}{\partial y} \right|_x + \left. \frac{\partial w}{\partial x} \right|_y \left. \frac{\partial x}{\partial y} \right|_z. \quad (5)$$

Wir eliminieren $\partial w / \partial y|_x$ (d.h. Gl. (5) in Gl. (4) einsetzen), und erhalten

$$\left. \frac{\partial w}{\partial x} \right|_z = \left. \frac{\partial w}{\partial y} \right|_z \left. \frac{\partial y}{\partial x} \right|_z.$$

Wir lösen nun $w = w(x, y)$ nach x auf, betrachten also x als Funktion von y und w , d.h. $x = x(y, w)$. Wir erhalten

$$dx = \left. \frac{\partial x}{\partial y} \right|_w dy + \left. \frac{\partial x}{\partial w} \right|_y dw$$

Die Gleichung $F(x, y, z) = 0$ lösen wir nach x auf, betrachten also x als Funktion von y und z , und erhalten daraus $w = w(x(y, z), y)$. Das Differential für $w(y, z)$ ist

$$dw = \left. \frac{\partial w}{\partial y} \right|_z dy + \left. \frac{\partial w}{\partial z} \right|_y dz.$$

Wir substituieren dies in die Gleichung für dx und erhalten schließlich

$$\left. \frac{\partial x}{\partial y} \right|_z = \left. \frac{\partial x}{\partial y} \right|_w + \left. \frac{\partial x}{\partial w} \right|_y \left. \frac{\partial w}{\partial y} \right|_z.$$

4. Ideales Boltzmann-Gas:

Die innere Energie eines idealen einatomigen Boltzmann-Gases beträgt $U = 3Nk_B T/2$, wobei die Zustandsgleichung $pV = Nk_B T$ lautet. Hierbei bezeichnet N die Zahl der Atome, T die Temperatur, p den Druck und V das Volumen des Systems.

- (a) Analysieren Sie den Carnot-Prozess für ein ideales Boltzmann-Gas. Der Carnot-Prozess setzt sich zusammen aus einer isothermen Expansion von einem Volumen V_1 zu einem Volumen V_2 bei der Temperatur T_1 , einer adiabatischen Expansion zu einer Temperatur $T_2 < T_1$, einer isothermen Kompression bei der Temperatur T_2 und einer adiabatischen Kompression zum Ausgangspunkt (T_1, V_1) . Berechnen Sie die Arbeit, die vom System in jedem Schritt geleistet wird und die Wärme, die vom Gas während der isothermen Expansion (Kompression) aufgenommen (abgegeben) wird. Berechnen Sie den Wirkungsgrad (vom System geleistete Arbeit/zugeführte Wärme) der Carnot-Maschine als Funktion von T_1 und T_2 .

Let us denote the initial state in the Carnot cycle (temperature T_1 , volume V_1) by 1. We denote by 2 the state reached by the system at the end of isothermal expansion (temperature T_1 , volume V_2). The state at the end of the adiabatic expansion (temperature $T_1 < T_2$, volume V_2') is denoted by 3, while the state at the end of isothermal compression (temperature T_2 , volume V_1') is denoted by 4.

We analyze the processes $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$ and $4 \rightarrow 3$ one by one.

- The process $1 \rightarrow 2$.

The work done by the gas in the isothermal expansion $1 \rightarrow 2$

$$W_{12} = \int_{V_1}^{V_2} p(V, T_1) dV = Nk_B T_1 \int_{V_1}^{V_2} \frac{dV}{V} = Nk_B T_1 \ln \frac{V_2}{V_1} \quad (6)$$

where we have used the equation of state to express the pressure.

Since the internal energy of the ideal gas does not depend on the volume the internal energy is constant in $1 \rightarrow 2$ process and the first law of thermodynamics gives for the heat absorbed by the gas

$$Q_{12} = W_{12} = Nk_B T_1 \ln \frac{V_2}{V_1} \quad (7)$$

- The process $2 \rightarrow 3$.

By definition of adiabatic process $Q_{23} = 0$. The work done by the system equals the absolute value of the change of its internal energy

$$W_{23} = \frac{3}{2} Nk_B (T_1 - T_2). \quad (8)$$

For the subsequent analysis we will need also the volume V_2' of the system in the state 3. In an adiabatic process the entropy is constant and, according to exercise 2a, we have

$$VT^{3/2} = \text{const.} \quad (9)$$

Thus,

$$V_2' = V_2 \left(\frac{T_1}{T_2} \right)^{3/2}. \quad (10)$$

- The process $3 \rightarrow 4$.
In full analogy with the process $1 \rightarrow 2$.

$$Q_{34} = W_{34} = Nk_B T_2 \ln \frac{V_1'}{V_2'} = Nk_B T_2 \ln \frac{V_1}{V_2} < 0. \quad (11)$$

Here we have used the relation (26) and analogous relation between V_1' and V_1 .

- The process $4 \rightarrow 1$.
In full analogy with the $2 \rightarrow 3$ process $Q_{41} = 0$ and $W_{41} = 3Nk_B(T_2 - T_1)/2$.

The efficiency of the Carnot cycle is now given by

$$\eta = \frac{W_{12} + W_{23} + W_{34} + W_{41}}{Q_{12}} = \frac{Q_{12} + Q_{34}}{Q_{12}} = \frac{T_1 - T_2}{T_1}. \quad (12)$$

- (b) *Untersuchen Sie den selben Carnot-Prozess in der umgekehrten Richtung (die isotherme Kompression des Gases findet bei der höheren Temperatur T_1 statt). Was ist der Zweck dieses Prozesses? Berechnen Sie die Wärme, die im Prozess aus dem kalten Wärmebad entnommen wird und vergleichen Sie sie mit der Arbeit, die von einer externen Maschine geleistet wird um den Prozess zu durchlaufen.*

The reversed Carnot process is used as a cooling machine. The amount of heat extracted from the cold reservoir in the reversed process can be read of from Eq. (27), where the volumes V_1 and V_2 should be exchanged

$$Q_{43} = Nk_B T_2 \ln \frac{V_2}{V_1}. \quad (13)$$

The cooling efficiency

$$\eta' = \frac{Q_{43}}{W_{12} + W_{23} + W_{34} + W_{41}} = \frac{T_2}{T_1 - T_2}. \quad (14)$$

- (c) *Berechnen Sie das Integral*

$$\Delta S = \oint \frac{\delta Q}{T},$$

über den Carnot-Prozess für das ideale Boltzmann-Gas. Dabei bezeichnet δQ die infinitesimale Menge an Wärme die vom System aufgenommen wird und das Integral läuft über den kompletten Carnot-Prozess. Interpretieren Sie das Ergebnis.

The integral

$$\Delta S = \oint \frac{\delta Q}{T} = \frac{Q_{12}}{T_1} + \frac{Q_{34}}{T_2} = 0. \quad (15)$$

The nullification of the integral is the manifestation of the fact that entropy is the proper function of the thermodynamic state.

- (d) Berechnen Sie die Entropie des Systems $S(T, V)$ als Funktion der Temperatur und des Volumens indem Sie von der inneren Energie ausgehen. Bestimmen Sie die freie Energie $F(T, V)$.

To determine the entropy $S(T, V)$ we start from the first law of thermodynamics together with the thermodynamic definition of entropy (we work with fixed number of particles)

$$dU = TdS - pdV = T \left. \frac{\partial S}{\partial T} \right|_V dT + \left(T \left. \frac{\partial S}{\partial V} \right|_T - p \right) dV \quad (16)$$

On the other hand for an ideal gas

$$dU = \frac{3}{2} Nk_B dT \quad (17)$$

Comparing Eqs. (15) and (16) we get

$$\left. \frac{\partial S}{\partial T} \right|_V = \frac{3Nk_B}{2T} \quad (18)$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \frac{p}{T} = \frac{Nk_B}{V} \quad (19)$$

Integration of Eq. (17) gives

$$S(T, V) = \frac{3}{2} Nk_B \ln T + \alpha(V) \quad (20)$$

with the unknown function $\alpha(V)$ which can be determined from Eq. (18). The final result reads

$$S(T, V) = Nk_B \ln (VT^{3/2}) + \text{const} \quad (21)$$

The unknown constant in Eq. (20) actually depends on the number of particles. If number of particles in the system is fixed the constant is irrelevant for thermodynamics and can be set to zero. We will discuss the dependence of the entropy on the number of particles in the next exercise sheet.

The free energy of the system follows now directly from $F(T, V) = U(T, V) - TS$. It is a good exercise to check that

$$dF = -SdT - pdV \quad (22)$$