

# 1 Schrödingergleichung

## 1.1 Allgemeines

“Herleitung” der SG

$$\Psi(x, t) = \Psi_0 \exp\left(\frac{i}{\hbar}(p_x x - Et)\right) \quad (\text{de Broglie})$$

$$\Rightarrow p_x \Psi(x, t) = -i\hbar \frac{\partial}{\partial x} \Psi(x, t)$$

$$\Rightarrow E \Psi(x, t) = i\hbar \frac{\partial}{\partial t} \Psi(x, t)$$

Via Korrespondenzprinzip gilt:  $E = \frac{\hat{p}^2}{2m}$

$$\Rightarrow E \Psi(x, t) = \underbrace{i\hbar \frac{\partial}{\partial t}}_E \Psi(x, t) = \underbrace{\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_H \Psi(x, t) = \frac{\hat{p}^2}{2m} \Psi(x, t)$$

Lösungsansatz (Separation der Variablen):  $\Psi(x, t) = \psi(x) \cdot \chi(t)$

$$\Leftrightarrow \psi(x) i\hbar \frac{\partial \chi(t)}{\partial t} = \chi(t) \cdot \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x)$$

$$\Leftrightarrow \frac{i\hbar \dot{\chi}(t)}{\chi(t)} = \frac{-\hbar^2 \psi''(x)}{2m \psi(x)} = E$$

$$\Rightarrow \text{ODE 1: } i\hbar \dot{\chi}(t) = E \chi(t) \Rightarrow \chi(t) = \exp\left(\frac{-i}{\hbar} E t\right)$$

$$\text{ODE 2: } \frac{-\hbar^2}{2m} \psi''(x) = E \psi(x)$$

allgemeine SG

$$\hat{H}\Psi = \hat{E}\Psi$$

allg. zeitabhängige

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-i\frac{E}{\hbar}t} = \psi(\mathbf{r}) e^{-i\omega t}$$

Lösung

Normierungsbedingung  $\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1$

Aufenthalts

$$P(x) = |\Psi(x)|^2$$

wahrscheinlichkeits-  
dichte

Delokalisation

vollständige Delokalisation eines Teilchens, falls  $P(x) = \text{konst.}$

Heisenberg'sche Un-  
schärferelation

$$\Delta x \Delta p \geq \frac{1}{2} \hbar$$

Kommutator

$$[\hat{A}, \hat{B}] \equiv \hat{A} \cdot \hat{B} - \hat{B} \cdot \hat{A} \quad \text{Falls } [\hat{A}, \hat{B}] = 0 \Rightarrow A \text{ und } B \text{ gleichzeitig messbar}$$

Operatoren

$$\hat{r} \quad \text{Orts-Operator} \quad \hat{r} = (x, y, z)^T$$

$$\hat{p} \quad \text{Impuls-Operator} \quad \hat{p} = -i\hbar \nabla = -i\hbar (\partial/\partial x, \partial/\partial y, \partial/\partial z)^T$$

$$\hat{H} \quad \text{Hamilton-Operator*} \quad \hat{H} = \frac{\hat{p}^2}{2m} + E_p(\hat{r}) = -\frac{\hbar^2}{2m} \nabla^2 + E_p(\hat{r})$$

\* für ein freies Teilchen im Potentialfeld

## 1.2 allgemeine Lösung für SG mit Potential

zeitunabhängige Schrödingergleichung (1-dim)	$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + E_{pot}(x)\psi(x) = E\psi(x)$
Lösung der zeitun- abhängigen SG	$\underbrace{\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{=:-C} \psi(x) = (E - E_{pot})\psi(x)$ <p>Ansatz: <math>\psi(x) = e^{ikx}</math></p> $\Rightarrow Ck^2 \cdot e^{ikx} = (E - E_{pot}) \cdot e^{ikx}$ $\Leftrightarrow k = \pm \sqrt{\frac{E - E_{pot}}{C}} = \pm \sqrt{\frac{(E - E_{pot}) \cdot 2m}{\hbar^2}}$ $\Rightarrow \psi_k(x) = A_k e^{ikx} + B_k e^{-ikx}$
Lösung für $E_{pot} = 0$	$\psi_1(x) = A e^{ikx} + B e^{-ikx} \quad k^2 = \frac{2mE}{\hbar^2}$
Lösung für $E < E_{pot}$	$\psi_2(x) = C e^{-\alpha x} + D e^{\alpha x} \quad \alpha^2 = \frac{2m}{\hbar^2} (E_{pot} - E)$
Lösung für $E > E_{pot}$	$\psi_3(x) = E e^{i\alpha' x} + F e^{-i\alpha' x} \quad \alpha'^2 = \frac{2m}{\hbar^2} (E - E_{pot})$
Stetigkeitsbedingungen	$\psi_i = \psi_j \quad \text{und} \quad \frac{\partial \psi_i}{\partial x} = \frac{\partial \psi_j}{\partial x} \quad \text{für } x = 0$
Teilchenstromdichte	$v A ^2 \quad v = \frac{p}{m} = \frac{\hbar k}{m}$
Transmissionskoeffizient	$\frac{k_C  C ^2}{k_A  A ^2}$
Reflexionskoeffizient	$\frac{k_B  B ^2}{k_A  A ^2}$
	Bedeutung von A,B,C wie unten Bsp. Potentialstufe
	$R + T = 1$

## 1.3 Spezifische Probleme

### 1.3.1 Potentialstufe

$E_{pot}$	$E_{pot} = \begin{cases} 0 & x < 0 \text{ (Bereich I)} \\ E_0 & x \geq 0 \text{ (Bereich II)} \end{cases}$
allg. Lösung ( $E < E_{pot}$ )	$\psi_I(x) = Ae^{ikx} + Be^{-ikx} \quad k^2 = \frac{2mE}{\hbar^2}$ $\psi_{II}(x) = Ce^{-\alpha x} + De^{\alpha x} \quad \alpha^2 = \frac{2m}{\hbar^2}(E_{pot} - E)$
Stetigkeitsbedingungen	$\psi_I _{x=0} = \psi_{II} _{x=0} \quad \text{und} \quad \left. \frac{\partial \psi_I}{\partial x} \right _{x=0} = \left. \frac{\partial \psi_{II}}{\partial x} \right _{x=0}$
Randbedingungen	$\lim_{x \rightarrow \infty} \psi_{II} < \infty$ (vgl. Normierungsbedingung)
spez. Lösung	$D = 0 \text{ (aus RB)}$ $B = \frac{(ik + \alpha)A}{ik - \alpha} \quad C = \frac{2ikA}{ik - \alpha}$
allg. Lösung ( $E > E_{pot}$ )	$\psi_I(x) = Ae^{ikx} + Be^{-ikx} \quad k^2 = \frac{2mE}{\hbar^2}$ $\psi_{II}(x) = Ee^{i\alpha'x} + Fe^{-i\alpha'x} \quad \alpha'^2 = \frac{2m}{\hbar^2}(E - E_{pot})$
spez. Lösung	$F = 0 \text{ (aus RB)}$ $B = \frac{(k - \alpha')A}{k + \alpha'} \quad E = \frac{2kA}{k + \alpha'}$
Transmissionskoeffizient	$\frac{v_{II} E ^2}{v_I A ^2} = \frac{\alpha'}{k} \left( \frac{2k}{k + \alpha'} \right)^2$
Reflexionskoeffizient	$\frac{v_I B ^2}{v_I A ^2} = \left( \frac{k - \alpha'}{k + \alpha'} \right)^2$

### 1.3.2 Potentialtopf (1D)

$E_{pot}$	$E_{pot} = \begin{cases} 0 & 0 < x < a \text{ Bereich I} \\ \infty & \text{sonst (Bereich II)} \end{cases}$
allg. Lösung	$\psi_I(x) = Ae^{ikx} + Be^{-ikx} \quad k^2 = \frac{2mE}{\hbar^2}$ $\psi_{II}(x) = 0$
Randbedingungen	$\psi_I(x=0) = \psi_I(x=a) = 0$
spez. Lösung	$\psi_I(x) = \sqrt{\frac{2}{a}} \sin(kx) \quad k = \frac{n\pi}{a} \quad \Rightarrow \lambda = \frac{2\pi}{k}$
Energieeigenwert	$E = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$

### 1.3.3 Potentialtopf (3D)

SG in 3 Dimensionen	$\psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z) \quad \psi_{1,2,3} \text{ sind Wellenfkt. im 1-dim. Kasten}$
Particle in a cube	$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_1\pi}{a}x\right) \sin\left(\frac{n_2\pi}{a}y\right) \sin\left(\frac{n_3\pi}{a}z\right)$ $E = \frac{\hbar^2 \pi^2}{2ma^2} (n_1^2 + n_2^2 + n_3^2)$

### 1.3.4 Der Tunneleffekt

Potentialstufe	$V(x) = \begin{cases} 0 & x < 0 & \text{Bereich A} \\ V & 0 \leq x \leq D & \text{Bereich B} \\ 0 & D < x & \text{Bereich C} \end{cases}$
SG	$\hat{H}\Psi_A(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_A(x) = E\Psi_A(x)$ $\hat{H}\Psi_B(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_B(x) + V\Psi_B(x) = E\Psi_B(x)$ $\hat{H}\Psi_C(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi_C(x) = E\Psi_C(x)$
Lösungen	$\Psi_A(x) = Ae^{ikx} + Be^{-ikx} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$ $\Psi_B(x) = A'e^{ik'x} + B'e^{-ik'x} \quad k' = \sqrt{\frac{2m(E-V)}{\hbar^2}} = i\kappa$ $\Psi_C(x) = A''e^{ikx} + B''e^{-ikx}$
Randbedingungen	$\Psi_A(0) = \Psi_B(0)$ $\frac{d}{dx}\Psi_A(0) = \frac{d}{dx}\Psi_B(0)$ $\Psi_B(D) = \Psi_C(D)$ $\frac{d}{dx}\Psi_B(D) = \frac{d}{dx}\Psi_C(D)$ $B'' = 0 \text{ (keine reflektierte Komponente rechts der Barriere erlaubt)}$

Letztlich hat man nur 5 Randbedingungen für 6 Unbekannte. Man kann also lediglich die Tunnelwahrscheinlichkeit  $P_T = \frac{|A''|^2}{|A|^2}$  angeben, indem man  $A''$  durch  $A$  ausdrückt.  $P_T = \frac{4E(V-E)}{4E(V-E) + V^2 \sinh^2(\kappa D)}$  Grundsätzlich wird die Tunnelwahrscheinlichkeit klein für breite Barrieren ( $D \rightarrow \infty$ ), hohe Barrieren ( $V \rightarrow \infty$ ) und grosse Massen  $m$

### 1.3.5 QM harmonischer Oszillator

Der QM harmonische Oszillator wird verwendet, um bspw. molekulare Vibrationsbewegungen zu modellieren.

SG	$\hat{H}\Psi = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right) \Psi = E\Psi$
Eigenwerte	$E_n = \left( n + \frac{1}{2} \right) \hbar\omega$
Eigenfunktionen	$\Psi_n = N_n H_n(\sqrt{\alpha}x) e^{-\alpha x^2/2} \quad \alpha = \frac{\sqrt{mk}}{\hbar} \quad H_n : \text{Hermite-Polynome}$

### 1.3.6 3D QM harm. Osz.

Eigenwerte	$E_n = \left( n_x + n_y + n_z + \frac{3}{2} \right) \hbar\omega$
Eigenfunktionen	$\Psi_n = \Psi_{n_x} \cdot \Psi_{n_y} \cdot \Psi_{n_z}$

## 1.4 Weiteres

Postulat # 2 der QM	Einzig mögliches Messresult einer physik. Grösse $A(\mathbf{r}, \mathbf{p})$ ist ein Eigenwert $a_n$ von Operator $\hat{A}(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \Rightarrow \hat{A}\psi_n = a_n\psi_n$
Postulat # 3 der QM	WSK dass $a_n$ Messresultat ist, ist $ c_n ^2$ , falls Zustand des Systems: $\Phi = \sum_n c_n \psi_n$
Erwartungswert	$\langle A \rangle = \int \Psi^* \hat{A} \Psi dx dy dz$
Beispiel	(1-dim) Energieerwartungswert: $\langle E_{kin} \rangle = \int \Psi^* \hat{H} \Psi dx$

## 2 Klassische Mechanik

### 2.1 Newton'scher Formalismus

Newton BGL	$m\ddot{\vec{x}} = \sum_{i=1}^N \vec{F}_i$
pot. Energie	$\vec{F}_i = -\vec{\nabla}_i E_{pot}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
kinet. Energie	$E_{kin} = \sum_{i=1}^N \frac{1}{2} m_i \dot{\vec{r}}_i^2 = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i}$

Obige Gleichungen nur in kartesischen Koordinaten erfüllt!

### 2.2 Lagrange'scher Formalismus

Unabhängig vom Koordinatensystem!	
verallgemeinerte Ort-skoordinaten	$\vec{q}^M = \{q_1, q_2, \dots, q_M\}$
verallgemeinerte Geschwindigkeiten	$\dot{\vec{q}}^M = \{\dot{q}_1, \dot{q}_2, \dots, \dot{q}_M\}$
Lagrangefunktion	$L(\vec{q}^M, \dot{\vec{q}}^M) := E_{kin}(\vec{q}^M, \dot{\vec{q}}^M) - E_{pot}(\vec{q}^M, \dot{\vec{q}}^M)$
Lagrange BGL	$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) = \frac{\partial L}{\partial q_i}$

### 2.3 Hamilton'scher Formalismus

konjugiert verallgemeinerter Impuls	$\vec{p}_i \equiv \frac{\partial L(\vec{q}^M, \dot{\vec{q}}^M)}{\partial \dot{q}_i}$
Hamiltonfunktion	$H(\vec{q}^M, \vec{p}^M) := \sum_{i=1}^M p_i \dot{q}_i - L(\vec{q}^M, \dot{\vec{q}}^M) = E_{kin}(\vec{q}^M, \vec{p}^M) + E_{pot}(\vec{q}^M, \vec{p}^M) = E_{Tot}$
Hamilton BGL	$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$

## 2.4 Zwangsbedingungen

Holonom	$C(\vec{q}^M) = 0$ Die Zwangsbedingung ist nur von Ortskoordinaten und Zeit abhängig.
Nicht-holonom	Die Zwangsbedingung ist zusätzlich abhängig von $\dot{\vec{q}}^M$
Implizite Bedingung	Sei z.B. $\dot{R} = 0$ (Kreisbahn). Dann ist $E_{kin} = \frac{1}{2}m \left[ 0 + R^2 \dot{\Theta}^2 \right]$ s. Skript 2.Woche S.10
Lagrange-Multiplikatoren	<p>Explizite Zwangsbedingung <math>C(\vec{q}^M) = 0</math></p> <p>neue Lagrangefunktion <math>L_{cons}(\vec{q}^M, \dot{\vec{q}}^M) = L(\vec{q}^M, \dot{\vec{q}}^M) + \lambda C(\vec{q}^M)</math></p> <p>Kraft der Zwangsbedingung <math>\frac{d^2}{dt^2} C(\vec{q}^M) = 0</math></p> <p><math>\Rightarrow</math> Lösung durch Anwendung der L-BGL auf <math>L_{cons}</math> und Einsetzen der Kraft der Zwangsbedingung</p>
Gauss-Prinzip	$\sum_{i=1}^M \frac{F_{Ci}^2}{2m_i} = MIN$ $\sum_{i=1}^M \frac{F_{Ci} \delta F_{Ci}}{m_i} = 0$ <ol style="list-style-type: none"> <li>1. Aus Zwangsbedingung Gleichung für <math>\ddot{\vec{r}}</math> herleiten.</li> <li>2. In <math>m\ddot{\vec{r}} = F_C = F_C + \delta F_C</math> einsetzen.</li> <li>3. Mit Lagrange-Multiplikator auf etwas in der Form <math>F_C = \lambda \vec{r}</math> kommen.</li> </ol>

# 3 Statistical Mechanics

## 3.1 Canonical Ensemble

Constants	$N, V, T$
Fluctuations	$E$
Distribution	A distribution of $m_i$ systems in quantum states $\psi_i$ with Energy $E_i$ is denoted as: $(m_1, m_2, \dots) \equiv \{m\}$ $\sum_i m_i = M \quad \sum_i m_i E_i = E_{tot}$
# Distributions (Permutations)	$\Omega(\{m\}) = \frac{M!}{\prod_i m_i!}$
Probability of quantum state $\psi_i$	$P_i = \frac{m_i}{M}$
Most probable distribution $m^*$	$\lim_{M \rightarrow \infty} \ln(\Omega(\{m^*\})) = \ln \left( \sum_{\{m\}} \Omega(\{m\}) \right)$ $- \sum_i P_i \ln(P_i) = MAX;$ $\sum_i P_i = 1;$ $\sum_i P_i E_i = \frac{E_{tot}}{M} = \langle E \rangle$ <div> <math display="block">P_i = \frac{1}{Z(N, V, T)} e^{-\beta E_j}</math> </div>
Canonical Partition Function	<div> <math display="block">Z(N, V, T) = \sum_j e^{-\beta E_j}</math> </div>
$\beta$ in an ideal gas	$\beta = \frac{1}{k_B T}$ $k_B$ is Boltzmann's Constant
Energy	$\langle E \rangle = - \left( \frac{\partial \ln Z(N, V, T)}{\partial \beta} \right)_{N, V}$
Pressure	$\langle p \rangle = \frac{1}{\beta} \left( \frac{\partial \ln Z(N, V, T)}{\partial V} \right)_{N, \beta}$
Uncertainty Principle	Shannon's information theory says, that $-\sum_i P_i \log P_i$ is the value for uncertainty If observer knows nothing about a system but the average energy, then his uncertainty
Ideal Gas Partition Function	$Z_{id} = V \left( \frac{m}{2\beta\pi\hbar^2} \right)^{\frac{3}{2}}$

## 3.2 Thermodynamical quantities and relations

Entropy	$S = -k_B \sum_i P_i \ln P_i$ $S = \frac{E}{T} + k_B \ln Z(N, V, T)$ $S = - \left( \frac{\partial F}{\partial T} \right)_V$
Helmholtz Free Energy	$F = E - TS = -k_B T \ln Z(N, V, T)$
Energy	$E = \langle E \rangle = -T \left( \frac{\partial F}{\partial T} \right)_V + F$
Gibbs Free Energy	$G = F + pV$

## 3.3 Isothermal-isobaric Ensemble

Constants	$N, P, T$
Fluctuations	$E, V$
System characterisation	<p>Various Volumes <math>V_k</math></p> <p>each with states <math>\Psi_{ki}</math></p> <p>and energies <math>E_{ki}</math></p>
Probability	$P_{ki}$ = probability that system is in state $\Psi_{ki}$
Most probable distribution	$- \sum_k \sum_i P_{ki} \ln(P_{ki}) = MAX;$ $\sum_k \sum_i P_{ki} = 1$ $\sum_k \sum_i P_{ki} E_{ki} = \langle E \rangle$ $\sum_k \sum_i P_{ki} V_k = \langle V \rangle$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 5px auto;"> <math display="block">P_{ki} = \frac{1}{Z(N, p, T)} e^{-\beta E_{ki} - \gamma V_k}</math> </div>
Isothermal-isobaric Partition Function	$Z(N, p, T) = \sum_k \sum_i e^{-\beta E_{ki} - \gamma V_k} = \sum_k Z(N, V_k, T) e^{-\gamma V_k}$
$\beta, \gamma$	$\beta = \frac{1}{k_B T} \quad \gamma = \frac{p}{k_B T}$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 5px auto;"> <math display="block">Z(N, p, T) = \int_0^\infty \sum_i e^{-[E_i(V) + pV]/k_B T} dV = \int_0^\infty \sum_i e^{-H_i(V)/k_B T} dV</math> </div>
Enthalpy	$H = E + pV$ $\langle H \rangle = - \left( \frac{\partial \ln Z(N, p, T)}{\partial \beta} \right)_{N, p}$
Volume	$V_i = \frac{\partial H_i}{\partial p} \quad \langle V \rangle = - \frac{1}{\beta} \left( \frac{\partial \ln Z(N, p, T)}{\partial p} \right)_{N, \beta}$



### 3.4 Thermodynamical quantities and relations

Entropy	$S = -k_B \int_0^\infty \sum_i P_i(V) \ln P_i(V) dV$ $S = \frac{H}{T} + k_B \ln Z(N, p, T)$
Free Enthalpy	$G = H - TS = -k_B T \ln Z(N, p, T)$
Other relations	$H = \langle H \rangle = -T \left( \frac{\partial G}{\partial T} \right)_p + G$ $S = - \left( \frac{\partial G}{\partial T} \right)_p$ $V = \langle V \rangle = \left( \frac{\partial G}{\partial p} \right)_T$ $dG = -SdT + Vdp$

### 3.5 Grand-Canonical Ensemble

Constants	$\mu, V, T$ $\mu$ = Chemisches Potential
Fluctuations	$E, N$
System characterisation	Various particle Numbers $N$ each with states $\Psi_{Ni}$ and energies $E_{Ni}$
Probability	$P_{Ni}$ = probability that system is in state $\Psi_{Ni}$
Most probable distribution	$-\sum_N \sum_i P_{Ni} \ln(P_{Ni}) = MAX;$ $\sum_N \sum_i P_N = 1$ $\sum_N \sum_i P_{Ni} E_{Ni} = \langle E \rangle$ $\sum_N \sum_i P_{Ni} N = \langle N \rangle$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 5px auto;"> <math display="block">P_{Ni} = \frac{1}{Z(\mu, V, T)} e^{-\beta E_{Ni} - \gamma N}</math> </div>
Grand Canonical Partition Function	$Z(\mu, V, T) = \sum_N \sum_i e^{-\beta E_{Ni} - \gamma N} = \sum_N Z(N, V, T) e^{-\gamma N}$
$\beta, \gamma$	$\beta = \frac{1}{k_B T} \quad \gamma = \frac{-\mu}{k_B T}$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 5px auto;"> <math display="block">Z(\mu, V, T) = \sum_N \sum_i e^{-[E_{Ni} - \mu N]/k_B T} = \sum_N e^{\beta \mu N} Z(N, V, T)</math> </div>
Particle Number	$\langle N \rangle = k_B T \left( \frac{\partial \ln Z(\mu, V, T)}{\partial \mu} \right)_{\beta, V}$

### 3.6 Thermodynamical quantities and relations

Entropy	$S = -k_B \sum_N \sum_i P_{Ni} \ln P_{Ni}$ $S = \frac{E - \mu N}{T} + k_B \ln Z(\mu, V, T) = \frac{E - \mu N + pV}{T}$
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### 3.7 Fluctuations

Average of a distribution of a quantity Q	$\langle Q \rangle = \sum_i P_i Q_i$
Variance	$\sigma_Q^2 = \langle Q^2 \rangle - \langle Q \rangle^2$
Standard deviation	$\sigma_Q = \sqrt{\sigma_Q^2}$
Canonical Ensemble	<p>Fluctuation of E</p> $\frac{\partial Z(N, V, T)}{\partial \beta} = \dots = -\langle E \rangle Z(N, V, T)$ $\frac{\partial \ln Z(N, V, T)}{\partial \beta} = \dots = -\langle E \rangle$ $\frac{\partial^2 \ln Z(N, V, T)}{\partial \beta^2} = \dots = \langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 \left( \frac{\partial E}{\partial T} \right)_V = k_B T^2 C_V$ <p><math>C_V</math> : Heat capacity of system at constant volume</p>
Isothermal-isobaric Ensemble	<p>Fluctuation of V</p> $\frac{\partial Z(N, p, T)}{\partial p} = \dots = -\beta \langle V \rangle Z(N, p, T)$ $\frac{\partial \ln Z(N, p, T)}{\partial p} = \dots = -\beta \langle V \rangle$ $\frac{\partial^2 \ln Z(N, p, T)}{\partial p^2} = \dots = \beta \langle V^2 \rangle - \beta \langle V \rangle^2 = -k_B T \left( \frac{\partial V}{\partial p} \right)_T = k_B T V \kappa_T$ <p><math>\kappa_T</math> : Isothermal compressibility</p>
Grand Canonical Ensemble	<p>Fluctuation of N</p> $\frac{\partial Z(\mu, V, T)}{\partial \mu} = \dots = -\beta \langle N \rangle Z(\mu, V, T)$ $\frac{\partial \ln Z(\mu, V, T)}{\partial \mu} = \dots = -\beta \langle N \rangle$ $\frac{\partial^2 \ln Z(\mu, V, T)}{\partial \mu^2} = \dots = \beta \langle N^2 \rangle - \beta \langle N \rangle^2 = N \rho k_B T \kappa_T$ <p><math>\rho = N/V</math> : Particle Density</p>

## 4 Non interacting Many-particle systems

### 4.1 Distinguishable particles

Canonical partition function for N distinguishable particles	$Z(N, V, T) = \sum_j e^{-\beta E_j} = \dots = [z(V, T)]^N$	all particles with same energy state
Examples for dist. particles	Atoms in a solid, Atoms in a macromolecule	

## 4.2 Indistinguishable particles

Examples for indist. part. Gas molecules, electrons in an atom, photons,...

Fermions All particles with spin  $\frac{1}{2}$ : Protons, Neutrons, Electrons,...

Wave function  $\Psi$  must be anti-symmetric

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} (\Psi_{k_1}(1)\Psi_{k_2}(2) - \Psi_{k_1}(2)\Psi_{k_2}(1))$$

$k_1 = k_2 \Rightarrow \Psi(1, 2) = 0$  Two particles cannot occupy the same state (Pauli)

Bosons All particles with integer spin: Photons, phonons, mesons

Wave function  $\Psi$  must be symmetric

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} (\Psi_{k_1}(1)\Psi_{k_2}(2) + \Psi_{k_1}(2)\Psi_{k_2}(1))$$

Many particles may occupy the same state

Indistinguishability No set of particles may be a permutation of another one

Boltzmann Limit If all  $N$  particles are in different states with different energies, we can sum the CPF as for indist. particles and divided by  $N!$

Boltzmann Limit is valid if the number of energy-levels is vastly larger than the number of particles

Then it's unlikely that two particles (bosons) occupy the same energy-level

## 4.3 Boltzmann Statistics

CPF in Boltzmann Limit  $Z(N, V, T) = \frac{1}{N!} [z(V, T)]^N$

Number of particle states with energies  $\leq \epsilon$   $n(\epsilon) = \frac{1}{8} \frac{4}{3} \pi R^3 = \frac{1}{6} \pi \left( \frac{2ma^2}{\pi^2 \hbar^2} \epsilon \right)^{\frac{3}{2}}$   $\epsilon = \frac{3}{2} k_B T$   $R^2 = n_x^2 + n_y^2 + n_z^2$

Boltzmann Statistics  $Z(N, V, T) = \frac{1}{N!} [z(V, T)]^N$  applicable if  $n(\epsilon) \gg N$   
 $\Leftrightarrow \frac{\pi}{6} \left( \frac{12mk_B T}{h^2} \right)^{\frac{3}{2}} \gg \frac{N}{a^3} = \frac{N}{V} = \rho$

B.Stats valid for: large mass  $m$ , high temperature  $T$ , low density  $\rho$

Examples Liquid Neon at 27K, liq. Argon at 86K; not Boltzmann: Electrons in a metal at 300K

Energy of  $N$ -particle system  $\langle E \rangle = - \left( \frac{\partial \ln Z(N, V, T)}{\partial \beta} \right)_{N, V} = \dots = N \langle \epsilon \rangle$

Average energy of a particle  $\langle \epsilon \rangle = \frac{\sum_k \epsilon_k e^{-\beta \epsilon_k}}{\sum_k e^{-\beta \epsilon_k}} = \frac{\sum_k \epsilon_k e^{-\beta \epsilon_k}}{z(V, T)}$

Probability of a particle for being in state  $k$   $\pi_k = \frac{e^{-\beta \epsilon_k}}{\sum_k e^{-\beta \epsilon_k}}$

## 4.4 Fermi-Dirac, Bose-Einstein partition functions

	Volume: $V$
	Number of particles: $N$
System	Energy levels: $E_j$
	1-particle energy levels: $\epsilon_k$
	Number of particles in a quantum state $\Psi_k : m_k$
	$E_j = \sum_k m_k \epsilon_k; N = \sum_k m_k$
Grand-canonical partition function	$Z(\mu, V, T) = \sum_{N=0}^{\infty} \sum_j e^{-\beta(E_j - \mu N)} = \dots = \prod_k \sum_{m_k} (e^{-\beta(\epsilon_k - \mu)})^{m_k}$
Fermi-Dirac partition function	$m_k = 0 \vee 1 \Rightarrow Z_{FD}(\mu, V, T) = \prod_k [1 + e^{-\beta(\epsilon_k - \mu)}]$
Bose-Einstein partition function	$m_k = 0, 1, 2, \dots \Rightarrow Z_{BE}(\mu, V, T) = \prod_k [1 - e^{-\beta(\epsilon_k - \mu)}]^{-1}$
Combined partition function	$Z_{FD/BE}(\mu, V, T) = \prod_k [1 \pm e^{-\beta(\epsilon_k - \mu)}]^{\pm 1}$

## 4.5 Fermi-Dirac Statistics

Avg. Number of particles	$\langle N \rangle = \frac{1}{\beta} \left( \frac{\partial \ln Z_{FD}(\mu, V, T)}{\partial \mu} \right)_{V, T} = \dots = \sum_k (e^{+\beta(\epsilon_k - \mu)} + 1)^{-1} = \sum_k \langle m_k \rangle$
$\langle m_k \rangle$	$\langle m_k \rangle \approx e^{-\beta(\epsilon_k - \mu)} \quad \langle m_k \rangle \ll 1 \text{ (Boltzmann Limit)}$
Avg. Energy	$\langle E \rangle = \sum_k \langle m_k \rangle \epsilon_k = \sum_k \frac{\epsilon_k}{e^{+\beta(\epsilon_k - \mu)} + 1}$
Pressure	$pV = k_B T \ln Z_{FD}(\mu, V, T) = k_B T \sum_k \ln (1 + e^{-(\epsilon_k - \mu)/k_B T})$

## 4.6 Bose-Einstein Statistics

Avg. Number of particles	$\langle N \rangle = \frac{1}{\beta} \left( \frac{\partial \ln Z_{BE}(\mu, V, T)}{\partial \mu} \right)_{V, T} = \dots = \sum_k (e^{+\beta(\epsilon_k - \mu)} - 1)^{-1} = \sum_k \langle m_k \rangle$
$\langle m_k \rangle$	$\langle m_k \rangle \approx e^{-\beta(\epsilon_k - \mu)}$
Avg. Energy	$\langle E \rangle = \sum_k \langle m_k \rangle \epsilon_k = \sum_k \frac{\epsilon_k}{e^{+\beta(\epsilon_k - \mu)} - 1}$
Pressure	$pV = k_B T \ln Z_{BE}(\mu, V, T) = -k_B T \sum_k \ln (1 - e^{-(\epsilon_k - \mu)/k_B T})$

## 4.7 Maxwell distribution

Avg. kinetic energy	$\langle \epsilon \rangle = \frac{3}{2} k_B T$
Avg. size of velocity	$\langle v \rangle = \left( \frac{8 k_B T}{m \pi} \right)^{\frac{1}{2}}$
Root mean square	$\langle v^2 \rangle^{\frac{1}{2}} = \left( \frac{3 k_B T}{m} \right)^{\frac{1}{2}}$

Ideal Gas

Avg. kinetic energy	$\langle E \rangle = N \frac{3}{2} k_B T$
Heat capacity	$\frac{dE}{dT} = \frac{3}{2} N k_B$
Free energy	$F = -N k_B T \left( \frac{3}{2} \ln \left( \frac{2 \pi m k_B T}{h^2} \right) - \ln \left( \frac{N}{V} \right) + 1 \right)$
Entropy	$S = N k_B \left( \frac{3}{2} \ln \left( \frac{2 \pi m k_B T}{h^2} \right) - \ln \left( \frac{N}{V} \right) + \frac{5}{2} \right)$

## 4.8 Distinguishable vs. indistinguishable particles

Ideal Gas	$Z_d(N, V, T) = [z(V, T)]^N$	$Z_i(N, V, T) = \frac{1}{N!} [z(V, T)]^N$
Free Energy	$F_d = -N k_B T (\ln z(V, T))$	$F_i = -N k_B T (\ln z(V, T) - \ln N + 1)$
Entropy	$S_d = N k_B (\ln z(V, T) + \frac{3}{2})$	$S_i = N k_B (\ln z(V, T) + \frac{3}{2} - \ln N + 1)$
Pressure	$P_d = N k_B T / V$	$P_i = N k_B T / V$

## 5 Computer Simulation

Generally, we want to solve the many-particle problem for a **liquid state of macromolecules by using classical mechanics**.

Van der Waals interaction between atoms

1. Short range repulsion due to electron overlap.
2. Long range attraction due induced dipoles.

Lennard-Jones (6,12) potential

A good approximation for van der Waals interaction is the L-J 12-6 function

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

$$V(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

$\sigma$  = Collision diameter     $\epsilon$  = well depth

$$r_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$

Force on atom  $i$  due to atom  $j$

$$f_{x_i}(r_{ij}) = -\frac{\partial}{\partial x_i} V(r_{ij}) = -4\epsilon \left[ -12 \left( \frac{\sigma}{r_{ij}} \right)^{12} + 6 \left( \frac{\sigma}{r_{ij}} \right)^6 \right] \frac{x_{ij}}{r_{ij}^2}$$

Covalent bond interaction

Approximation is harmonic function:

$$V(\vec{r}(t), K_n^b, b_n^0) = \sum_n \frac{1}{2} K_n^b (b_n(t) - b_n^0)^2$$

$$b_n = r_{ij}$$

Newton's equation of motion

$$m \frac{dv(t)}{dt} = f(x(t)) = -\frac{\partial}{\partial x} V(x(t))$$

$$\frac{dx(t)}{dt} = v(t)$$

Leap-Frog integration

Integration of Newton's equation of motion

$$v\left(t_n + \Delta \frac{t}{2}\right) = v\left(t_n - \Delta \frac{t}{2}\right) + \frac{f(x(t_n))}{m} \Delta t + O((\Delta t)^3)$$

$$x(t_n + \Delta t) = x(t_n) + v\left(t_n + \Delta \frac{t}{2}\right) \Delta t + O((\Delta t)^3)$$

Periodic boundary conditions

### 5.1 Metropolis Monte-Carlo Method

Metropolis Monte-Carlo method can be used to evaluate multidimensional integrals.

Häufig ist der Raum  $\Omega$  so groß, dass die Summation nicht vollständig durchgeführt werden kann. Stattdessen erzeugt man nun eine Markow-Kette  $x_1, x_2, x_3, \dots$  von Zuständen in  $\Omega$ , deren Häufigkeit wie das vorgegebene Gewicht  $P(x)$  verteilt ist. Bereiche des Raumes  $\Omega$  mit hohem Gewicht sollen also häufiger in der Markow-Kette vertreten sein als Bereiche mit niedrigem Gewicht. (Importance Sampling) Gelingt dies, so lassen sich die Erwartungswerte einfach als arithmetisches Mittel der Größe  $\mathcal{A}$  zu diesen Zuständen der Markow-Kette berechnen, also als

$$\langle \mathcal{A} \rangle \approx \frac{1}{N} \sum_{i=1}^N \mathcal{A}(x_i).$$

Man muss sicherstellen, dass die Markow-Kette tatsächlich den gesamten Raum  $\Omega$  bedeckt und nicht nur einen Teil des Raumes abtastet. Man sagt, der Algorithmus muss ergodisch sein.

## Algorithm

For large number of steps, do

1. Make a step  $\Delta\vec{r}$  in configuration space:  $\vec{r}_{n+1}^N = \vec{r}_n^N + \Delta\vec{r}$  (This is the Markov-Chain)
2. Calculate the change in energy  $\Delta E = E_{n+1} - E_n$
3. **if**  $\Delta E \leq 0$  **then**  
    Accept new configuration  $\vec{r}_{n+1}^N$   
**else if**  $\exp\left(\frac{-\Delta E}{k_B T}\right) > \text{random number} \in [0, 1]$  **then**  
    Accept  $\vec{r}_{n+1}^N$   
**else**  
     $\vec{r}_{n+1}^N = \vec{r}_n^N$   
**end if**

## Remarks

- It is better to perform N 1-particle moves rather than 1 N-particle move.
- If  $T \rightarrow \infty$  then  $\exp\left(\frac{-\Delta E}{k_B T}\right) \rightarrow 1$  (For high temperature, change of configuration is more likely)

## 5.2 Replica-exchange simulation

Replica-exchange is done to improve metropolis method. You get a very robust ensemble. Essentially, one runs N copies of the system, randomly initialized, at different

a ) temperatures

b ) Hamiltonians

Then, based on the Metropolis criterion one exchanges configurations at different temperatures or Hamiltonians.

$$\Delta_T = \frac{H(\vec{r}_{s2}) - H(\vec{r}_{s1})}{\frac{1}{k_B T_{s1}} - \frac{1}{k_B T_{s2}}} \text{ for a)}$$

$$\Delta_H = \frac{(H(\vec{r}_{s2}; \lambda_{s1}) - H(\vec{r}_{s1}; \lambda_{s1})) - (H(\vec{r}_{s2}; \lambda_{s2}) - H(\vec{r}_{s1}; \lambda_{s2}))}{k_B T} \text{ for b)}$$

## 5.3 Stochastic Dynamics

Langevin-Equation	$m_i \dot{v}_i(t) = f_i(t) - m_i \gamma_i v_i(t) + f_i^{st}(t)$ $\gamma_i$ = Friction coefficient (of solvent) $f_i^{st}$ = Stochastic force (random punches of solvent) $\langle f_i^{st}(t) \rangle = 0$ $P(f_i^{st})$ ist standard-normalverteilt.
Solution of Langevin-Eq	$v(t) = v_0 e^{-\gamma t} + e^{-\gamma t} \int_0^t e^{\gamma t'} \frac{f^{st}(t')}{m} dt'$
Average velocity	$\langle v(t) \rangle = v_0 e^{-\gamma t} \quad \lim_{t \rightarrow \infty} \langle v(t) \rangle = 0$
Average squared velocity	$\langle v^2(t) \rangle = \frac{3k_B T}{m} + \left( v_0^2 - \frac{3k_B T}{m} \right) e^{-2\gamma t} \quad \lim_{t \rightarrow \infty} \langle v^2(t) \rangle = \frac{3k_B T}{m}$
Average $E_{kin}$	$\langle \frac{1}{2} m v^2(t) \rangle = \frac{3k_B T}{2} + \left( \frac{1}{2} m v_0^2 - \frac{3k_B T}{2} \right) e^{-2\gamma t}$
Probability distribution	<i>Gaussian</i>
Average displacement	$\langle r(t) - r_0 \rangle = v_0 \frac{1}{\gamma} (1 - e^{-\gamma t})$
Average square displacement	$\lim_{t \rightarrow 0} \langle (r(t) - r_0)^2 \rangle \Rightarrow r(t) = r_0 + v_0 t$  $\lim_{t \rightarrow \infty} \langle (r(t) - r_0)^2 \rangle = \lim_{t \rightarrow \infty} 6Dt \quad D = \frac{k_B T}{m\gamma} \quad \text{Diffusion constant}$

## 6 Thermodynamic Boundary Conditions

Coupling to an external temperature or pressure bath. (Measure T and P rather than E and V)

Coupling	temperature	by scaling	velocities
	pressure	by scaling	positions
Intensive vs. extensive variables	Intensive variable		Extensive variable
	independent of system size		
	Temperature		Energy
	Pressure		Volume
	Chemical Potential ( $\mu$ )		Particle Number
Keeping intensive variables constant	1. Weak coupling methods		
	2. Extended system methods		
	3. Stochastic methods		



## 6.1 Constant Temperature

### 6.1.1 Weak coupling method (Heat bath)

Coupling equation	$\frac{dT(t)}{dt} = \frac{1}{\tau_T} [T_0 - T(t)]$
Relation $T \leftrightarrow v_i$	$E_{kin}(t) = \sum_{i=1}^N \frac{1}{2} m_i v_i^2(t) = \frac{1}{2} N_{df} k_B T(t)$
Velocity scaling	$v_{new} = \lambda v_{old}$
Modified eqn of motion	$m_i \frac{dv_i(t)}{dt} = m_i \lambda(t) v_i(t)$
	$\lambda = 1 + \frac{c_V^{df}}{k_B} \frac{\Delta t}{\tau_T} \left[ \frac{T_0}{T(t)} - 1 \right]$
	$\tau > 0.1 \text{ should be o.k.}$
Energy distribution in L-J Fluid	$\sigma_{E_{tot}}^2 = k_B T^2 C_V N^{-2}$

### 6.1.2 Stochastic method

Collision model	$\langle T \rangle = T_0$
Langevin model	$m_i \frac{dv_i(t)}{dt} = f_i(t) - m_i \gamma_i v_i(t) + f_i^{st}(t)$

## 6.2 Constant Pressure

### 6.2.1 Weak coupling method

Coupling equation	$\frac{dP(t)}{dt} = \frac{1}{\tau_P} [P_0 - P(t)]$
Virial	$W \equiv -\frac{1}{2} \sum_{i < j}^N \vec{r}_{ij} \cdot \vec{f}_{ij}$
Relation $P \leftrightarrow x_i, V$	$P(t) = \frac{2}{3V} [\langle E_{kin} \rangle - \langle W \rangle] \quad (\text{Virial theorem})$
Velocity scaling	$x_{new} = \mu x_{old}$
Modified eqn of motion	$\frac{dx_i(t)}{dt} = m_i \mu(t) x_i(t)$
	$\mu(t) = \left[ 1 - \frac{\beta_T \Delta t}{\tau_P} [P_0 - P(t)] \right]^{1/3}$

## 7 Biased Sampling