Statistical Physics

1. Laws of Thermodynamics
2. Kinetic approach and Boltzmann transport theory
3. Classical statistical mechanics
4. Quantum statistical Physics
5. Phase transitions
6. Linear response theory
7. Renormalization group

Laws of Thermodynamics

Thermodynamics: (developed in 19th century)

phenomenological theory to describe equilibrium properties of macro-scopic systems based on few macroscopically measurable quantities

thermodynamic limit (boundaries unimportant)

Laws of Thermodynamics

Thermodynamics: (developed in 19th century)

phenomenological theory to describe equilibrium properties of macro-scopic systems based on few macroscopically measurable quantities

thermodynamic limit (boundaries unimportant)

state variables / state functions:

describe equilibrium state of TD system uniquely

intensive: homogeneous of degree 0, independent of system size

extensive: homogeneous of degree 1, proportional to system size

intensive state variables serve as *equilibrium parameters*

Laws of Thermodynamics

state variables / state functions:

intensive		extensive	
T	temperature	S	entropy
p	pressure	V	volume
H	magnetic field	M	magnetization
E	electric field	P	dielectric polarization
μ	chemical potential	N	particle number

conjugate state variable: combine together to an energy

$T\,S,\ \ pV,\ \ HM,\ EP,\ \ \mu N$ unit [energy]

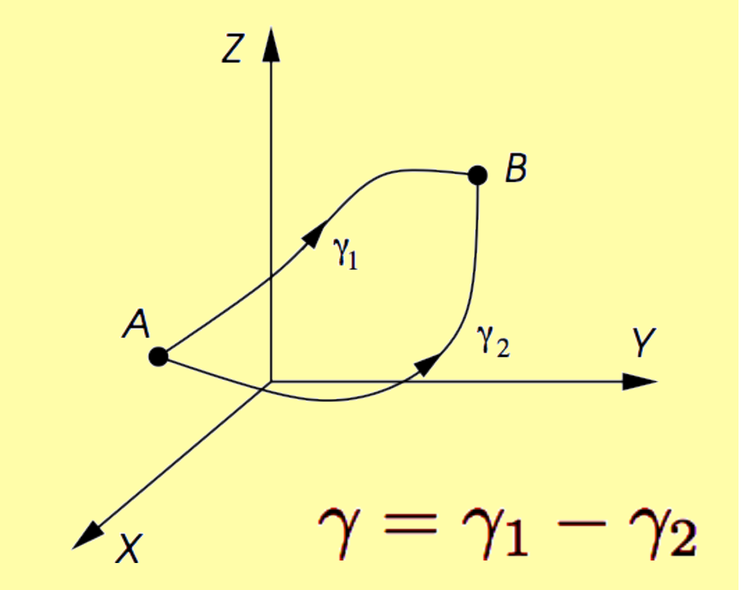
Laws of Thermodynamics

state variable: *Z(X,Y)*

$$Z(B) = Z(A) + \int_{\gamma_1} dZ$$

$$= Z(A) + \int_{\gamma_2} dZ$$

$$\Rightarrow \quad \oint_{\gamma} dZ = 0$$



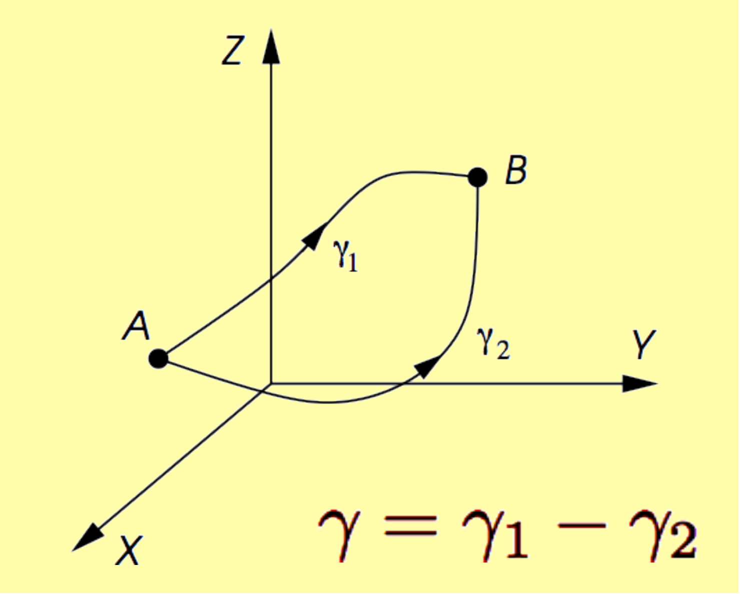
$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial y}\right)_X dY$$

Laws of Thermodynamics

state variable: *Z(X,Y)*

$$Z(B) = Z(A) + \int_{\gamma_1} dZ$$

$$= Z(A) + \int_{\gamma_2} dZ$$



➡ $$\oint_{\gamma} dZ = 0$$

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial y}\right)_X dY$$

Z: exact differential

➡ $$\left[\frac{\partial}{\partial Y}\left(\frac{\partial Z}{\partial X}\right)_Y\right]_X = \left[\frac{\partial}{\partial X}\left(\frac{\partial Z}{\partial Y}\right)_X\right]_Y$$

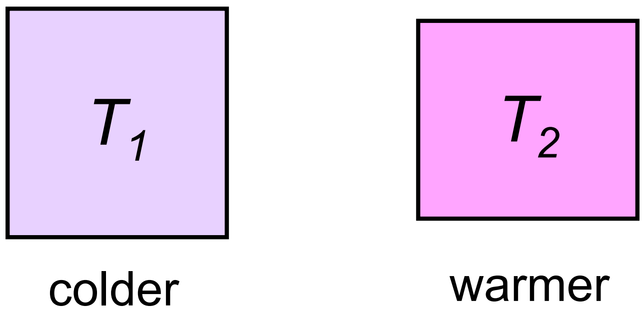
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0th law of thermodynamics)

characterizes state of TD systems



$$T_1 < T_2$$

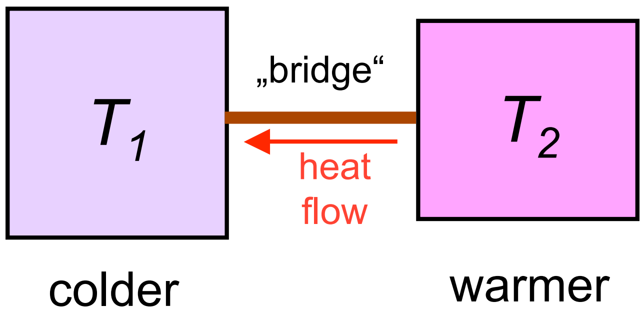
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0^{th} law of thermodynamics)

characterizes state of TD systems



$T_1 < T_2$

Fick‘s law

$$\vec{J}_Q = -K\vec{\nabla}T(\vec{r})$$

heat current — temperature gradient

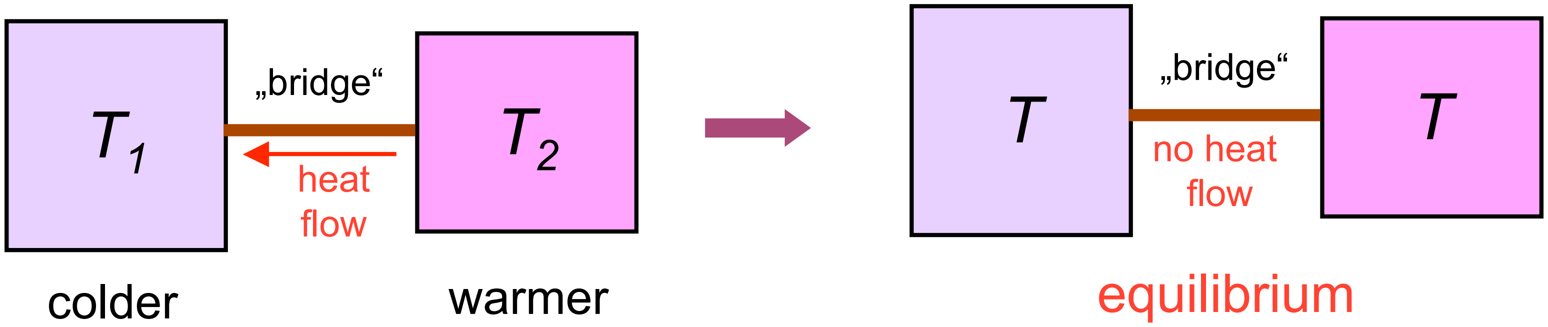
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0^{th} law of thermodynamics)

characterizes state of TD systems



$$T_1 < T < T_2$$

Fick‘s law

$$\vec{J}_Q = -K\vec{\nabla}T(\vec{r})$$

heat current — temperature gradient

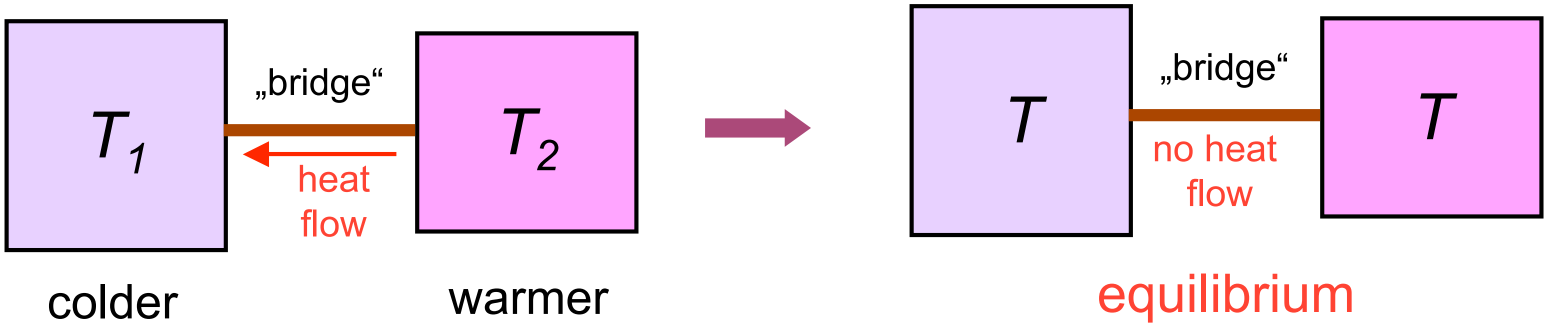
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0^{th} law of thermodynamics)

characterizes state of TD systems



$$T_1 < T < T_2$$

other equilibrium parameters:

- pressure p
- chemical potential μ

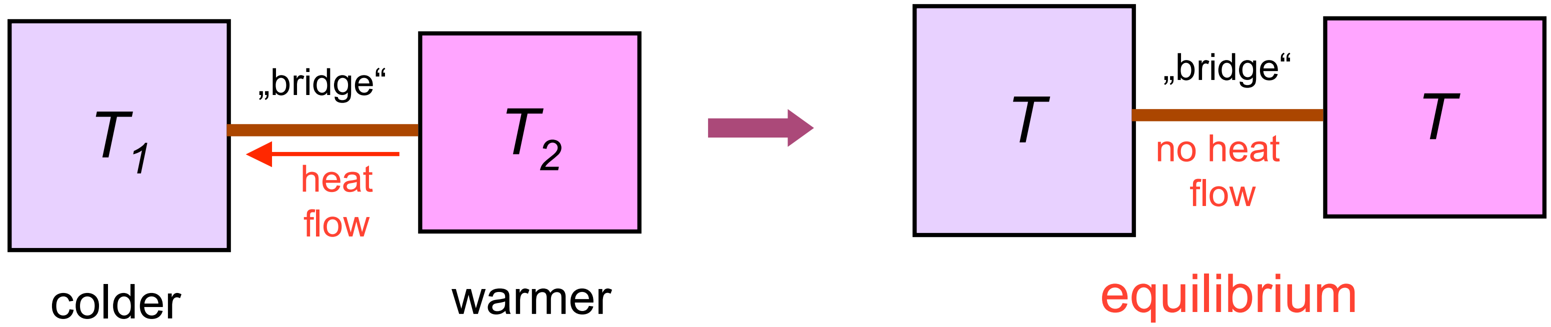
Laws of Thermodynamics

Equilibrium parameters:

intensive state variables can serve as equilibrium parameters

Temperature (existence: 0^{th} law of thermodynamics)

characterizes state of TD systems



equilibrium parameter
constant everywhere
in TD system

other equilibrium parameters:

pressure p

chemical potential μ

Laws of Thermodynamics

Equations of state:

consider TD system described by state variables $\{Z_1, Z_2, ..., Z_n\}$

subspace of equilibrium states:

$$f(Z_1, Z_2, ..., Z_n) = 0$$

equation of state (EOS)

Laws of Thermodynamics

Equations of state:

consider TD system described by state variables $\{Z_1, Z_2, ..., Z_n\}$

subspace of equilibrium states:

$$f(Z_1, Z_2, ..., Z_n) = 0$$

equation of state (EOS)

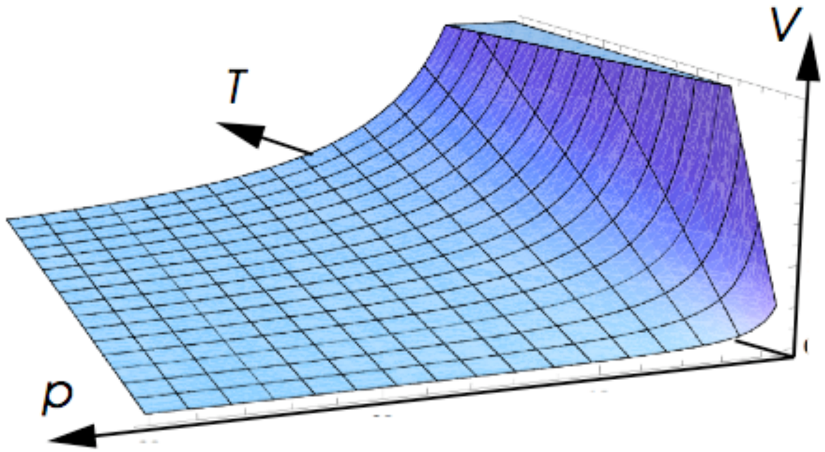
Ideal gas: $\{T, p, V\}$

thermodynamic EOS

$$pV = Nk_BT$$

Boltzmann constant

$$k_B = 1.381 \cdot 10^{-23} JK^{-1}$$



Laws of Thermodynamics

Equations of state:

consider TD system described by state variables $\{Z_1, Z_2, ..., Z_n\}$

subspace of equilibrium states:

$$f(Z_1, Z_2, ..., Z_n) = 0$$

equation of state (EOS)

Ideal gas: $\{T, p, V\}$

thermodynamic EOS

$$pV = Nk_BT$$

Boltzmann constant

$$k_B = 1.381 \cdot 10^{-23} JK^{-1}$$

response functions

reaction of TD system to change of state variables

isobar thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}$$

isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p}$$

Laws of Thermodynamics

1^{st} law of thermodynamics

J.R. Mayer, J.P. Joule & H. von Helmholtz ~1850

„heat is like work a form of energy“

heat

$$\delta Q = C dT$$

specific heat

C_V : constant V

C_p : constant p

work

$$\delta W = F dq$$

force displacement

$$\delta W = -p dV$$ gas

$$\delta W = H dM$$ paramagnet

Laws of Thermodynamics

1st law of thermodynamics

J.R. Mayer, J.P. Joule & H. von Helmhotz
~1850

„heat is like work a form of energy“

heat

$$\delta Q = C dT$$

specific heat

C_V : constant V

C_p : constant p

work

$$\delta W = F dq$$

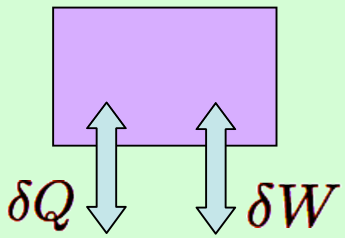
force displacement

$$\delta W = -p dV$$ gas

$$\delta W = H dM$$ paramagnet

internal energy U

$$dU = \delta Q + \delta W$$



isolated TD system

➡ $dU = 0$

$$\delta Q = \delta W = 0$$

Laws of Thermodynamics 1^{st} law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2} N k_B T$ (equipartition)

caloric EOS

Specific heat: $\delta Q = dU - \delta W = dU + pdV$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

constant *V*

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Laws of Thermodynamics 1^{st} law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2} N k_B T$ (equipartition)

caloric EOS

Specific heat: $\delta Q = dU - \delta W = dU + pdV$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

constant *p*

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Laws of Thermodynamics 1st law

internal energy

$$dU = \delta Q + \delta W$$

ideal gas (single atomic): $U = \frac{3}{2} N k_B T$ (equipartition)

caloric EOS

Specific heat:

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] V \alpha$$

ideal gas: $\begin{cases} \left(\frac{\partial U}{\partial V} \right)_T = 0 \\ \alpha = \frac{1}{T} \end{cases}$ and $pV = N k_B T$ ➡

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N k_B$$

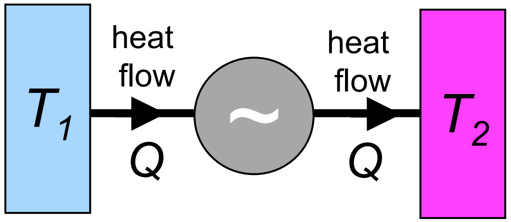
$$C_p - C_V = N k_B$$

Laws of Thermodynamics

2^{nd} law of thermodynamics

two equivalent formulations

R. Clausius: there is no cyclic process whose only effect is to transfer heat from a reservoir of lower temperature to one with higher temperature



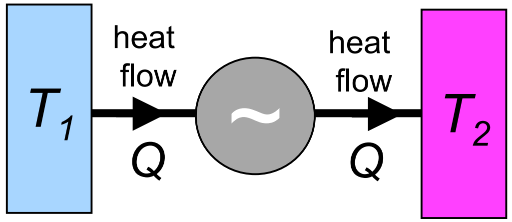
$$T_1 < T_2$$

Laws of Thermodynamics

2^{nd} law of thermodynamics

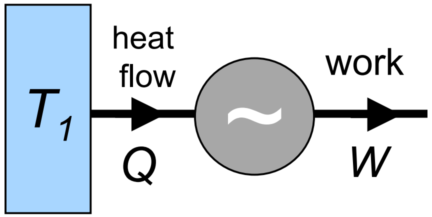
two equivalent formulations

R. Clausius: there is no cyclic process whose only effect is to transfer heat from a reservoir of lower temperature to one with higher temperature



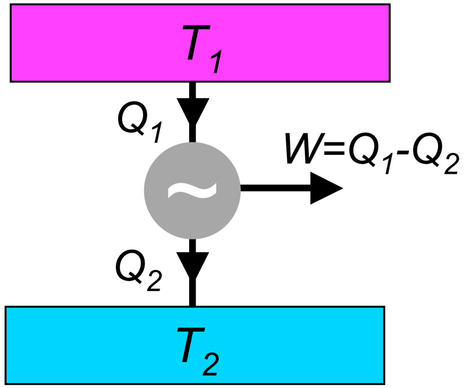
$T_1 < T_2$

W. Thomson (Lord Kelvin): there is no cyclic process whose effect is to take heat from a reservoir and transform it completely into work;
there is no perpetuum mobile of the 2^{nd} kind



Laws of Thermodynamics — 2^{nd} law

Carnot engine



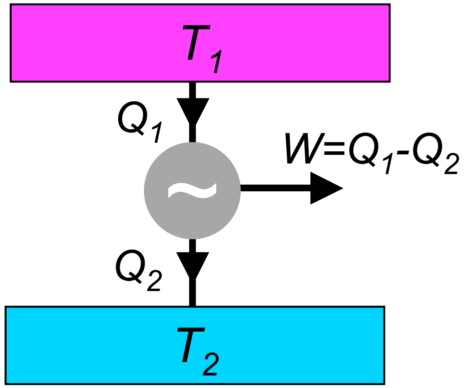
reversible Carnot process
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

➡ definition of absolute temperature T

irreversible process
$$\frac{Q_1}{Q_2} < \frac{T_1}{T_2}$$

Laws of Thermodynamics — 2^{nd} law

Carnot engine



reversible Carnot process $$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

➡ definition of absolute temperature T

irreversible process $$\frac{Q_1}{Q_2} < \frac{T_1}{T_2}$$

entropy as new state variable

$$dS = \frac{\delta Q}{T}$$

Clausius' theorem →

$$dS \geq \frac{\delta Q}{T}$$

$$\oint \frac{\delta Q}{T} \leq 0$$

$$\oint \frac{\delta Q}{T} = 0$$ cyclic process reversible

$$\oint \frac{\delta Q}{T} < 0$$ cyclic process irreversible

Laws of Thermodynamics 2nd law

entropy

$$dS \geq \frac{\delta Q}{T} \quad \Rightarrow \quad \int_A^B \frac{\delta Q}{T} \leq \int_A^B dS = S(B) - S(A)$$

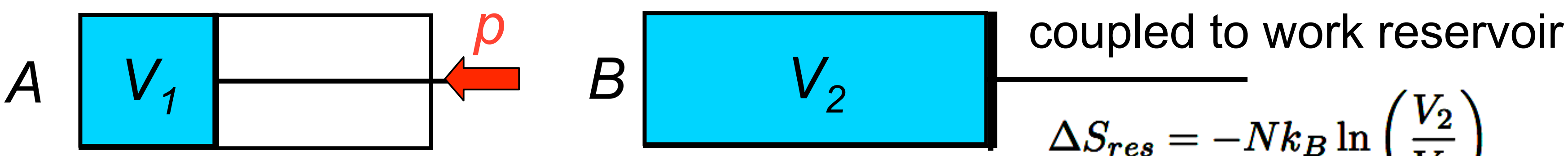
Laws of Thermodynamics 2nd law

entropy

$$dS \geq \frac{\delta Q}{T} \quad \rightarrow \quad \int_A^B \frac{\delta Q}{T} \leq \int_A^B dS = S(B) - S(A)$$

ideal gas:

reversible isothermal process $dU=0$ $\delta Q = -\delta W$



$$\Delta S_{res} = -Nk_B \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = \int_A^B \frac{\delta Q}{T} = -\frac{1}{T}\int_{V_1}^{V_2} pdV = Nk_B \ln\left(\frac{V_2}{V_1}\right)$$

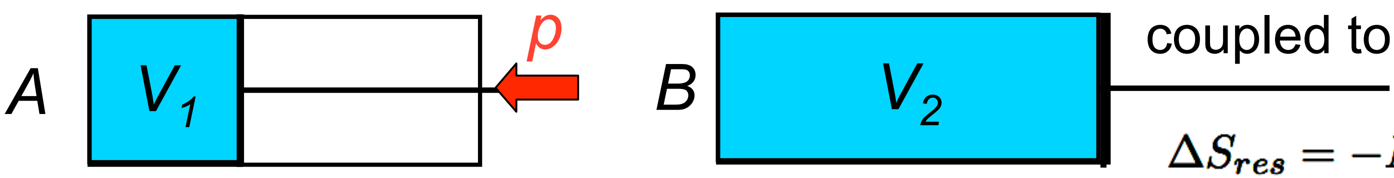
$$\Delta S_{tot} = \Delta S + \Delta S_{res} = 0$$

entropy

$$dS \geq \frac{\delta Q}{T} \quad \rightarrow \quad \int_A^B \frac{\delta Q}{T} \leq \int_A^B dS = S(B) - S(A)$$

ideal gas:

reversible isothermal process $dU=0$ $\quad \delta Q = -\delta W$



coupled to work reservoir

$$\Delta S_{res} = -N k_B \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = \int_A^B \frac{\delta Q}{T} = -\frac{1}{T}\int_{V_1}^{V_2} p dV = N k_B \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{tot} = \Delta S + \Delta S_{res} = 0$$

irreversible process $\Delta S_{res} = 0$

$$\Delta S_{tot} = \Delta S + \Delta S_{res} > 0$$

increase of entropy

waste of potential energy

Laws of Thermodynamics — 2^{nd} law

application to gas: $$TdS = \delta Q = dU - \delta W = dU + pdV$$

dS exact differential *S(U,V)*

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

Laws of Thermodynamics 2nd law

application to gas: $$TdS = \delta Q = dU - \delta W = dU + pdV$$

dS exact differential *S(U,V)*

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

- $\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$ ➡ $T = T(U,V)$ ➡ $U = U(T,V)$
  caloric EOS
- $\left(\frac{\partial S}{\partial V}\right)_S = \frac{p}{T}$ ➡ $p = Tf(T,V)$ thermodynamic EOS

Laws of Thermodynamics

Thermodynamic potentials

natural state variables → convenient simple relations

internal energy (gas) *U(S,V)*

$$dU = TdS - pdV \quad \rightarrow \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

response functions:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

specific heat

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = \left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_s}$$

adiabatic compressibility

dS=0

Laws of Thermodynamics

Thermodynamic potentials

natural state variables → convenient simple relations

internal energy (gas) $U(S,V)$

$$dU = TdS - pdV \rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Maxwell relations:

dU exact differential

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Laws of Thermodynamics

Thermodynamic potentials

natural state variables → convenient simple relations

other variables: *(S,V)* → *(T,V)* Legendre transformation

Helmholtz free energy (gas) *F(T,V)*

$$F(T,V) = \inf_S \left\{ U - S \left(\frac{\partial U}{\partial S} \right)_V \right\} = \inf_S \{ U - ST \}$$

$$dF = dU - d(ST) = dU - SdT - TdS = -SdT - pdV$$

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

response functions →

$$\left\{ \begin{aligned} \left(\frac{\partial^2 F}{\partial T^2} \right)_V &= -\frac{C_V}{T} \quad \text{specific heat} \\ \left(\frac{\partial^2 F}{\partial V^2} \right)_T &= \frac{1}{V \kappa_T} \quad \text{isothermal compressibility} \end{aligned} \right.$$

Laws of Thermodynamics

Thermodynamic potentials

natural state variables → convenient simple relations

other variables: $(S,V) \rightarrow (T,V)$ Legendre transformation

Helmholtz free energy (gas) $F(T,V)$

$$F(T,V) = \inf_S \left\{ U - S \left(\frac{\partial U}{\partial S} \right)_V \right\} = \inf_S \{U - ST\}$$

$$dF = dU - d(ST) = dU - SdT - TdS = -SdT - pdV$$

$$\left(\frac{\partial F}{\partial T} \right)_V = -S$$

$$\left(\frac{\partial F}{\partial V} \right)_T = -p$$

Maxwell relation →

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

Laws of Thermodynamics

Thermodynamic potentials

natural state variables → convenient simple relations

Enthalpy (gas) *H(S,p)*

$$dH = TdS + Vdp \xrightarrow[\text{relation}]{\text{Maxwell}} \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Gibbs free energy (gas) *G(T,p)*

$$dG = -SdT + Vdp \xrightarrow[\text{relation}]{\text{Maxwell}} \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Laws of Thermodynamics

Equilibrium condition

entropy:

$$dS \geq 0$$ general

$$dS = 0$$ in equilibrium

S maximal

↑

U,V fixed variables

closed system: $dU=dV=0$

fixed variables	potential
T,V	F minimal
T,p	G minimal
S,V	U minimal
S,p	H minimal

Laws of Thermodynamics

3rd law of thermodynamics

Nernst 1905

entropy $S = S(T, q, \ldots)$

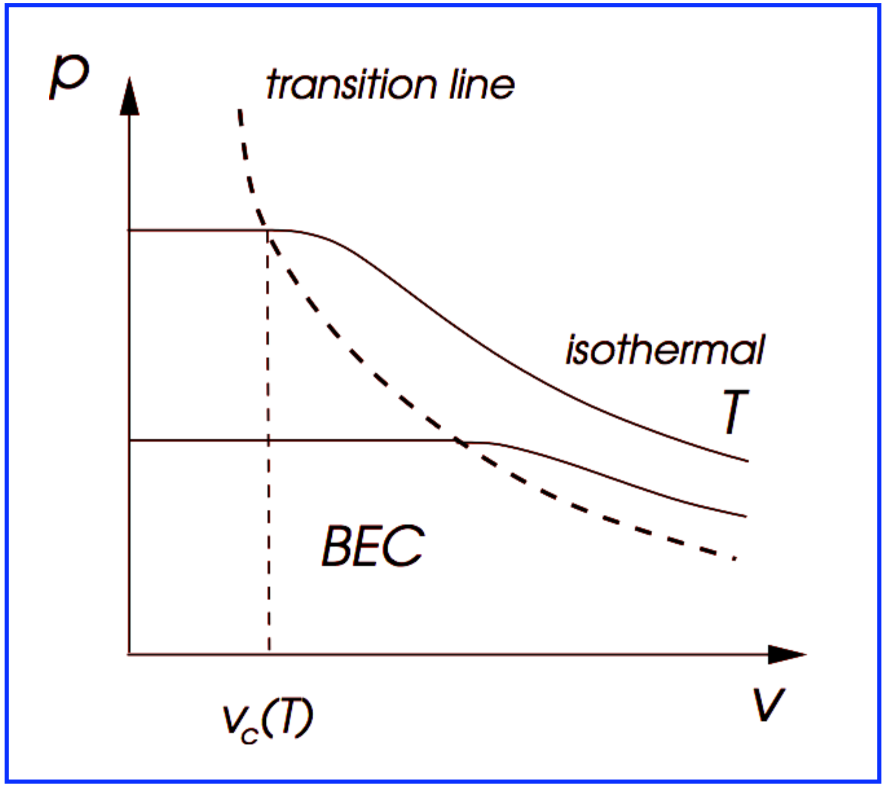
$$\lim_{T \to 0} \left(\frac{\partial S}{\partial q} \right)_T = 0 \qquad \lim_{T \to 0} \left(\frac{\partial S}{\partial T} \right)_q = 0$$

e.g.: $C_V(T = 0) = 0 \qquad \alpha(T = 0) = 0$

$$\lim_{T \to 0} S(T, q, \ldots) = S_0$$ independent of $T, q, \ldots$

Planck: $S_0 = 0$ only within quantum statistical physics equation of state

$$p = \begin{cases} \dfrac{k_B T}{\lambda^3} g_{5/2}(z)\,, & V > V_c \\[2ex] \dfrac{k_B T}{\lambda^3} g_{5/2}(1)\,, & V < V_c \end{cases}$$



compressibility $V > V_c$

$$\kappa_T = \frac{N\lambda^6}{V k_B T g_{3/2}(z)^2} \frac{g'_{3/2}(z)}{g'_{5/2}(z)}$$

diverges at $z = 1$

entropy (fixed μ)

$$S(T,V,\mu) = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = \begin{cases} Nk_B\left(\frac{5v}{2\lambda^3}g_{5/2}(z) - \ln z\right), & T > T_c\,, \\ Nk_B\frac{5}{2}\frac{g_{5/2}(1)}{g_{3/2}(1)}\left(\frac{T}{T_c}\right)^{3/2}, & T < T_c \end{cases}$$

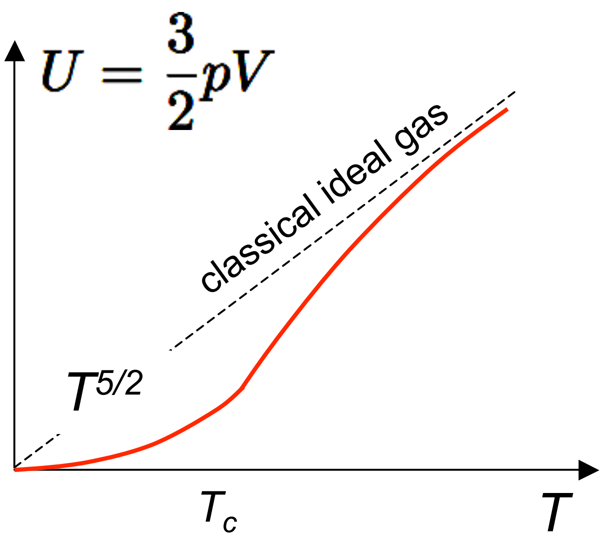
entropy per particle

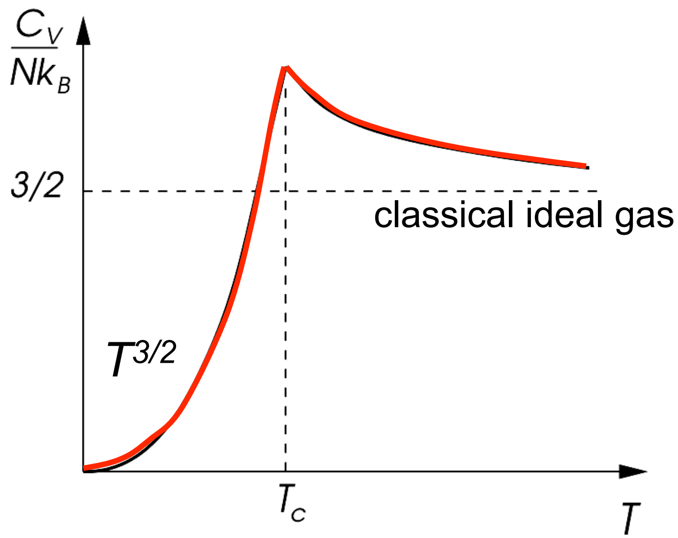
$$\frac{S}{N} = s\left(\frac{T}{T_c}\right)^{3/2} = \frac{n_n(T)}{n}s \qquad \text{with} \quad s = \frac{5}{2}k_B\frac{g_{5/2}(1)}{g_{3/2}(1)}$$

contribution to entropy from normal particles only

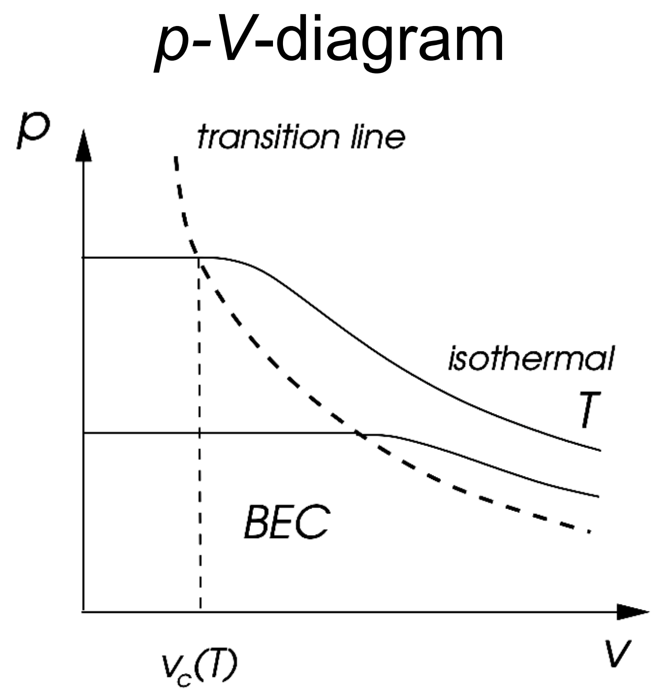
specific heat (fixed *N*)

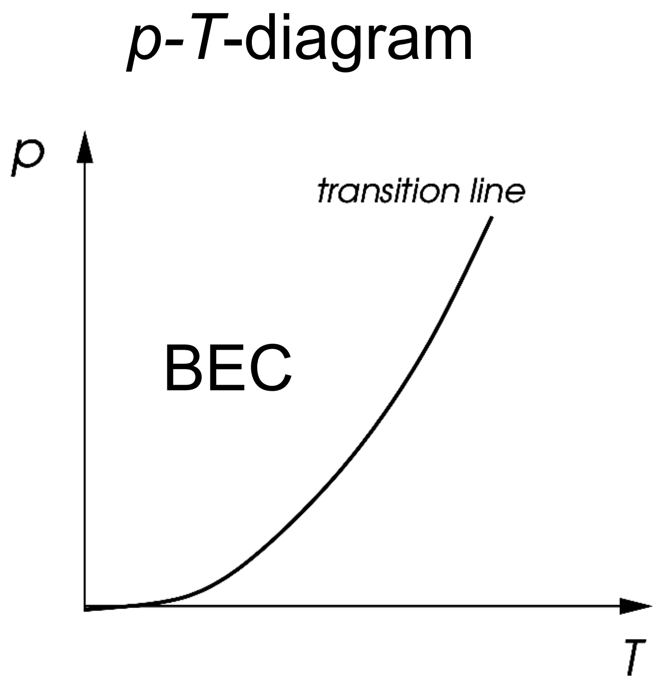
$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \begin{cases} Nk_B\left(\frac{15v}{4\lambda^3}g_{5/2}(z) - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right), & T > T_c\,, \\ Nk_B\frac{15}{4}\frac{g_{5/2}(1)}{g_{3/2}(1)}\left(\frac{T}{T_c}\right)^{3/2}, & T < T_c \end{cases}$$





phase diagram



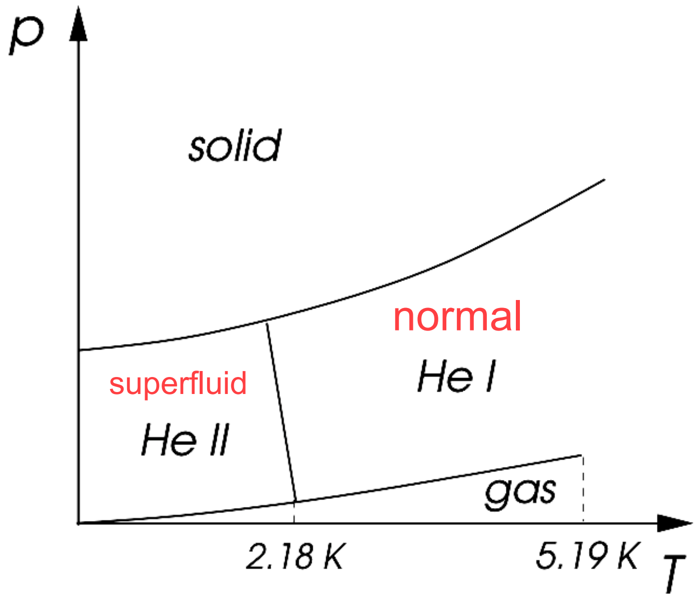


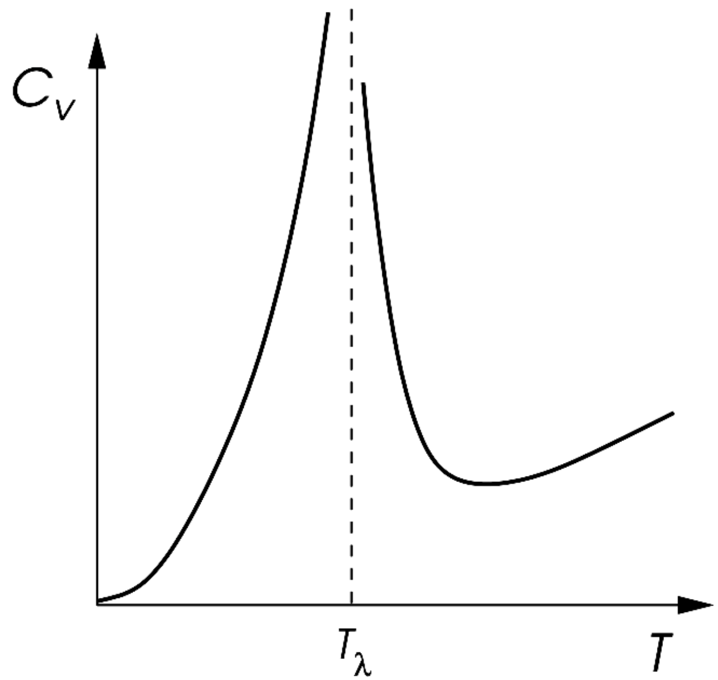
$$p_0 v^{5/3} = \frac{h^2}{2\pi m} \frac{g_{5/2}(1)}{[g_{3/2}(1)]^{5/3}}$$

$$p_0 = \frac{k_B T}{\lambda^3} g_{5/2}(1) \propto T^{5/2}$$

superfluid ^{4}He bosonic atoms

BEC ➡ supefluid ➡ frictionless flow
rigidity of condensate





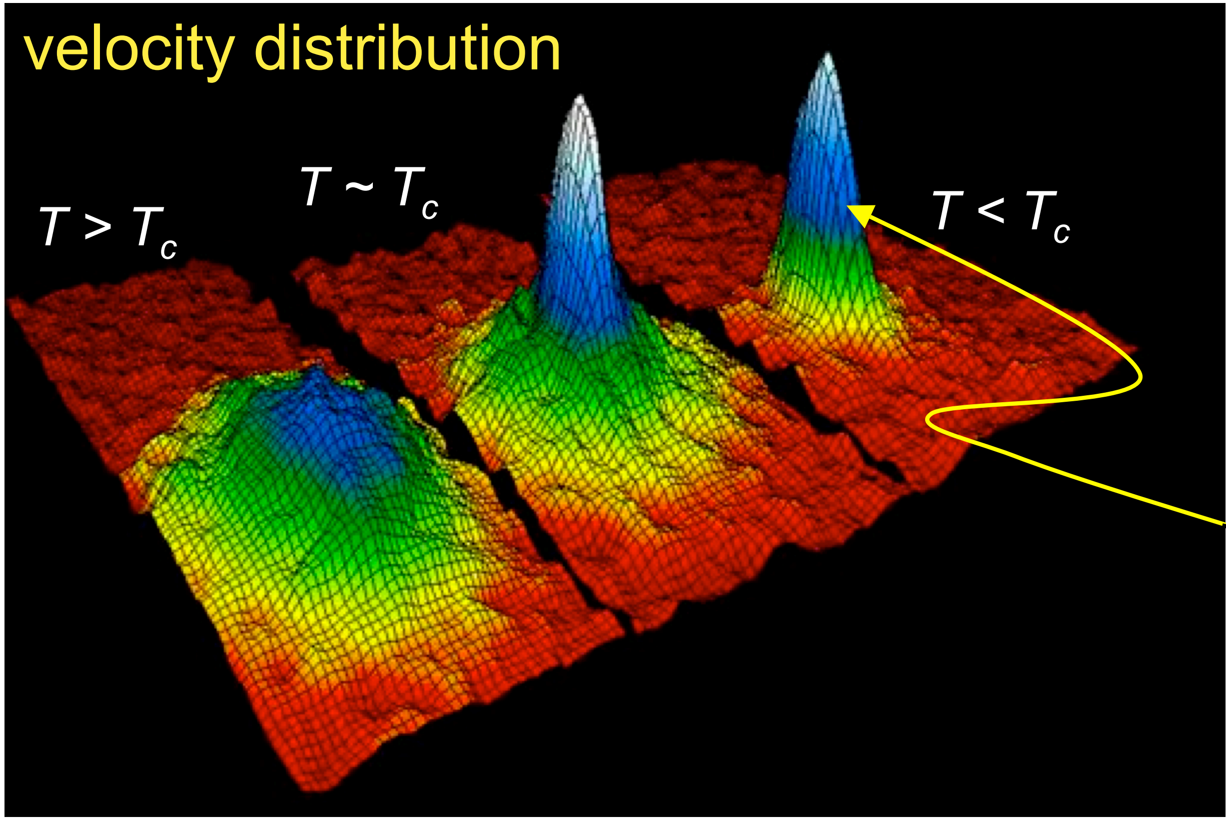
„ λ - transition “

Bose-Einstein condensation BEC

ultra-cold atomic gases

^{87}Rb 37 electrons + 87 nucleons = 124 Fermions ➡ Boson

2000 Rb atoms in a trap $T_c = 170\ nK$



macroscopic occupation of state with $p = 0$

Electromagnetic wave - harmonic oscillator

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \vec{\nabla}^2 \right) \vec{A} = 0 \qquad \vec{\nabla} \cdot \vec{A} = 0$$

plane waves in cavity (*L x L x L*):

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k},\lambda} \left\{ A_{\vec{k}\lambda} \vec{e}_{\vec{k}\lambda} e^{i\vec{k}\cdot\vec{r} - i\omega t} + A^*_{\vec{k}\lambda} \vec{e}^{\,*}_{\vec{k}\lambda} e^{-i\vec{k}\cdot\vec{r} + i\omega t} \right\}$$

$$\omega = \omega_{\vec{k}} = c|\vec{k}| \qquad \vec{e}_{\vec{k}\lambda} \cdot \vec{k} = 0$$

Periodic boundary conditions:

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

Electromagnetic wave - Canoncial quantization

$$Q_{\vec{k}\lambda} = \frac{1}{\sqrt{4\pi c}}\left(A_{\vec{k}\lambda} + A^*_{\vec{k}\lambda}\right) \qquad P_{\vec{k}\lambda} = \frac{i\omega_{\vec{k}}}{\sqrt{4\pi c}}\left(A_{\vec{k}\lambda} - A^*_{\vec{k}\lambda}\right)$$

Hamiltonian: $$\mathcal{H} = \int d^3r \frac{\vec{E}^2 + \vec{B}^2}{8\pi} = \sum_{\vec{k},\lambda} \frac{\omega_{\vec{k}}}{2\pi c} \left|A_{\vec{k}\lambda}\right|^2 = \frac{1}{2}\sum_{\vec{k},\lambda}\left(P^2_{\vec{k}\lambda} + \omega^2_{\vec{k}} Q^2_{\vec{k}\lambda}\right)$$

canonical quantization $$[Q_{\vec{k},\lambda}, P_{\vec{k}',\lambda'}] = i\hbar\delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}$$

raising / lowering operators

$$A^*_{\vec{k}\lambda} \rightarrow a^\dagger_{\vec{k}\lambda}$$

$$A_{\vec{k}\lambda} \rightarrow a_{\vec{k}\lambda}$$

$$[a_{\vec{k}\lambda}, a^\dagger_{\vec{k}'\lambda'}] = \delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'}$$

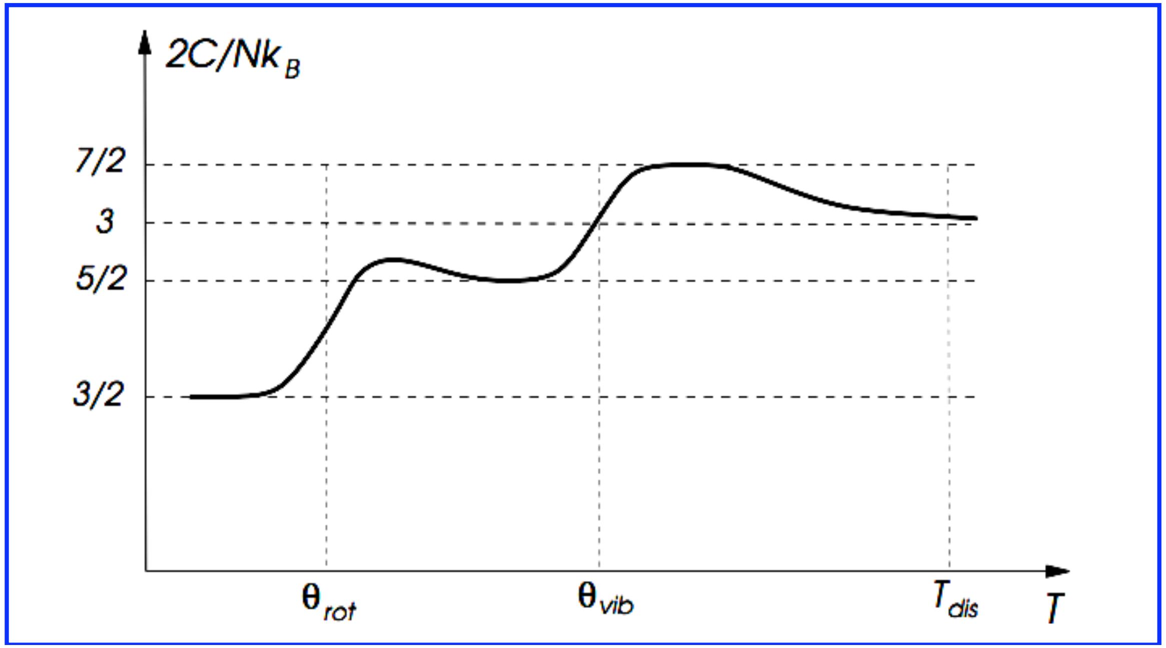
$$\mathcal{H} = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k}}\left(a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda} + \frac{1}{2}\right) = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k}}\left(n_{\vec{k}\lambda} + \frac{1}{2}\right)$$

create bosonic particles in mode

$(\vec{k}, \lambda)$ with $\omega_{\vec{k}}$ photon

Specific heat of diatomic molecule

$$\frac{2C(T)}{N} = \begin{cases} \frac{3}{2}k_B + 3k_B\left(\frac{\theta_{rot}}{T}\right)^2 e^{-\theta_{rot}/T} & T_c \ll T \ll \theta_{rot} \\ \frac{3}{2}k_B + k_B + k_B\left(\frac{\theta_{vib}}{2T}\right)^2 e^{-\theta_{vib}/T} & \theta_{rot} \ll T \ll \theta_{vib} \\ \frac{3}{2}k_B + k_B + k_B & \theta_{vib} \ll T \ll T_{dis} \\ 3k_B & T_{dis} \ll T \end{cases}$$



Linear Response

small perturbation by external field $\int d^3r \hat{A}(\vec{r}) h(\vec{r}, t)$

measured response $\Rightarrow$ $\langle \hat{B}(\vec{r}) \rangle (t) = \int dt' \int d^3r' \, \chi_{BA}(\vec{r} - \vec{r}', t - t') h(\vec{r}', t')$

Kubo formula / retarded Green's function

$$\chi_{BA}(\vec{r} - \vec{r}', t - t') = -\frac{i}{\hbar} \Theta(t - t') \langle [\hat{B}_H(\vec{r}, t), \hat{A}_H(\vec{r}', t')] \rangle_{\mathcal{H}}$$

causality

$$\langle \hat{C} \rangle_{\mathcal{H}} = \frac{tr\{\hat{C} e^{-\beta \mathcal{H}}\}}{tr\{e^{-\beta \mathcal{H}}\}}$$

thermal average

$$\hat{A}_H(t) = e^{i\mathcal{H}t/\hbar} \hat{A} e^{-i\mathcal{H}t/\hbar}$$

Heisenberg representation

Linear Response

Fourier transform

$$\chi(\vec{q},\omega) = \int d^3\tilde{r} \int_{-\infty}^{+\infty} d\tilde{t}\, \chi(\tilde{\vec{r}},\tilde{t}) e^{i\omega\tilde{t} - i\vec{q}\cdot\tilde{\vec{r}}} \quad \Rightarrow \quad B(\vec{q},\omega) = \chi(\vec{q},\omega) h(\vec{q},\omega)$$

dynamical structure factor

$$\chi(\vec{q},\omega) = \int_0^{\infty} d\omega'\, S(\vec{q},\omega') \left\{ \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' + i\eta} \right\}$$

$$S(\vec{q},\omega) = \sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} \underbrace{|\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 \delta(\hbar\omega - \epsilon_{n'} + \epsilon_n)}$$

stationary states

$$\mathcal{H}|n\rangle = \epsilon_n |n\rangle$$

and $\hat{A} = \hat{B}^\dagger$

Fermi Golden rule

transition rates between
different states of the system

$\eta \rightarrow 0_+$

causality

Linear Response

real- and imaginary part $\chi = \chi' + i\chi''$

$$\chi'(\vec{q},\omega) = \int_0^\infty d\omega' \, S(\vec{q},\omega') \left\{ \mathcal{P}\frac{1}{\omega-\omega'} - \mathcal{P}\frac{1}{\omega+\omega'} \right\} ,$$

$$\chi''(\vec{q},\omega) = -\pi \left\{ S(\vec{q},\omega) - S(\vec{q},-\omega) \right\} .$$

Kramers-Kronig relations

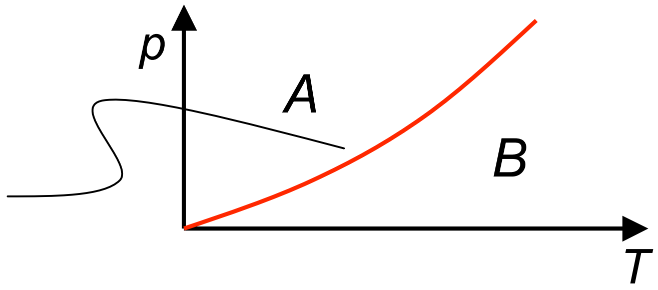
$$\chi'(\vec{q},\omega) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega' \, \mathcal{P}\frac{\chi''(\vec{q},\omega')}{\omega-\omega'} ,$$

$$\chi''(\vec{q},\omega) = \frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega' \, \mathcal{P}\frac{\chi'(\vec{q},\omega')}{\omega-\omega'} .$$

Ehrenfest relation for 2nd order phase transition

transition between phase *A* and *B*

$$\left.\begin{aligned} S_A(T,p) &= S_B(T,p) \\ V_A(T,p) &= V_B(T,p) \end{aligned}\right\} \quad \text{continuous}$$



differentials
$$\begin{cases} \left(\dfrac{\partial S_A}{\partial T}\right)_p dT + \left(\dfrac{\partial S_A}{\partial p}\right)_T dp = \left(\dfrac{\partial S_B}{\partial T}\right)_p dT + \left(\dfrac{\partial S_B}{\partial p}\right)_T dp\,, \\[2ex] \left(\dfrac{\partial V_A}{\partial T}\right)_p dT + \left(\dfrac{\partial V_A}{\partial p}\right)_T dp = \left(\dfrac{\partial V_B}{\partial T}\right)_p dT + \left(\dfrac{\partial V_B}{\partial p}\right)_T dp\,. \end{cases}$$

Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha$$

thermal expansion coefficient

Ehrenfest relations

experimentally testable

$$\frac{dp}{dT} = -\frac{\left(\frac{\partial S_B}{\partial T}\right)_p - \left(\frac{\partial S_A}{\partial T}\right)_p}{\left(\frac{\partial S_B}{\partial p}\right)_T - \left(\frac{\partial S_A}{\partial p}\right)_T} = \frac{\Delta C_p}{TV\Delta\alpha}$$

$$\frac{dp}{dT} = -\frac{\left(\frac{\partial V_B}{\partial T}\right)_p - \left(\frac{\partial V_A}{\partial T}\right)_p}{\left(\frac{\partial V_B}{\partial p}\right)_T - \left(\frac{\partial V_A}{\partial p}\right)_T} = \frac{\Delta\alpha}{\Delta\kappa_T}$$

Critical exponents

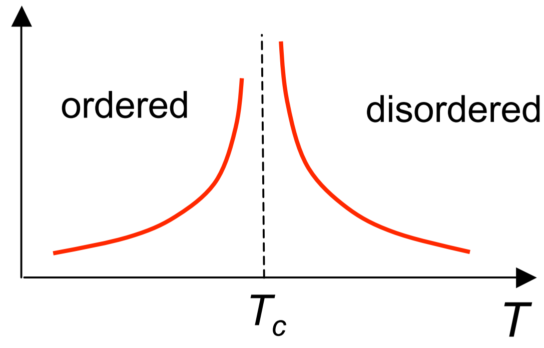
singular behavior at $T = T_{c+/-}$ control parameter $\tau = 1 - \frac{T}{T_c}$

$$\tau > 0\,, \tau < 0$$

heat capacity $C(T) \propto |\tau|^{-\alpha}$

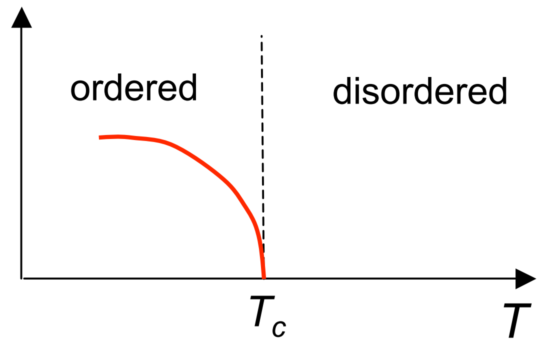
susceptibility $\chi(T) \propto |\tau|^{-\gamma}$

correlation length $\xi(T) \propto |\tau|^{-\nu}$



$$\tau > 0 \quad (T < T_c)$$

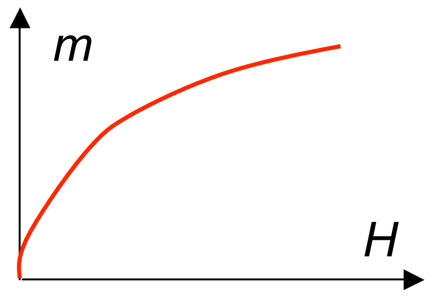
order parameter $m(T) \propto |\tau|^{\beta}$



Critical exponents

singular behavior at $T=T_{c+/-}$ control parameter $\tau = 1 - \frac{T}{T_c}$

$\tau = 0 \quad (T = T_c)$



order parameter $m \propto H^{1/\delta}$

correlation function $\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}}$

scaling laws

Rushbrooke scaling: $\alpha + 2\beta + \gamma = 2$

Widom scaling: $\gamma = \beta(\delta - 1)$

Fisher scaling: $\gamma = (2 - \eta)\nu$

Josephson scaling: $\nu d = 2 - \alpha$

Critical exponents

Fisher scaling: $\gamma = (2 - \eta)\nu$

general correlation function $\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}} g(r/\xi)$ $\xi(T) \propto |\tau|^{-\nu}$

susceptibility $\chi(T) \propto |\tau|^{-\gamma}$

$$\chi \propto \int d^d r \, \Gamma_{\vec{r}} \propto \int d^d r \, \frac{1}{r^{d-2+\eta}} g(r/\xi)$$

$$\propto \xi^{2-\eta} \int d^d y \frac{1}{y^{d-2+\eta}} g(y) \propto |\tau|^{-\nu(2-\eta)}$$

Critical exponents

Mean field exponents:

$$-A'\tau m + Bm^3 - H - \kappa\vec{\nabla}^2 m = 0$$

$\tau < 0 \quad (T > T_c)$

$$\xi^2 = -\frac{\kappa}{A'\tau} \propto |\tau|^{-2\nu}$$

$$\chi = -\frac{1}{A'\tau} \propto |\tau|^{-\gamma}$$

$\tau > 0 \quad (T < T_c)$

$$m^2 = \frac{A'\tau}{B} \propto |\tau|^{2\beta}$$

$\tau = 0 \quad (T = T_c)$

$$Bm^3 = H \propto H^{3/\delta}$$

$$\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2}} \propto \frac{1}{r^{d-2+\eta}}$$

$$C \propto \Theta(\tau) \propto |\tau|^{-\alpha}$$

$$\nu = \frac{1}{2}$$

$$\gamma = 1$$

$$\beta = \frac{1}{2}$$

$$\delta = 3$$

$$\eta = 0$$

$$\alpha = 0$$

Spontaneous symmetry breaking - long range order

Ginzburg-Landau theory (Ising model of ferromagnet)

order parameter $m \propto \begin{cases} 0 & T > T_c \\ \pm|\tau|^{1/2} & T < T_c \end{cases}$

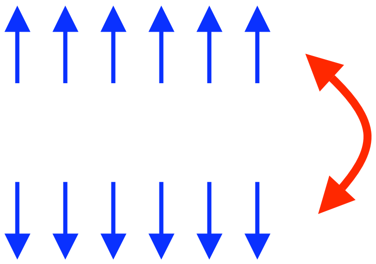
high symmetry $\mathcal{G}$

U

low symmetry $\mathcal{G}'$

choice between 2 states

two-fold degeneracy



time reversal

broken symmetry

free energy functional

$$F[m;H,T] = \int d^d r \left\{ \frac{A}{2} m(\vec{r})^2 + \frac{B}{4} m(\vec{r})^4 - H(\vec{r}) m(\vec{r}) + \frac{\kappa}{2} [\vec{\nabla} m(\vec{r})]^2 \right\}$$

scalar (invariant) under symmetry operations in $\mathcal{G} = G \times \mathcal{K}$

space group (G) — time reversal ($\mathcal{K}$)

Spontaneous symmetry breaking - long range order

correlation function

$$\Gamma_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \xrightarrow{\vec{r} = \vec{r}_j - \vec{r}_i} \Gamma_{\vec{r}} \propto \frac{e^{-r/\xi}}{r^b}$$

for $T < T_c$, $T > T_c$

$$\lim_{r\to\infty} \Gamma_{\vec{r}} = 0 \quad \Rightarrow \quad \lim_{r\to\infty} \langle s_i s_j \rangle = \langle s_i \rangle \langle s_j \rangle$$

$T > T_c$ $\quad \langle s_i \rangle = 0$ $\quad \lim_{r\to\infty} \langle s_i s_j \rangle = 0$

$T < T_c$ $\quad \langle s_i \rangle = \pm m$ $\quad \lim_{r\to\infty} \langle s_i s_j \rangle = m^2 > 0$

long range order

correlation over arbitrary distance

Renormalization group

Analysis of critical phenomena, e.g. at 2nd-order phase transitions

Method: decimation of high-energy degrees of freedom to reach a low-energy effective Hamiltonian without changing the partition function

$$\mathcal{H}(\vec{K},\{s_i\},N) = NK_0 + K_1\sum_i s_i + K_2 \sum_{\langle i,j\rangle} s_i s_j + \cdots$$

Ising model

$$K_0 = 0\,, \quad K_1 = H/k_B T\,, \quad K_2 = J/K_B T\,, \quad K_{n>2} = 0 \qquad \vec{K} = (K_0, K_1, K_2, \ldots)$$

$$Z(\vec{K},N) = \sum_{\{s_i\}} e^{\mathcal{H}(\vec{K},\{s_i\},N)}$$

separate $\{s_i\}$ → $\{S_b\}$ decimate, $\{s'\}$ keep

$$Z(\vec{K},N) = \sum_{\{s'\}}\sum_{\{S_b\}} e^{\mathcal{H}(\vec{K},\{S_b\},\{s'\},N)} = \sum_{\{s'\}} e^{\mathcal{H}(\vec{K}',\{s'\},Nb^{-d})} = Z(\vec{K}',Nb^{-d})$$

Renormalization group

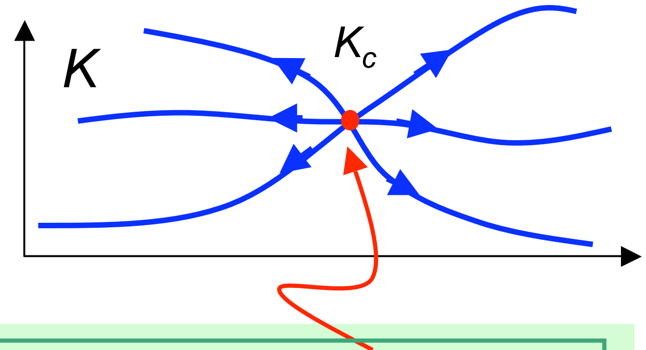
$$Z(\vec{K},N) = \sum_{\{s'\}} \sum_{\{S_b\}} e^{\mathcal{H}(\vec{K},\{S_b\},\{s'\},N)} = \sum_{\{s'\}} e^{\mathcal{H}(\vec{K}',\{s'\},Nb^{-d})} = Z(\vec{K}',Nb^{-d})$$

renormalization group step $\vec{K} \rightarrow R\vec{K} = \vec{K}'$ $\quad \vec{K}^{(n)} = R^n \vec{K}$

change of length scale b $\quad \xi \rightarrow \xi' = \xi/b$

number of spins $N \rightarrow N' = N/b^d$

fixed point in flow of $\vec{K}$ $\quad R\vec{K}_c = \vec{K}_c$



$$R\vec{K} \approx \vec{K}_c + \Lambda(\vec{K} - \vec{K}_c)$$
$$= \vec{K}_c + \Lambda \sum_i c_i \vec{e}_i$$
$$= \vec{K}_c + \sum_i c_i b^{y_i} \vec{e}_i$$

$y_i > 0$	relevant	➡	unstable FP
$y_i < 0$	irrelevant	➡	stable FP
$y_i = 0$	marginal		

Renormalization group

$$
\begin{aligned}
R\vec{K} &\approx \vec{K}_c + \Lambda(\vec{K} - \vec{K}_c) \\
&= \vec{K}_c + \Lambda \textstyle\sum_i c_i \vec{e}_i \\
&= \vec{K}_c + \textstyle\sum_i c_i b^{y_i} \vec{e}_i
\end{aligned}
$$

relevant direction $\vec{e}_1$ $\quad y_1 > 0$

$c_1 = -A\tau \qquad \tau = 1 - T/T_c$

$$R\tau = \tau' = b^{y_1}\tau$$

correlation length

$$\xi' = \xi/b$$

$$|\tau'|^{-\nu} = \frac{|\tau'|^{-\nu}}{b}$$

$\Rightarrow$ $$\nu = \frac{1}{y_1}$$

specific heat

$$C \propto |\tau|^{-\alpha}$$

$$2 - \alpha = \frac{d}{y_1} = d\nu$$

Josephson scaling