

Statistical Physics

Kathrin Laxhuber

Janik Schüttler

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Contents

1	The Laws of Thermodynamics	2
2	Thermodynamic Potentials	3
2.1	Further Thermodynamic Potentials	5
2.1.1	Free energy	5
2.1.2	Enthalpy	5
2.1.3	Gibbs free energy	6
2.1.4	Grand canonical potential	6
2.2	Van der Waals gas	6
3	Classical Statistical Mechanics	7
3.1	Microcanonical ensemble	7
3.1.1	Equilibrium: Ergodic hypothesis	7
3.1.2	Equilibrium: Entropy & Gibbs variational principle	7
3.2	Equipartition theorem	9
3.3	Canonical ensemble	9
3.4	Grand canonical ensemble	10
3.5	Real classical gas	10
4	The Ising Model	12
4.1	The model	12
4.2	The mean-field approximation	12
4.3	Peierls argument	14
4.4	The exact solution in $d = 2$	15
5	The Renormalization Group	17
5.1	Scaling hypothesis	17
5.2	Renormalization: block spin transformation	18
5.3	An explicit RG computation	20
6	Second Quantization	22
7	Ideal Quantum Gases	23
7.1	Formalism	23
7.2	Independent particles	23
7.3	Bose-Einstein condensation	24
7.4	Thermodynamics of ideal gas	25
7.5	Non-degenerate Bose/Fermi gases (Classical limit)	25
7.6	Degenerate Bose gas	25

1 The Laws of Thermodynamics

Thermodynamic System is spatially delimited and characterized by possible changes from outside.

Equilibrium attained in a closed system by waiting. State determined by state variables, e.g. $p, V, T \dots$

Process p generally connects (equilibrium) states z_1, z_2 , but need not proceed along equilibrium states.

- **Reversible:** $\exists p' : p' \circ p = \text{id}$ on whole world.
- **Quasistatic:** System in equilibrium at all time. Can be realized reversibly (but no work process).
- **Cyclic:** $z_2 = z_1$.
- **Work process:** Any exchange of energy seen from outside can be accounted for as work, i.e. no flow of heat (adiabatic) or substance.

Any quasistatic p can be reversible, not nec converse

First law of thermodynamics

- For any two states z_1, z_2 there is a work process from $z_1 \rightarrow z_2$ or $z_2 \rightarrow z_1$.
- Work $W(z_1 \rightarrow z_2)$ related to the process depends only on the ordered pair (z_1, z_2) (not on process).

$W(z_2 \rightarrow z_1) := -W(z_1 \rightarrow z_2)$ if $z_2 \rightarrow z_1$ impossible.

Energy $U(z)$ is defined relative to a reference state z_0 with arbitrary energy constant $U(z_0)$ as

$$U(z) - U(z_0) := W(z_0 \rightarrow z).$$

Infinitesimal Work

$$\delta W := -p dV \quad (\text{rev quasist work proc})$$

$$\delta W := -p dV \quad (\text{general rev quasist proc})$$

Heat for general quasistatic processes is defined as

$$\delta Q = dU - \delta W$$

State variables have exact differential.

0th law Write $(U_1, V_1) \sim (U_2, V_2)$ for thermal equilibrium. Then \sim is transitive and defines an equivalence relation (with “temperature” classes).

Heat reservoir is a thermodynamic system with no work coordinates $dU = \delta Q$ and large, thus constant T for finite ΔQ . Equilibrated states form isotherm.

Boyle, Gay-Lussac Ideas gas gas has isotherms $pV = \text{const}$ (Boyle) & $U = \text{const}$ (Gay-Lussac)

Second law exists in different formulations:

”No process is possible, the only result of which is that heat is taken from a system and work is done.”

”There is no cyclic machine that takes heat from each of the involved reservoirs and does work”.

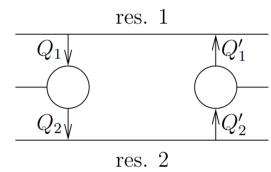
I.e. there must also be heat given.

Carnot Theorem

- For all *reversible*, cyclic machines operating between two heat reservoirs, $\frac{Q_1}{Q_2} \equiv \tau_{12} > 0$ is universal (i.e. depends only on T_1, T_2 , equivalence class of reservoirs w.r.t. \sim).
- For *any* cyclic machines, $\frac{Q_1}{Q_2} \leq \tau_{12}$.

Proof Any (left) & reversible (right) cyclic machine.

Choose #cycles s.t. $Q'_2 = Q_2 (> 0)$. Then by 2nd law: $Q'_1 \geq Q_1$, thus $\frac{Q'_1}{Q'_2} \geq \frac{Q_1}{Q_2}$, and $Q'_1 \geq 0$.



Absolute temperature Assign $T_0 > 0$ to standard reservoir 0 (e.g. 273.15 K at triple point of water). Set $T_1 = \tau_{10} T_0 > 0$ for any other reservoir 1.

Efficiency $\frac{W}{Q_1}$ inherits Carnot inequality: $\frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \leq \eta_{12} \equiv 1 - \tau_{12}^{-1} = 1 - \frac{T_2}{T_1}$ (because $\tau_{12} = \frac{\tau_{10}}{\tau_{20}}$).

Clausius For any cyclic process of a system

$$\oint \frac{\delta Q}{T} \leq 0 \quad (\text{i})$$

with equality iff the process is possible without change of the environment (ii).

Equality holds for quasistatic processes if T & δQ are defined in the system itself (not just via reservoirs).

Proof Extend system to machine in dashed box.

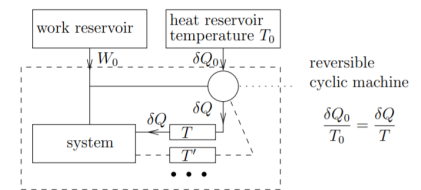
2nd law: $Q_0 =$

$$\oint \delta Q_0 \leq 0 \Rightarrow (\text{i})$$

$$Q_0 + W_0 = 0:$$

$$Q_0 = 0 \Rightarrow W_0 =$$

$$0 \Rightarrow (\text{ii})$$



Entropy is defined relative to a reference state z_0 as $S(z) - S(z_0) = \int_{z_0}^z \frac{\delta Q}{T}$ with integration along any quasistatic path (needed for exact differential). Hence, $dU = T dS - p dV$ for quasistatic processes

Entropy Theorem For adiabatically closed systems and *any* process $z_1 \rightarrow z_2$ we have $S(z_1) \leq S(z_2)$ and equality iff $z_2 \rightarrow z_1$ is possible without change of environment.

Proof Adiabatically closed: $\delta Q = 0$. Add quasistatic return, Clausius: $\oint \frac{\delta Q}{T} = S(z_1) - S(z_2) \leq 0$.

Equations of state thermal $p = p(T, V)$ and caloric $U = U(T, V)$ equations of state specify thermodynamic properties. They are related by $\left. \frac{\partial U}{\partial V} \right|_T = T^2 \left. \frac{\partial p}{\partial T} \right|_T$, hence the entropy $S = S(U, V)$ equivalently describes all thermodynamic properties

$$S = S(U, V) \longleftrightarrow \begin{cases} p = p(T, V) \\ U = U(T, V) \end{cases}$$

by $\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T}$, $\left. \frac{\partial S}{\partial V} \right|_U = \frac{p}{T}$ and solving for U, p .

Derivation Use that dS is exact differential, i.e. mixed derivatives agree: $dS = \frac{1}{T}(dU + p dV) = \frac{1}{T} \left. \frac{\partial U}{\partial T} \right|_V dT + \frac{1}{T} \left(\left. \frac{\partial U}{\partial V} \right|_T + p \right) dV$, take mixed derivatives $0 = \frac{\partial}{\partial V} \left[\left. \frac{1}{T} \frac{\partial U}{\partial T} \right|_V \right]_T - \frac{\partial}{\partial T} \left[\left. \frac{1}{T} \frac{\partial U}{\partial V} \right|_T + \frac{p}{T} \right]_V = \frac{1}{T^2} \left. \frac{\partial U}{\partial V} \right|_T - \frac{\partial(p/T)}{\partial T} \Big|_V$

Maxwell relations $\left. \frac{\partial(1/T)}{\partial V} \right|_V = \frac{\partial^2 S}{\partial U \partial V} = \left. \frac{\partial(p/T)}{\partial U} \right|_V$
Equivalent to coupling of thermal and caloric state equations (both express exactness of dS)

Heat capacity $C_V := \left. \frac{\delta Q}{\delta T} \right|_V = \left. \frac{\partial U}{\partial T} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V$

Entropy (ideas gas) $S - S_0 = R \log \frac{V}{V_0} + \int_{T_0}^T C_V(T) \frac{dT}{T}$

Third law In short: $\lim_{T \rightarrow 0} S(T, x) = \text{const.}$ Detailed:

- Existence of limit: $S(T, V) = \int_{T_0}^T d\tau \frac{C_V(\tau, V)}{\tau}$ converges at $\tau = 0$. Requires $C_V \rightarrow 0$ as $T \rightarrow 0$
- Independence: $\lim_{T \rightarrow 0} \left. \frac{\partial S}{\partial V} \right|_T = C$, requ $\left. \frac{\partial p}{\partial V} \right|_T \rightarrow 0$

Thus also $C_V \rightarrow 0$ and any derivatives of S w.r.t. state variables. The law can be violated.

2 Thermodynamic Potentials

Introduce amount of substance N : states (U, V, N)

Constrained equilibria state (z_1, z_2) (isolated sub-states): $U(z_1, z_2) = U(z_1) + U(z_2), S(z_1, z_2) = S(z_1) + S(z_2)$

Derivation U additive (bc W), same reference state

Maximum entropy principle "In a closed system the entropy is maximal in complete equilibrium." Comparison between the entropy $S(z)$ and that $S(z_1) + S(z_2)$ of all constrained equilibria (z_1, z_2) with $z_1 + z_2 = z$

$$S(z) = \max_{\substack{z_1, z_2 \\ z_1 + z_2 = z}} [S(z_1) + S(z_2)]$$

Derivation

- Remove constraint, call state $z_1 + z_2$

- $U(z_1, z_2) = U(z_1 + z_2)$ since $W = 0$
- Thus $z_1 + z_2 = (U_1 + U_2, V_1 + V_2, N_1 + N_2)$
- $S(z_1) + S(z_2) = S(z_1, z_2) \leq S(z_1 + z_2)$ (Superadditivity) by entropy theorem
- Complete equilibrium for equality

Homogeneity is $U(\lambda z) = \lambda U(z), S(\lambda z) = \lambda S(z)$, ($\lambda > 0$). Functions homogeneous of degree 1 (0) are called extensive (intensive).

Derivation Apply constrained equilibria λ times, then $\lambda U(z_0) = U(z_0, \dots, z_0) = U(\lambda z_0)$ with reference state $z_0 = (U_0, V_0, N_0 = 1)$. Implies result for any state z with $\lambda z = (\lambda U, \lambda V, \lambda N)$. Technicality: for λ integer $\lambda z = z + \dots + z$, $\lambda^{-1} z$ such that $\lambda \cdot \lambda^{-1} z = z$.

Chemical potential defined as $\mu := \left. \frac{\partial U}{\partial N} \right|_{S, V}$

Homogeneity relation

$$U = TS - pV + \mu N, \quad S = \frac{1}{T} (U + pV - \mu N)$$

Thus $\left. \frac{\partial S}{\partial U} \right|_{V, N} = \frac{1}{T}$, $\left. \frac{\partial S}{\partial V} \right|_{U, N} = \frac{p}{T}$, $\left. \frac{\partial S}{\partial N} \right|_{U, V} = -\frac{\mu}{T}$. Requires the assumption of continuous differentiability of S . Physically justified since (U, V, N) determines p, T (not necessarily conversely, not even at fixed N) and S strictly monotonically increasing in $T > 0$

Derivation $\frac{d}{d\lambda} [U(\lambda S, \lambda V, \lambda N)] = \frac{d}{d\lambda} [\lambda U(S, V, N)]$

Concavity of entropy

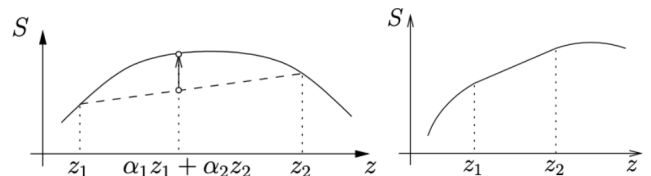
$$S(\alpha_1 z_1 + \alpha_2 z_2) \geq \alpha_1 S(z_1) + \alpha_2 S(z_2)$$

Physically, concavity means that $S(\alpha_1 z_1 + \alpha_2 z_2)$ is greater or equal to entropy of constrained equilibrium $S(z_1) + \alpha_2 S(z_2)$. Points on graph $S(z)$ are equilibrium points, points below are constrained equilibria. Equivalent to semidefiniteness of hesse matrix

$$\partial^2 S = \begin{pmatrix} \frac{\partial^2 S}{\partial U^2} & \frac{\partial^2 S}{\partial U \partial V} \\ \frac{\partial^2 S}{\partial V \partial U} & \frac{\partial^2 S}{\partial V^2} \end{pmatrix}$$

i.e. $\frac{\partial^2 S}{\partial U^2} \leq 0, \det \partial^2 S \geq 0$.

Derivation Use superadditivity and homogeneity.



Complete equilibrium in entropy is characterized by linear stretch. The following are equivalent:

- z_1, z_2 are in equilibr: $S(z_1 + z_2) = S(z_1) + S(z_2)$
- $S(z)$ is linear in between z_1, z_2 , i.e. for $\alpha \in (0, 1)$ $S(\alpha z_1 + (1 - \alpha) z_2) = \alpha S(z_1) + (1 - \alpha) S(z_2)$

iii) $\nabla S(z_1) = \nabla S(z_2)$, i.e. $(T_1, p_1, \mu_1) = (T_2, p_2, \mu_2)$

Derivation i) $\iff S\left(\frac{z_1+z_2}{2}\right) = \frac{1}{2}S(z_1) + \frac{1}{2}S(z_2)$

- (i) \implies (ii): Tangent at $\frac{z_1+z_2}{2}$ must contain z_1, z_2 , otherwise $S(z_1)$ or $S(z_2)$ would lie beneath it due to concavity, which would violate i) $S\left(\frac{z_1+z_2}{2}\right) = \frac{S(z_1)+S(z_2)}{2}$. *Alternative:* i) means that entropy at midpoint $S\left(\frac{z_1+z_2}{2}\right)$ equals the average entropy of endpoints $\frac{S(z_1)+S(z_2)}{2}$. Concavity requires the connection between z_1, z_2 to be linear.
- (ii) \implies (i): is a special case with $\alpha = 1/2$
- (ii) \implies (iii): chord is contained in tangent at z_1 , hence contains $(z_2, S(z_2))$, thus is tangent at z_2 .
- (iii) \implies (ii): tangent planes at z_1, z_2 are parallel, hence must coincide for otherwise lower would not be above $(z_1, S(z_1))$ or $(z_2, S(z_2))$.

Gibbs-Duhem relation $S dT - V dp + N d\mu = 0$
Only 2 of intensive variables T, p, μ are independent.

Derivation $T dS + S dT = d(TS) = dU + p dV - \mu dN + V dp - N d\mu = T dS + V dp - N d\mu$ using homogeneity relation and entropy's differential dS .

Incomplete equilibria

- Fixed diathermal wall (exchange of heat only):
 $T_1 = T_2$ by maximum entropy principle $0 = \frac{\partial S(U_1 - \Delta U)}{\partial(\Delta U)} + \frac{\partial S(U_2 - \Delta U)}{\partial(\Delta U)} = \frac{1}{T_1} - \frac{1}{T_2}$
- Movable adiabatic wall (exchange of volume only): has $p_1 = p_2$, follows from $dU_i = -p_1 dV_i$, $dU_1 + dU_2 = 0, dV_1 + dV_2 = 0$.
- Exchange of two quantities: full equilibrium

Stability conditions

- Heat capacity: $0 < C_V \equiv \frac{\partial U}{\partial T} \Big|_V \leq +\infty$
- Isoth compressibility: $0 < \kappa_T \equiv -\frac{1}{V} \frac{\partial V}{\partial p} \Big|_T \leq \infty$

Can be used to derive $C_p - C_V = -T \frac{(\partial V / \partial T)_p^2}{(\partial V / \partial p)_T} \geq 0$

Derivation Concavity of entropy is equivalent with $\frac{\partial^2 S}{\partial U^2} \leq 0, \det \partial^2 S \geq 0$. It is enough to consider $N = 1$ since $\alpha_1(U_1, V_1, N_1) + \alpha_2(U_2, V_2, N_2) = N \left[\beta_1 \left(\frac{U_1}{N_1}, \frac{V_1}{N_1}, 1 \right) + \beta_2 \left(\frac{U_2}{N_2}, \frac{V_2}{N_2}, 1 \right) \right]$ with $N = \alpha_1 N_1 + \alpha_2 N_2, \beta_i = \alpha_i N_i / N$. Then:

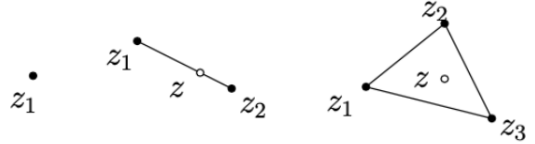
- $0 \geq \frac{\partial^2 S}{\partial U^2} \Big|_V = \frac{\partial(T^{-1})}{\partial U} \Big|_V = -T^{-2} \left(\frac{\partial U}{\partial T} \right)_V^{-1}$, hence $C_V \geq 0$. $C_V = 0$ is unphysical, hence $C_V > 0$.
- $0 \leq \det \partial^2 S = \det \frac{\partial \left(\frac{1}{T}, \frac{p}{T} \right)}{\partial (T, V)} \det \frac{\partial (T, V)}{\partial (U, V)} = -\frac{1}{T^2} \frac{1}{T} \frac{\partial p}{\partial V} \Big|_T \cdot \frac{\partial T}{\partial U} \Big|_V$ (off-diagonals cancel)
- $C_p = \frac{\partial(U+pV)}{\partial T} \Big|_p = \frac{\partial U}{\partial T} \Big|_p + p \frac{\partial V}{\partial T} \Big|_p = \frac{\partial U}{\partial T} \Big|_V +$

$\left(\frac{\partial U}{\partial V} \Big|_T + p \right) \frac{\partial V}{\partial T} \Big|_p$, use $\frac{\partial U}{\partial V} \Big|_T = T^2 \frac{\partial p / T}{\partial T} \Big|_V$ to obtain $\frac{\partial U}{\partial V} \Big|_T + p = T \frac{\partial p}{\partial T} \Big|_V = -T \frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T}$

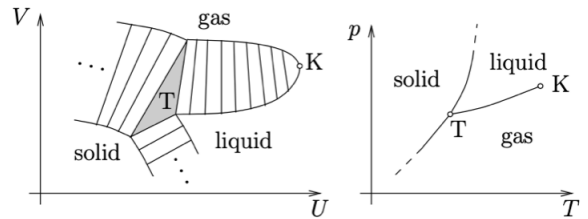
Pure and mixed phases S differentiable, hence each point has one tangent. Since surface is concave, any value of (T, p) determines exactly one tangent plane, but not necessarily one point of contact, but a set of points which are in equilibrium are possible:

- Contact at a point: $z_1 = (U, V)$ uniquely determined by (T, p)
- Contact along a segment: each state with same (T, p) can be uniquely represented as a mixture
- Contact at a triangle: each state with same (T, p) can be uniquely represented as a mixture

A mixture is characterized by $z = \sum_{i=1}^k \alpha_i z_i, \alpha_i \geq 0, \sum_{i=1}^k \alpha_i = 1$ with pure phases z_i and $k = 1, 2, 3$ is for point/segments/triangles.



Entropy surface & phase diagram One segment correspond to one point in p, T -diagram. Vapour pressure curve ends in critical point K . In white areas (pure phases) entropy strictly concave and $(U, V) \leftrightarrow (T, p)$ bijective. Liquid and gas cannot strictly be distinguished.

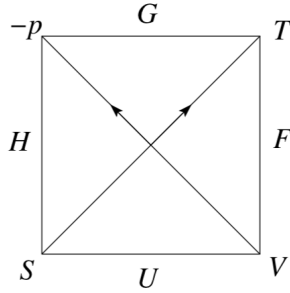


Gibbs rule

- The allowed convex contact sets are simplices.
- For a system with two coordinates (U, V) the number of degrees of freedom (independent intensive variables (T, p)) is $f = 3 - n$, where n is the number of coexisting pure phases.

Order of phase transitions Second order in critical point, elsewhere first order.

2.1 Further Thermodynamic Potentials



$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN, S = \frac{1}{T}(U + pV - \mu N)$$

$$dU = T dS - p dV + \mu dN, U = TS - pV + \mu N$$

$$dF = -S dT - p dV + \mu dN, F = U - TS = -pV + \mu N$$

$$dH = T dS + V dp + \mu dN, H = U + pV = TS + \mu N$$

$$dG = -S dT + V dp + \mu dN, G = F + pV = \mu(T, p)N$$

$$d\Omega = -S dT - p dV - N d\mu, \Omega = F - \mu N = -pV$$

U, F, G, Ω are concave in T, p, μ .

$U, F, H (G, \Omega)$ are convex (linear) in V, N .

From S to U Internal energy U determines thermodynamics as $\nabla U = (T, -p, \mu)$ like $S(U, V, N)$. $U(S, V, N)$ is subadditive, convex and homogeneous of degree 1 in S, V, N .

Derivation S strictly monotonically increasing in U , relation $S \leftrightarrow U$ bijective at fixed V, N .

Motivation for other potentials Often const T and/or p , then maximum entropy principle not directly applicable.

2.1.1 Free energy

Legendre transformation Map $T \mapsto -F(T, V, N)$ is Legendre transform of U w.r.t. S .

$$\begin{aligned} F(T, V, N) &= \inf_S [U(S, V, N) - TS] \\ &= U(S, V, N) - TS \\ &= -pV + \mu N \end{aligned}$$

with S a solution of $\frac{\partial U}{\partial S}(S, V, N) = T$ if existent.

$$\begin{aligned} dF &= dU - T dS - S dT \\ &= -S dT - p dV + \mu dN \end{aligned}$$

i.e. $\frac{\partial F}{\partial T}|_{V, N} = -S, \frac{\partial F}{\partial V}|_{T, N} = -p, \frac{\partial F}{\partial N}|_{T, V} = \mu$ (one-sided derivatives where $T \mapsto F(T)$ has a corner).

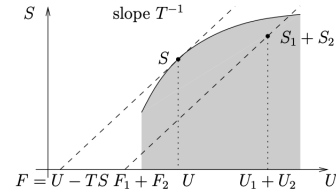
Remark (Thermodynamics from F) Map $(S, V, N) \mapsto (T, V, N)$ not invertible if energy surface contains flat piece, thermodynamics still described by free energy since Legendre transform invertible.

Concavity $F(T, V, N)$ strictly concave in $T > 0$ and convex in (V, N) .

Minimum principle for F At fixed total volume and substance and of fixed temperature the free energy is minimal in complete equilibrium.

$$F(T, V_1, N_1) + F(T, V_2, N_2) \geq F(T, V_1 + V_2, N_1 + N_2)$$

Derivation Using max entropy principle:

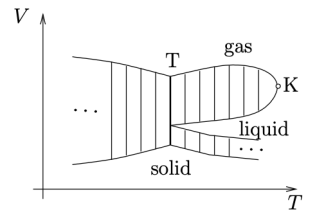


Intercepts of dashed lines (same slope = $1/T$) express minimum principle for free energy.

Stability conditions for F

- i) From $0 > \frac{\partial^2 F}{\partial T^2}|_V = -\frac{\partial S}{\partial T}|_V = -\frac{1}{T} \frac{\partial Q}{\partial T}|_V = -\frac{C_V}{T}$:
 $0 < C_V \leq +\infty$ with divergence in corner of $F(T)$
- ii) $0 \leq \frac{\partial^2 F}{\partial V^2}|_T = -\frac{\partial p}{\partial V}|_T = \frac{1}{V \kappa_T}$: $0 < \kappa_T \leq +\infty$

$F(T, V)$ surface has a corner as function of T above the line of the triple point T .



Relation to pressure

$$-p(T, \mu) = \inf_{\rho} [f(T, \rho) - \mu \rho]$$

$\rho = \frac{N}{V}$. Along phase coexistence (linear stretch, figure above) p, μ are constant in $F = -pV + \mu N$, hence $\frac{F}{V} = f(T, \rho) = -p + \mu \rho$ has such a stretch in ρ .

2.1.2 Enthalpy

Legendre transform Map $-p \mapsto -H(S, p, N)$ is Legendre transform of U w.r.t. V .

$$\begin{aligned} H(S, p, N) &= \inf_V [U(S, V, N) + pV] \\ &= U(S, V, N) + pV \\ &= TS + \mu N \end{aligned}$$

with V a solution of $\frac{\partial U}{\partial V}(S, V, N) = -p$ if existent.

$$\begin{aligned} dH &= dU + p dV + V dp \\ &= T dS + V dp + \mu dN \end{aligned}$$

Concavity $H(S, p, N)$ strictly concave in p and convex in (S, N) .

2.1.3 Gibbs free energy

Legendre transform

$$\begin{aligned} G(T, p, N) &= \inf_{S, V} [U(S, V, N) - TS + pV] \\ &= \inf_V [F(T, V, N) + pV] \\ &= \inf_S [H(S, p, N) - TS] \\ &= \mu(T, p) \cdot N \end{aligned}$$

with V a solution of $\frac{\partial U}{\partial V}(S, V, N) = -p$ if existent.

$$\begin{aligned} dG &= dU - d(TS) + d(Vp) \\ &= -S dT + V dp + \mu dN \end{aligned}$$

Concavity $G(T, p, N)$ strictly concave in T, p and linear in N .

Relation to chemical potential μ is the Gibbs free energy per mole.

G surface has a ridge (1-parameter family of corners) above the transition curves seen in the phase diagram.

2.1.4 Grand canonical potential

Legendre transform

$$\begin{aligned} \Omega(T, V, \mu) &= \inf_{S, N} [U(S, V, N) - TS - \mu N] \\ &= \inf_N [F(T, V, N) - \mu N] \\ &= -p(T, \mu) \cdot V \\ d\Omega &= -S dT - p dV - N d\mu \end{aligned}$$

Concavity $\Omega(T, V, \mu)$ concave in T, μ , linear in V .

2.2 Van der Waals gas

Van der Waals equation generalizes ideal gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

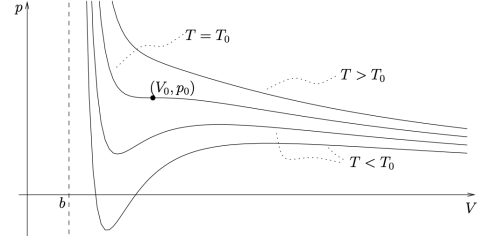
by taking molecule interactions into account.

Derivation

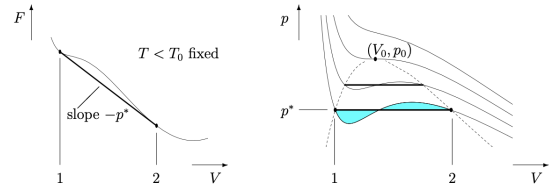
- Use potential $\phi(r)$: repulsive at small r and attractive at large r with minimum in between.
- Modify ideal gas $p'V' = RT$
- Volume is effectively smaller due to the presence of other molecules, $V' = V - b$
- Real molecules attract each other, hence molecules near the wall will be drawn inward.

Proportional to number of particles near wall and of neighbors, hence quadratic in density $1/V$. Thus $p' = p + \frac{a}{V^2}$.

Physical problem Isotherms violate stability conditions and convexity of $F(T, V)$ in parts where $\frac{\partial p}{\partial V}|_T > 0$ that occur for $T < T_0$.



Maxwell construction Replace unphysical non-convex parts of $F(T, V)$ by convex hull, i.e. by a linear part between point 1 and 2 in the following figure. This corresponds to a phase coexistence seen in the free energy surface plot earlier. Within this region, p becomes a constant (in V) called the vapor pressure $p = p^*(T)$, determined by $p^*(V_2 - V_1) = -(F_2 - F_1) = \int_1^2 p dV$.



Critical point is stationary $\frac{\partial p}{\partial V}|_T = p_1(T_0) = 0$ and of inflection $\frac{\partial^2 p}{\partial V^2}|_T = p_2(T_0) = 0$ for $p_n(T) = \frac{\partial^n p}{\partial V^n}|_{V=V_0(T)}$. Additionally $p_3(T_0) < 0$. Parameters are given by $V_0 = 3b, RT_0 = \frac{8}{27} \frac{a}{b}, p_0 = \frac{1}{27} \frac{a}{b^2}$. Thus, the following quotient is universal

$$\frac{RT_0}{p_0 V_0} = \frac{8}{3}.$$

Reduced $\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T}, \tilde{p} = \frac{p}{p_0}, \tilde{V}, \tilde{T} = \dots$

Behavior near critical point (Landau)

$$p(T, V) = p_0(T) + p_1(T)v + p_3(T)v^3 + \dots$$

$$F(T, V) = F_0(T) + F_1(T)v^2 + F_4(T)v^4 + \dots$$

with $F_{n+1}(T) = -\frac{p_n(T)}{n+1}$ and $F_2(T_0) = 0, F_4(T_0) > 0$. This energy is postulated in Landau theory of second order phase transitions. For van der Waals gas $F_1(T) = -1, F_2(T) = 3(T - 1), F_4(T) = 3/8$ at leading order.

Derivation Taylor $p(T, V)$ in V for $T \approx T_0$ using relative $v = V - V_0(T_0)$, then $F(T, V) = F_0(T) - \int_{V_0(T)}^V p(T, V') dV'$.

3 Classical Statistical Mechanics

3.1 Microcanonical ensemble

Classical system is described by

- i) **phase space** $\Gamma = (\Lambda \times \mathbb{R}^3)^N$ s.t. $x \in \Gamma = (x_1, \dots, x_N)$ with $x_i = (q_i, p_i)$, equipped with
- ii) **Hamiltonian** $H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i<j} \varphi(q_i - q_j)$

States are distributions over phase space elements.

$$d\mu(x) = \omega(x) dx \quad (\text{Macrostates, mixed})$$

$$x_0 \in \Gamma \quad (\omega(x) = \delta(x - x_0)) \quad (\text{Microstates, pure})$$

Their time evolution is given by the Hamiltonian flow $x \mapsto \phi_t(x)$ through $\omega_t(x) = \omega(\phi_{-t}(x))$.

Observables are functions f on the phase space Γ .

Liouville theorem states that $D\phi_t = 1$, i.e.

$$\int_{\phi_t(\Omega)} dy = \int_{\Omega} dx$$

Expectation values simplify by Liouville theorem

$$\langle f \rangle_t = \int_{\Gamma} \omega(x) f(\phi_t(x)) dx = \int_{\Gamma} \omega_t(x) f(x) dx$$

3.1.1 Equilibrium: Ergodic hypothesis

Poincare Recurrence A pure state $\phi_t(x_0)$ comes arbitrarily close to x_0 ever and ever again.

Consequence No convergence of $\langle f \rangle_t$ as $t \rightarrow \infty$. Alternate definition of the equilibrium value is needed.

Time average (Birkhoff) of an observable f

$$\langle f \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \langle f \rangle_t dt$$

exists for any ω (Birkhoff theorem).

The state average is defined correspondingly as

$$\bar{\omega} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \omega_t dt = \lim_{T \rightarrow \infty} \bar{\omega}_T.$$

Equilibrium We interpret $\langle f \rangle$ as the expectation value in thermodynamic equilibrium.

Energy shell is the ϕ_t -invariant set

$$\Gamma(E) = \{x \in \Gamma_N \mid H(x) = E\}.$$

Ergodic hypothesis Almost all orbits of energy E come arbitrarily close to any point on $\Gamma(E)$ ever and ever again, and they do this uniformly often.

Precisely: $d\mu_E(x)$ (defined below) is the unique probability measure on $\Gamma(E)$ that is invariant under ϕ_t .

Microcanonical ensemble

$$d\mu_E(x) = \Sigma(E)^{-1} \delta(H(x) - E) dx \quad (\text{ensemble})$$

$$\Sigma(E) = \int_{\Gamma} \delta(H(x) - E) dx \quad (\text{partition function})$$

Consequence For an arbitrary distribution on $\Gamma(E)$, i.e. of form $d\mu = \tilde{\omega}(t) \delta(H(x) - E) dx$, time average is equal to ensemble average

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \langle f \rangle_t dt = \int_{\Gamma} f(x) d\mu_E(x).$$

Thus, $\bar{\omega} = \omega_E$ (time avg. = microcan.) for any ω .

Derivation Equate l.h.s. to $\int_{\Gamma} f(x) \omega(x) dx$. Then $\omega_t = \omega$, thus $\omega = \omega_E$ (uniqueness in ergodicity).

Energy distribution of a general state is

$$W_E = \int \omega(x) \delta(H(x) - E) dx.$$

The resulting thermodynamic equilibrium

$$\langle f \rangle = \int dE W_E \int_{\Gamma} f(x) d\mu_E(x),$$

is solely determined by W_E , as in thermodynamics.

Boltzmann Postulate "The equilibrium state of a system of energy E is the microcanonical ensemble."

Remarks

- **(Failure of ergodic hypothesis)** e.g. for systems with more constraints than just $E = \text{const.}$ Replace $\Gamma(E)$ appropriately.
- **(Macroscopic observables)** approach average fast and deviate little, perceived "approach to equilibrium". Ergodic time scale is experimentally irrelevant (\sim age of universe).

3.1.2 Equilibrium: Entropy & Gibbs variational principle

Entropy of a state ωdx is defined as

$$S(\omega) = -k \int_{\Gamma} \omega(x) \log \omega(x) dx.$$

Remarks

- **(Dimensions)** Replace $\log \omega \rightsquigarrow \log h^{3N} \omega(x)$ (h : units of action). Only adds constant to S , irrelevant due to normalization. May be understood as partitioning Γ into cells.
- **(Uncertainty)** S measures the uncertainty we have about the microstate given the macrostate. It is the only additive and normalized measure.
- **(Motivation)** For the classical case of N particles in k boxes, $-\log \Omega = -N \sum_{i=1}^k \frac{N_i}{N} \log \frac{N_i}{N}$

with $\Omega = \#\text{microstates of the macrostate}$.

Stirling's formula $\log n! \approx n \log n - n$ for $n \rightarrow \infty$

Useful $\log \frac{N!}{\prod n_i!} \approx -\sum n_i \log \frac{n_i}{N}$ if $\sum n_i = N$

Properties of entropy

i) **(Strict Concavity)** For any $\omega_{1,2}$,
 $S(\lambda\omega_1 + (1-\lambda)\omega_2) \geq \lambda S(\omega_1) + (1-\lambda)S(\omega_2)$,
 with equality iff $\lambda = 0, 1$ or $\omega_1 = \omega_2$.

ii) **(Separation)** For ω a state on $\Gamma_1 \times \Gamma_2$, the marginal distributions $\omega_i = \int \omega(x_1, x_2) dx_i$ are states on Γ_i ($i = 1, 2$) and fulfill

$$S(\omega) \leq S(\omega_1) + S(\omega_2).$$

"=" iff $\omega(x_1, x_2) = \omega_1(x_1)\omega_2(x_2)$ (uncorrelated).

iii) **(Hamiltonian conservation)** $S(\omega_t) = S(\omega)$

iv) **(Increase with time)** $S(\bar{\omega}_{nT}) \geq S(\bar{\omega}_T)$ for $T > 0, n \in \mathbb{N}$.

Proof

- i) Follows from strict concavity of $t \mapsto -t \log t$.
- ii) Start with $S(\omega) - S(\omega_1) - S(\omega_2)$, enter the ω_i definitions (outside log) and pull log's together. Use $t \log t \geq t - 1$ and normalization of ω, ω_i .
- iii) Use $\omega_t(x) = \omega(\phi_{-t}(x))$, substitute $y := \phi_{-t}(x)$.
- iv) Like in (iii): $S\left(\frac{1}{T} \int_{t_0}^{T+t_0} \omega_t dt\right) = S\left(\frac{1}{T} \int_0^T \omega_t dt\right)$. Apply (i), induction.

Arrow of time Imagine one ordered state x and one unordered state y . For these pure states the entropy is always $-\infty$ (point in phase space, volume is zero) as $S(x) = \log |\{x\}| = -\infty$. Define macroscopically similar states $\Gamma_{f(x)} = \{x' \in \Gamma \mid |f(x') - f(x)| \leq \epsilon\}$ for some macroscopic observable f . The entropy for a microstate $S(x) = k \log |\Gamma_{f(x)}|$ is then well-defined. Note that $\phi_t(\Gamma_{f(x)}) \neq \Gamma_{f(\phi_t(x))}$ and due to Liouville $\text{vol}(\Gamma_{f(x)}) = \text{vol}(\phi_t(\Gamma_{f(x)}))$. Irreversibility is contained in the initial condition, not within the laws.

Gibbs variational principle Among all states with fixed $E, N, V = |\Gamma|$, the equilibrium state has the maximum entropy.

Microcanonical ensemble maximizes entropy, thus all states of fixed E, N, V are equiprobable.

Proof

- Technical difficulty: S of $\omega(x) = \tilde{\omega}(x)\delta(H(x) - E)$ is $-\infty$ (because $\Gamma(E) = 0$). Replace δ with $\delta_\epsilon(H(x) - E) = \frac{1}{2\epsilon}\theta(|H(x) - E| < \epsilon)$.

- Use $\delta_\epsilon \log \delta_\epsilon = -(\log 2\epsilon)\delta_\epsilon$ to show that $S(\omega_2) - S(\omega_1) \rightarrow \tilde{S}(\tilde{\omega}_2) - \tilde{S}(\tilde{\omega}_1)$ for $\epsilon \rightarrow 0$ (any ω_1, ω_2) (split up in 2 terms: ω_i (vanishes) & $\omega_i \log \omega_i$). Here, $\tilde{S}(\tilde{\omega}) = -k \int dx \delta(H(x) - E) \tilde{\omega}(x) \log \tilde{\omega}(x)$.
- Drop tilde. Set $\omega_2(x) = \Sigma(E)^{-1}$ (microcanon.).
- Use normalization to pull out ω : $S(\omega) - S = -k \int dx \delta(H(x) - E) \omega (\log \omega - \log \Sigma(E)^{-1})$
- Use $t \log t \geq t - 1$ with $t = \frac{\omega}{\Sigma(E)^{-1}}$: integrand $\geq \delta(\dots)(\omega - \Sigma(E)^{-1})$. Integral 0 (normalization).

Entropy in microcanonical ensemble as in proof above we find: $S = k \log \Sigma(E)$ (bzw. $k \log \frac{\Sigma(E)}{h^{3N}}$).

Approximation by θ -function For large N ,

$$\omega dx = \phi(E)^{-1} \theta(H(x) - E) dx$$

$$\phi(E) = \int_{H(x) \leq E} dx$$

yields the same S as the microcanonical ensemble. Independent of this, $\frac{d}{dx} \theta(x) = \delta(x)$ can be used.

Entropy of ideal gas (Sackur-Tetrode)

$$S(U, V, N) = kN \left(\log \left(\frac{V}{N} \cdot \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right)$$

Derivation

- Calculate $\Sigma = \frac{d}{dU} \int_{\{H \leq U\}} dp dq$: $H = \sum_{i=1}^N \frac{p_i^2}{2m}$, thus $\Sigma = V^N \frac{d}{dU} A_{3N} (2mU)^{3N/2}$ with $A_k = \frac{\pi^{k/2}}{\Gamma(\frac{k}{2}+1)}$ volume of unit ball in \mathbb{R}^k .
- A priori: $S = k \log \frac{\Sigma(E)}{h^{3N}}$.
- Large system (U, V, N) : neglect intensive term.
- In thermodynamics: extensive normalization. Here: can add C_N . Same result as $\Sigma \rightsquigarrow \frac{\Sigma}{N!}$.
- Calculate $S = k \log \frac{\Sigma(E)}{N!h^{3N}}$ using Stirling.

Gamma function $\Gamma(n+1) = n!$

Comparison to thermodynamics requires $k := \frac{R}{N_A}$, $c_V := \frac{C_V}{N} = \frac{3}{2}k$. Then: $k^{-1}S(U, V, N) = nc_V \log \frac{U}{U_0} + N \dots$

Remarks

- **(QM)** result agrees for large T and $h = 2\pi\hbar$.
- **(3rd law)** is violated as $S \rightarrow -\infty$ for $T \rightarrow 0$ at fixed V, N since $\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3}{2}k \frac{N}{U}$ ($\Rightarrow U \rightarrow 0$).
- **(Interpretation of Gibbs normalization)** $\Sigma \rightsquigarrow \frac{\Sigma}{N!}$ is the indistinguishability of particles.
- **(Entropy of mixtures)** of 2 particle types ($N_1 + N_2 = N$) is $S(U, V, N_1, N_2) = S(U, V, N) - k \sum_i N_i \log \frac{N_i}{N}$. Understood by $N! \rightsquigarrow N_1!N_2!$ in derivation above: $k \log \frac{N!}{N_1!N_2!} \approx -k \sum N_i \log \frac{N_i}{N}$.

3.2 Equipartition theorem

Energy equipartition theorem For a Hamiltonian system $(x_1, \dots, x_{2f}) = (q_1, p_1, \dots, q_f, p_f)$ with f degrees of freedom and $H(x) \rightarrow +\infty$ for $x \rightarrow \infty$:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} kT.$$

Proof

- $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \Sigma^{-1} \frac{d}{dE} \int_{H(x) \leq E} dx x_i \frac{\partial H}{\partial x_j}$
- Rewrite: $x_i \frac{\partial H}{\partial x_j} = \frac{\partial}{\partial x_j} (x_i (H(x) - E)) - \delta_{ij} (H(x) - E)$. First term 0 (integration in x_j , boundaries).
- Thus $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} \frac{\phi(E)}{\Sigma(E)} = \delta_{ij} \frac{d}{dE} (\log \phi(E))^{-1}$.
- Enter $S \approx k \log \phi(E)$, $\frac{\partial S}{\partial E} = \frac{1}{T}$.

Applied form For a typical Hamiltonian $H = \sum_{i,k} g^{ik} (q_1, \dots, q_f) p_i p_k + V(q_1, \dots, q_f)$ ($g^{ik} = g^{ki}$) follows: $\left\langle \sum_k g^{ik} p_i p_k \right\rangle = \frac{1}{2} kT$ ($i = 1, \dots, f$), where the l.h.s. is kinetic energy of i -th degree of freedom (if g^{ik} diagonal). Similarly for potential energy.

Example virial theorem For $H(q, p) = K(p) + V(q)$ with $K(\lambda p) = \lambda^2 K(p)$, $V(\lambda q) = \lambda^r V(q)$: $\langle K \rangle = \frac{f}{2} kT$ (see above) and $\langle V \rangle = \frac{1}{r} \sum_{i=1}^f q_i \frac{\partial H}{\partial q_i} = \frac{f}{r} kT$. Thus $2 \langle K \rangle = r \langle V \rangle$.

Example ideal diatomic gas has energy (center of mass system) $\frac{P^2}{2M} + \frac{1}{2m} \left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2 \sin^2 \theta} \right) + V(r)$

- $r = \text{const}$: $f = 3 + 2$ (transl + rot) per molecule, thus $\langle H \rangle = \frac{5}{2} NkT$, hence $c_V = \frac{5}{2} R$
- Small osc.: $f = 3 + 2 + 1$ (+ osc), $c_V = \left(\frac{6}{2} + \frac{1}{2} \right) R$. $\frac{1}{2}$ accounts for degree of freedom in potential.

Remark The transition (i) to (ii) is discontinuous in c_V . This issue is resolved in QM-treatment.

3.3 Canonical ensemble

Canonical ensemble is equilibrium state of system with fixed V, N and given T .

$$\omega(x) = Z(\beta)^{-1} e^{-\beta H(x)}$$

$$Z(\beta) = \int_{\Gamma} e^{-\beta H(x)} dx$$

Derivation

- Thermal contact to reservoir $V' \gg V$, $N' \gg N$. Neglect interactions: $H_0(x, x') = H(x) + H'(x)$.
- Combined system "0" has fixed E, V, N , thus microcan. state. Marginalize that: $\omega(x) = \frac{1}{\Sigma_0(E)} \int_{\Gamma'} dx' \delta(H(x) + H'(x) - E) = \frac{\Sigma'(E-H(x))}{\Sigma_0(E)}$.

- Rewrite $\Sigma'(E-H(x)) = e^{k^{-1} S'(E-H(x))}$ because S' slowly varying, can Taylor around E .
- Neglect $\mathcal{O}(\frac{1}{N^r})$ terms (determine order using S , E extensive): $S'(E-H(x)) \approx S'(E) - \frac{\partial S'}{\partial E} \cdot H(x)$.
- $\omega(x) = \frac{\Sigma'(E)}{\Sigma_0(E)} e^{-\beta H(x)}$, define Z as normalization.

Gibbs & canonical ensemble Among all macrostates of fixed V, N and energy expectation $\langle H \rangle$, the canonical ensemble has maximal entropy.

Entropy in canonical ensemble $S(\beta) = k\beta \langle H \rangle + k \log Z(\beta)$ (by taking $\log \omega$, inserting into S).

Free energy in canonical ensemble Partition function determines thermodynamics via $F(T, V, N)$:

$$F(\beta) = -\frac{1}{\beta} \log Z(\beta) \quad \left(U - TS = \langle H \rangle - \frac{1}{k\beta} S \right)$$

This is analogous to S with ϕ (microcanon.).

Mean energy in canonical ensemble

$$\langle H \rangle = U = -\frac{\partial}{\partial \beta} \log Z = \frac{\partial}{\partial \beta} (\beta F)$$

Derivation $U = \frac{\int dx H(x) e^{-\beta H(x)}}{\int dx e^{-\beta H(x)}} = \left(-\frac{\partial Z}{\partial \beta} \right) / Z$

Fluctuation identity of energy U

$$\langle (\Delta H)^2 \rangle = \langle H(x)^2 \rangle - \langle H(x) \rangle^2 = -\frac{\partial U}{\partial \beta} = \frac{\partial^2}{\partial \beta^2} (\beta F)$$

$$C_V = \frac{\partial U}{\partial T} = -\frac{1}{kT^2} \frac{\partial U}{\partial \beta} = \frac{1}{kT^2} \langle (\Delta H)^2 \rangle > 0$$

Derivation Take $-\frac{\partial U}{\partial \beta} = \frac{\int dx H(x) e^{-\beta H(x)}}{\int dx e^{-\beta H(x)}}$ (\rightsquigarrow fraction).

Thermodynamical consequences $C_V > 0$ is thermodyn. stability condition. Implies: $U(T)$ increases monoton., $S(U)$ & $\beta F(\beta)$ & $F(T)$ are concave.

Derivation $\frac{\partial^2 S}{\partial U^2} = -\frac{1}{T^2} \frac{\partial T}{\partial U} \cdot \frac{1}{k} \frac{\partial^2 F}{\partial T^2} = \beta^3 \frac{\partial^2}{\partial \beta^2} (\beta F)$.

Magnitude of fluctuations Usually (if C_V extensive for $N, V \rightarrow \infty$, i.e. $\frac{C_V}{N}$ bounded), fluctuations are small, thus the energy appears sharp macroscopically. However, fluctuations are large near triple point.

$$\langle (\Delta H)^2 \rangle^{1/2} \propto N^{1/2} \ll N \quad (\text{usually})$$

$$\langle (\Delta H)^2 \rangle^{1/2} \propto N \quad (\text{kink in } F, \text{ e.g. triple point})$$

Derivation Usually: $C_V \propto N$. Triple point: energy of phases differs extensively, $\langle (\Delta H)^2 \rangle, C_V \propto N^2$.

Remark (thermodynamics) Thermodynamics: C_V has δ -singularity from $\frac{\partial F}{\partial T}$ -discontinuity. Here: δ is approximate, height $\mathcal{O}(N^2)$, width $\mathcal{O}(N^{-1})$ ($\int_{T_0-\epsilon}^{T_0+\epsilon} C_V dT = \mathcal{O}(N)$).

Equivalence of ensembles The diagram below connects the ensembles and commutes for large systems.

$$\begin{array}{ccc} \Sigma(E) & \xrightarrow{\text{Laplace}} & Z(\beta) \\ \log \downarrow & & \downarrow \log \\ k^{-1}S(E) & \xrightarrow{\text{Legendre}} & -\beta F(\beta) \end{array}$$

Derivation

- Legendre: $-\beta F(\beta) = -\beta \inf_S (U(S) - TS) = \sup_E (\frac{1}{k}S(E) - \beta E)$.
- $Z(\beta) = \int dE e^{g(E)}$, $g(E) = -\beta E + \log \Sigma(E)$. Concavity \Rightarrow saddle point approximation (i.e. Taylor $g(E)$ to 2. order around maximum ($g'(E_0) = 0$, $g''(E_0) = -(kT^2 C_V)^{-1}$) gives $Z(\beta) = e^{-\beta E_0 + \frac{1}{k}S(E_0)} \int dE \exp\left(-\frac{(E-E_0)^2}{2kT^2 C_V}\right)$.
- From $g'(E_0) = 0$: $\frac{1}{k} \frac{dS}{dE} \Big|_{E_0} = \beta$. I.e. E_0 corresponds to β , hence $Z(\beta) = e^{-\beta F(\beta)} \sqrt{2\pi kT^2 C_V}$.
- With $C_V \propto \mathcal{O}(N)$ (more careful at phase transitions): $\log Z(\beta) = -\beta F(\beta) + \mathcal{O}(\log N)$.

3.4 Grand canonical ensemble

Grand canonical ensemble is equilibrium state of system with fixed V and given T, μ .

$$\begin{aligned} \omega(N, x) &= \frac{1}{\Xi(\beta, \mu)} e^{-\beta(H(x) - \mu N)} \\ \Xi(\beta, \nu) &= \sum_{N=0}^{\infty} \int_{\Gamma_N} dx e^{-\beta(H(x) - \mu N)} \\ &= \sum_{N=0}^{\infty} z^N Z_N(\beta), \quad z = e^{\beta\mu} \text{ (fugacity)} \end{aligned}$$

Derivation

- Reservoir: thermal contact & material exchange.
- Marginalize canonical ensemble of total system $\omega(x, N) = \frac{1}{Z_0(\beta)} \int_{\Gamma_{N_0-N}} dx' e^{H'(x') - H(x)}$.
- Expand $F'(\beta, N_0 - N) \approx F'(\beta, N_0) - \mu N$.

Gibbs & grand canonical ensemble Among all macrostates of fixed V and expectation values $\langle H \rangle, \langle N \rangle$, the grand canonical ensemble has maximal entropy.

Entropy in grand canonical ensemble $S(\beta, \mu) = k\beta(\langle H \rangle - \mu \langle N \rangle) + k \log \Xi(\beta, \mu)$ (take $\log \omega$).

Grand canonical potential Ξ determines thermo-

dynamics via p with $\beta p(\beta, \mu) = \frac{1}{V} \log \Xi(\beta, \mu)$ from

$$\Omega(\beta, \mu) = -\frac{1}{\beta} \log \Xi(\beta, \mu) \quad (U - TS - \mu N)$$

Particle number in grand canonical ensemble

$$N = -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \Xi(\beta, \mu).$$

Alternatively show this like U in canonical ensemble.

3.5 Real classical gas

Real classical gas N identical interacting particles.

$$\begin{aligned} H &= \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i<k}^{1\dots N} \phi(x_i - x_k), \quad (x_i \in \Lambda), \\ Z_N(\beta) &= \underbrace{\int_{\Gamma^N} \frac{dx}{N!} e^{-\beta \sum_{i<k} \phi(x_i - x_k)}}_{=: \hat{Z}_N(\beta)} \cdot \underbrace{\int_{\mathbb{R}^{3N}} dp e^{-\beta \sum_i \frac{p_i^2}{2m}}}_{\left(\frac{2\pi m}{\beta}\right)^{3N/2}} \end{aligned}$$

We calculate $\hat{Z}_N(\beta)$ via a cluster expansion of $W(x)$.

Definitions for cluster expansion

- $(C_1, \dots, C_n) =$ partition of $\{1, \dots, N\}$ in subsets C_1, \dots, C_n ("clusters")
- $x_C = (x_{i_1}, \dots, x_{i_l})$ if $C = (i_1, \dots, i_l)$
- $|x_C| = \max_{i,k \in C} |x_i - x_k|$: diameter of C
- $d(x_{C_1}, x_{C_2}) = \min_{i \in C_1, k \in C_2} |x_i - x_k|$: distance between C_1, C_2

Cluster expansion Assume $\phi(y) = 0$ for $|y| > a$ (interaction range is finite). Then $W(x)$ has the cluster property: for any 2-cluster partition (C_1, C_2) with $d(x_{C_1}, x_{C_2}) > a$ one has $W(x) = W(x_{C_1})W(x_{C_2})$. We can expand in clusters:

$$W(x) = \sum_{(C_1, \dots, C_n)} U(x_{C_1})U(x_{C_2}) \dots U(x_{C_n}).$$

This is recursive definition of Ursell function U (the part of W that can't be credited to subsystems of x):

$$U(x) = W(x) - \sum_{\substack{(C_1, \dots, C_n) \\ n > 1}} U(x_{C_1}) \dots U(x_{C_n})$$

$$(U(x_1) = W(x_1) = 1, U(x_1, x_2) = W(x_1, x_2) - 1, \dots)$$

Lemma

- If there exists a partition (C, C') such that $d(x_C, x_{C'}) > a$, then $U(x) = 0$.
- This is the case in particular if $|x| > (N-1)a$.

Proof

- Induction. $N = 1$: Nothing to prove. Inductive step: $U(x) + \sum_{(D_1, \dots, D_k), k > 1} U(x_{D_1}, \dots, x_{D_k}) = W(x) = W(x_C)W(x_{C'}) = \sum_{(C_1, \dots, C_n)} \sum_{(C'_1, \dots, C'_m)} \dots$

Thus $U(x) = - \sum_{\substack{(D_1, \dots, D_k) \\ k > 1}} U(x_{D_1}) \dots U(x_{D_k})$ (sum

over partitions that are **not** refinements of (C, C')). There is at least one D_j that contains particles from both C and C' . Then $U(x_{D_j}) = 0$ by applying induction assumption to $(D_j \cap C, D_j \cap C')$. Thus $U(x) = 0$.

- ii) There is always a partition (C, C') s.t. $d(x_C, x_{C'}) \geq |x|/(N-1)$.

Grand canonical partition function for real (interacting) classical gases using $z = e^{\beta\mu} \cdot \left(\frac{2\pi m}{\beta}\right)^{3/2}$

$$\Xi = \exp\left(V \sum_{l=1}^{\infty} b_l z^l\right),$$

$$b_l(T) = \frac{1}{l!} \int_{\mathbb{R}^{3(N-1)}} dy_2 \dots dy_l U(0, y_2, \dots, y_N)$$

Derivation

- $W(x)$ & $U(x)$ translation invariant, introduce $y_i = x_i - x_1$. Then $\int_{\Gamma^N} U(x) = \int_{\Gamma} dx_1 \int_{(\Gamma - x_1)^{N-1}} dy_2 \dots dy_l U(0, y_2, \dots, y_N)$.
- From lemma: if distance $x_1 \leftrightarrow \partial\Gamma$ is $> (N-1)a$, then we can replace $(\Gamma - x_1)^{N-1} \rightsquigarrow \mathbb{R}^{3(N-1)}$. Boundary layer negligible for large Γ . Thus: $\frac{1}{N!} \int_{\Gamma^N} U(x) = V \cdot b_N(T)$.
- Let n_l = number of clusters of l particles, l_i = number of particles in C_i .
- Thus $\hat{Z}_N = \frac{1}{N!} \sum_{(C_1, \dots, C_n)} \prod_{i=1}^n l_i! (V b_{l_i})$.
- Number of distinct ways of grouping labels $1, \dots, N$ into bins of n_l l -clusters: $\frac{N!}{\prod_l n_l! (l!)^{n_l}}$ (permute each cluster of same number of particles $n_l!$, permute particles within cluster $(l!)^{n_l}$). Constraint $\sum_{l=1}^{\infty} l n_l = N$ (\star).
- $\hat{Z}_N = \sum'_{(n_1, n_2, \dots)} \frac{1}{\prod_l n_l! (l!)^{n_l}} \prod_{i=1}^n l_i! (V b_{l_i} \cdot l!)^{n_i} = \sum'_{(n_1, n_2, \dots)} \prod_l \frac{(V b_l)^{n_l}}{n_l!}$ (\sum' : constraint (\star)).
- Grand canonical ensemble: $\Xi = \sum_{N=0}^{\infty} z_0^N Z_N = \sum_{N=0}^{\infty} z^N \hat{Z}_N = \sum_{(n_1, n_2, \dots)} \prod_{l=1}^{\infty} \frac{(V b_l z^l)^{n_l}}{n_l!} = \prod_{l=1}^{\infty} \sum_{n=0}^{\infty} \frac{(V b_l z^l)^n}{n!} = \prod_{l=1}^{\infty} e^{V b_l z^l}$ (removed constraint)

Virial expansion Equation of state follows as

$$\frac{p}{kT} = \sum_{l=1}^{\infty} \frac{a_l(T)}{v^l}, \quad \sum_{l=1}^{\infty} b_l z^l = \sum_{l=1}^{\infty} a_l \left(\sum_{k=1}^{\infty} k b_k z^k \right)^l.$$

2nd equation: $a_1 = 1, a_2 = -b_2, a_3 = 4b_2^2 - 2b_3, \dots$

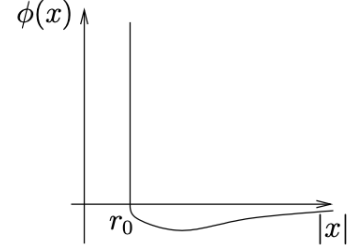
Derivation

- $\frac{p}{kT} = \sum_{l=1}^{\infty} b_l(T) z^l$ from $\beta p = \frac{1}{V} \log \Xi$.

- $\frac{1}{v} = \sum_{i=1}^{\infty} l b_l(T) z^l$ from $\frac{1}{v} = \frac{N}{V} = \frac{1}{\beta V} \frac{\partial}{\partial \mu} \log \Xi$ and $\frac{\partial}{\partial \mu} = \beta z \frac{\partial}{\partial z}$.

Relation to ideal gas $z \rightarrow 0$ ($\mu \rightarrow -\infty$) leads to the ideal gas $\frac{p}{kT} = \frac{1}{v}$. Corrections are obtained iteratively by computing the lowest cluster integrals, starting with $b_2(T) = \frac{1}{2} \int d^3x (e^{-\frac{\phi(x)}{kT}} - 1)$.

Comparison to van der Waals $\frac{p}{kT} = \frac{1}{v-b} - \frac{\tilde{a}/kT}{v^2} = \frac{1}{v} + \left(\tilde{b} - \frac{\tilde{a}}{kT}\right) \frac{1}{v^2} + \dots$ gives $a_2(T) = \tilde{b} - \frac{\tilde{a}}{kT}$.



Example hard-core interaction at large T :

$$e^{-\phi(x)/kT} - 1 \begin{cases} = -1, & (|x| \leq r_0), \\ \approx -\frac{\phi(x)}{kT}, & (|x| > r_0). \end{cases}$$

We then find

$$a_2 = -b_2 = \underbrace{\frac{1}{2} \left(\frac{4\pi}{3} r_0^3 \right)}_{\tilde{b}} + \frac{1}{kT} \cdot \underbrace{\frac{1}{2} \int_{|x| \geq r_0} \phi(x) dx}_{-\tilde{a}}.$$

4 The Ising Model

4.1 The model

Setup Square lattice $\Lambda = (1, 2, \dots, i, \dots, N)$ with periodic boundary conditions and spins $s_i = \pm 1$ at every lattice site i . The system has 2^N spin configurations: $s = (s_1, s_2, \dots, s_N)$.

Generalizations: d dimensions, different geometries.

Energy for a configuration s

$$H(s) = -\frac{1}{2} \sum_{ik} J_{ik} s_i s_k - h \sum_i s_i$$

Hom. external magnetic field h , couplings $J_{ki} = J_{ik}$.

Example (anti-)ferromagnet Couplings

$$J_{ik} = \begin{cases} J & \text{if } i, k \text{ nn} \\ 0 & \text{otherwise} \end{cases}$$

For $J > 0$ ferromagnet, for $J < 0$ antiferromagnet.

Canonical partition function

$$Z(\beta, h, \Lambda) = \sum_s e^{-\beta H(s)} = e^{-\beta F(\beta, h, \Lambda)}$$

Free energy is real-analytic in β, h . Only in the thermodynamic limit

$$f(\beta, h) := \lim_{N \rightarrow \infty} \frac{1}{N} F(\beta, h, \Lambda)$$

of the free energy per spin, a phase transition can manifest as a singularity.

Thermodynamic quantities (per spin)

- Energy $u = \frac{\langle H \rangle}{N} = -\frac{1}{N} \frac{\partial \log Z}{\partial \beta} = \frac{\partial}{\partial \beta} (\beta f)$
- Heat capacity (at fixed h) $c_h = \frac{\partial u}{\partial T} = -k\beta^2 \frac{\partial^2}{\partial \beta^2} (\beta f) = \frac{k\beta^2}{N} \left(\langle H^2 \rangle - \langle H \rangle^2 \right) \geq 0$
- Magnetization $m = \langle s_i \rangle = \frac{1}{N} \sum_i \langle s_i \rangle$ (translation invariance) $= \frac{1}{\beta N} \frac{\partial}{\partial h} \log Z = -\frac{\partial f}{\partial h}$
- Susceptibility $\chi = \frac{\partial m}{\partial h} = -\frac{\partial^2 f}{\partial h^2} = \frac{\beta}{N} \left(\langle (\sum_i s_i)^2 \rangle - \langle \sum_i s_i \rangle^2 \right) (\geq 0) = \frac{\beta}{N} \sum_{ik} \langle s_i s_k \rangle - \langle s_i \rangle \langle s_k \rangle$ (i fixed, translation invariance)

Lattice gas has one or zero particle(s) per site i :

$$n_i \in \{0, 1\} \quad \text{for } i \in \Lambda \quad (\text{particle per site})$$

$$n = (n_1, n_2, \dots, n_N) \quad (\text{configuration})$$

$$\tilde{H}(n) = \frac{1}{2} \sum_{ik} W_{ik} n_i n_k \quad (\text{energy})$$

Lattice gas \longleftrightarrow **Ising model** Use substitution

$$s_i = 2n_i - 1.$$

Then

$$\tilde{H}(n) - \mu \sum_i n_i = H(s) - C|\Lambda|$$

with $J_{ik} = -\frac{W_{ik}}{4}$, $h = \frac{\mu}{2} - \frac{W_0}{4}$, $W_0 = \sum_k W_{ik}$ (i -independent, translation invariance) and $C = \frac{\mu}{2} - \frac{W_0}{8}$. This relates grand canonical partition function of lattice gas to canonical one of the Ising model. Thereby

$$-\Omega(\beta, \Lambda, \mu) = -F(\beta, \Lambda, h) + C|\Lambda|,$$

$$p(\beta, \mu) = -f(\beta, h) + C,$$

$$n(\beta, \mu) \equiv \frac{1}{|\Lambda|} \left\langle \sum_i n_i \right\rangle = \frac{1}{2} (m(\beta, h) + 1).$$

4.2 The mean-field approximation

Assume ferromagnetic coupling $J_{ik} > 0$.

Mean-field approximation Replace

$$s_i s_k \longrightarrow s_i m(s), \quad m(s) := \frac{1}{N} \sum_{k=1}^N s_k, \quad \text{or}$$

$$J_{ik} \longrightarrow J, \quad J := \frac{1}{N} \sum_k J_{ik}.$$

Then

$$H \longrightarrow \tilde{H}, \quad \tilde{H}(s) = -\frac{N}{2} J m(s)^2 - N h m(s)$$

with $m \in \{-1, -1 + \frac{2}{N}, -1 + \frac{4}{N}, \dots, 1 - \frac{2}{N}, 1\} \equiv M_N$.

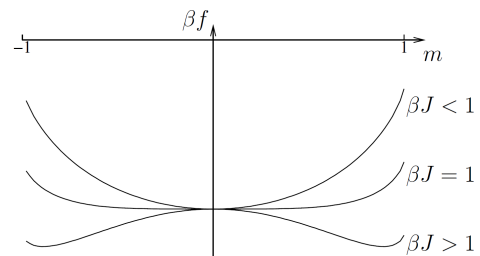
The function f ($-1 \leq m \leq +1$)

$$\beta f(m) := \beta f(m, \beta, h) = -\beta \left(\frac{J}{2} m^2 + h m \right) + \frac{1+m}{2} \log \frac{1+m}{2} + \frac{1-m}{2} \log \frac{1-m}{2}$$

$$\beta f'(m) = -\beta(Jm + h) + \operatorname{arctanh} m$$

$$\beta f''(m) = -\beta J + \frac{1}{1-m^2}$$

See graph of $f(m)$ for $h = 0$ below.



Remark (concavity/convexity of f) Note: first term in f is concave, last two are convex ($x \log x$).

Partition function With f as above we obtain

$$\tilde{Z} = \sum_{m \in M_N} e^{-N\beta f(m) + o(N)} \approx e^{-N\beta f(m_0) + o(N)}.$$

Derivation

- #spins ± 1 for given m : $N_{\pm} = \frac{1 \pm m}{2} N$ (use $N_+ + N_- = N$, $N_+ - N_- = Nm$). Thus #configurations: $\binom{N}{N_+} = \frac{N!}{(\frac{1+m}{2}N)!(\frac{1-m}{2}N)!}$.
- $\tilde{Z} = \sum_{m \in M_N} \frac{N!}{(\frac{1+m}{2}N)!(\frac{1-m}{2}N)!} e^{\beta N(\frac{1}{2}Jm^2 + Hm)}$.
Use Stirling $\log n! = n(\log n - 1) + o(n)$.

Thermodynamic limit = $N \rightarrow \infty$, $V \rightarrow \infty$, $\frac{N}{V} = \text{const}$. There, macroscopic thermodynamics is valid.

Free energy per spin in equilibrium the minimum free energy f . In the thermodynamic limit it is

$$\tilde{f}(m_0) = \lim_{N \rightarrow \infty} -\frac{1}{\beta N} \log \tilde{Z},$$

where $m_0 \in (-1, 1)$ denotes a minimum of $f(m)$. This minimum m_0 fulfills the transcendental eq

$$m_0 = \tanh(\beta(Jm_0 + h)) \iff$$

$$\frac{x - \beta h}{\beta J} = \tanh x, \quad \text{with } x = \beta(Jm_0 + h).$$

with $x = \beta(Jm + h)$.

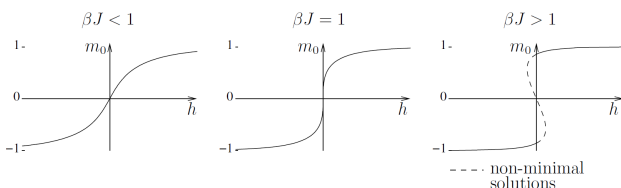
Derivation

- Let m_0 be an absolute minimum of $f(m)$. Then $\min_{m \in M_N} f(m) = f(m_0) + o(1)$ for $N \rightarrow \infty$ (despite M_N discrete) because of continuity of f .
- Rewrite $\binom{N}{N_+} = \frac{N!}{(\frac{1}{2}(1+m)N)!(\frac{1}{2}(1-m)N)!}$.
- With $e^{o(N)} \leq \sum \leq N e^{o(N)} = e^{o(N)}$ & sandwich lemma follows $\tilde{Z} = e^{-N\beta f(m_0) + o(N)}$ ($N \rightarrow \infty$).
- Minima located in open interval $(-1, +1)$ because $f'(\pm 1) = \pm \infty$ at $m = \pm 1$. Thus $f'(m) = 0$ at minimum. Solve.
- Alternative (usual) intuition: self-consistency condition requires $m = \frac{\partial \log Z_1}{\partial h} = \tanh \beta h' = \tanh[\beta(h + Jm)]$, where h' denotes the effective mean-field.

Magnetization The minimum m_0 fulfills the self-consistency condition for $\beta J < 1$ or $h \neq 0$

$$m = -\frac{\partial f}{\partial h} = +m_0(\beta, h)$$

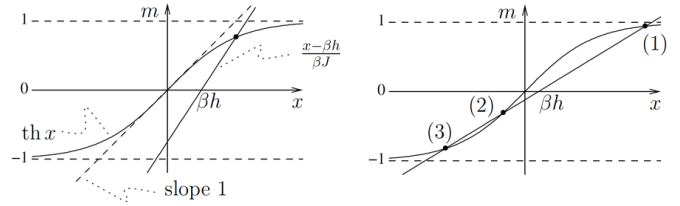
and results in the following isotherms (m_0 as a function of h for given β)



Derivation $m_0(\beta, h)$ differentiable for $\beta J < 1$ or $h \neq 0$, and $-\frac{\partial}{\partial h} f(m_0(\beta, h), \beta, h) = -f'(m_0, \beta, h) \frac{\partial m_0}{\partial h} - \frac{\partial f}{\partial h}(m_0, \beta, h)$ with $f'(m_0, \beta, h) = 0$ (minimum). Define critical temperature $\beta_c J = \frac{J}{kT_c} = 1$. Then

- for $\beta J \leq 1$ ($T \geq T_c$) there is 1 solution $m_0(\beta, h)$,
- for $\beta J > 1$ we have 1 solution if h large, 3 solutions if h small. The positive solution is absolute minimum $m_0(\beta, h)$ (because $f(m) - f(-m) = -2hm$, is < 0 for $m > 0$). Exception: $h = 0$, there $\pm m_0(\beta, h)$ are both absolute minima.

See plot below for graphical sol: (i) left & ii) right.



Spontaneous magnetization means net magnetization $|m| > 0$ without external field. It occurs for $T < T_c$ ($\beta > \beta_c$): $m_0 > 0$ remains for $h \searrow 0$. In fact,

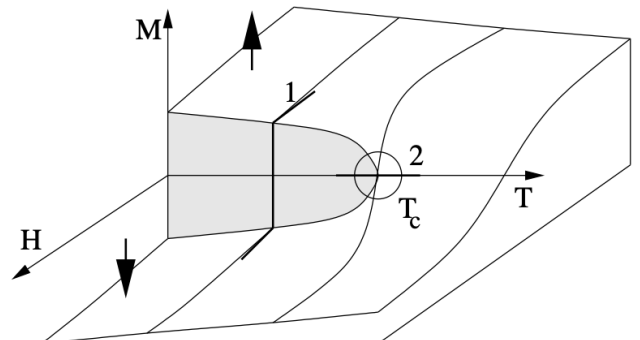
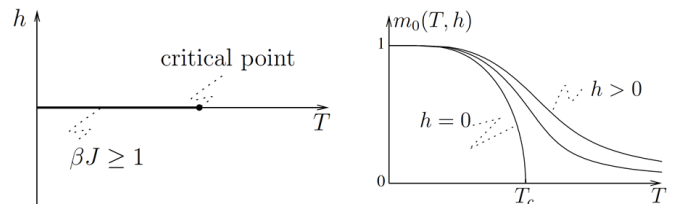
$$m(T, 0) \approx \begin{cases} \sqrt{3(1 - \frac{T}{T_c})} \propto (T_c - T)^\beta, & (T \nearrow T_c) \\ 1 - 2e^{-2T/T_c}, & (T \searrow 0) \end{cases}$$

with $\beta = 1/2$ (critical exponent).

Derivation

- Expand $\tanh x \approx \begin{cases} x - \frac{1}{3}x^3, & (x \rightarrow 0) \\ 1 - 2e^{-2x}, & (x \rightarrow \infty) \end{cases}$
- From before: $\tanh x = \frac{x}{\beta J}$ ($h = 0$), solve for x .

Phase diagrams are shown below.



Susceptibility

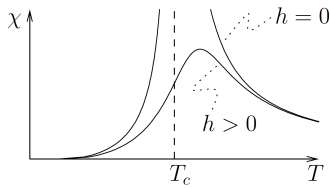
$$\chi = f''(m_0)^{-1} = \frac{1}{\beta^{-1}(1 - m_0^2)^{-1} - J}$$

Derivation

- Take $\frac{d}{dh}$ of $\frac{\partial f}{\partial m}(m_0(\beta, h), \beta, h) = 0$.
- Enter $\frac{\partial m_0}{\partial h} =: \chi$ & $\frac{\partial^2 f}{\partial h \partial m} = -1$ and then $f''(m)$ (all from definition of f).

Curie-Weiss law For $h = 0$ the susceptibility is

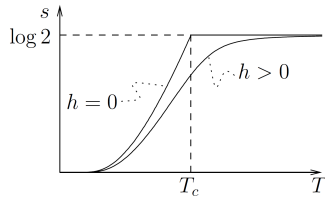
$$\chi(T, h = 0) \begin{cases} = \frac{1}{k(T - T_c)} & T > T_c \\ \approx \frac{1}{2} \frac{1}{k(T_c - T)} & T \uparrow T_c \\ \sim |T - T_c|^{-\gamma} & (\gamma = 1) \end{cases}$$



Derivation

- $T > T_c \Rightarrow m_0 \rightarrow 0 \Rightarrow \chi \approx \frac{1}{\beta^{-1} - J}$
- Expand $\beta^{-1}(1 - m_0^2)^{-1} - J \sim \beta^{-1}(1 + m_0^2 + \dots) - J = \beta^{-1} - J + \beta^{-1}3(1 - \frac{T}{T_c}) = 2k(T_c - T)$.

Entropy $s = k\beta^2 \frac{\partial f}{\partial \beta}$ is in agreement with 3rd law:



Energy

$$u = \frac{\partial}{\partial \beta}(\beta f) = -\frac{J}{2}m_0^2 - hm_0$$

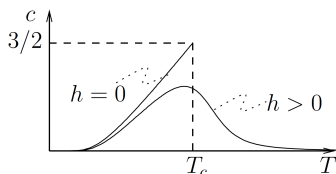
$$u(T, h = 0) = -\frac{J}{2}m_0^2 \approx \begin{cases} 0 & T > T_c \\ \frac{3}{2}k(T - T_c) & T \uparrow T_c \end{cases}$$

Heat capacity

$$c_h(T, h) = \left. \frac{\partial u}{\partial T} \right|_h = -(Jm_0 + h) \left. \frac{\partial m_0}{\partial T} \right|_h$$

$$c_h(T, h = 0) \approx \frac{3}{2}k \sim |T - T_c|^{-\alpha} \quad (T \uparrow T_c)$$

with critical exponent $\alpha = 0$. See also the plot below.



Remarks

i) (**Lattice dimension**) d is irrelevant for MFT, but not for Ising model. There:

- $d = 1$: no phase transition for $T > 0$ ($T = 0$: spontaneous magnetization),
- $d \geq 2$: phase diagrams as in MFT: phase transition curve ($T < T_c, h = 0$) with spontan. magnetization, ends in critical point.

Ising critical exponents match MFT for $d \geq 4$:

	α	β	γ
$d = 2$	0	1/8	7/4
$d = 3$	0.109	$\simeq 0.327$	$\simeq 1.237$
$d \geq 4$	0	0.5	1

ii) (**Phase coexistence in lattice gas**) The two phases of opposite m match liquid & gas phase interpretation of model as lattice gas.

4.3 Peierls argument

Setting Ising model. Take nearest neighbors & $J > 0$ (ferromagnet) as example. Let $h = 0$.

Question At $T = 0$ either $s_i = +1, \forall i \in \Lambda$, or -1 . Is there spontaneous magnetization for small $T > 0$? Yes if typical configs of the canonical ensemble are still mostly “+” or “-”, but not when large “islands” of opposite spins become very probable.

Qualitative Argument

Qualitative answer

- **Case $d = 1$:** No spontaneous magnetization.
- **Case $d = 2$:** Spontaneous magnetization for $T > 0$ small enough.

Qualitative reasoning through discussion of island probability vs. prob. of $\forall i \in \Lambda : s_i = +1 (= p_0)$.

Note: energy difference between 2 aligned vs. opposite spins is $J - (-J) = 2J$ for $k = 2$ nn interaction.

- **Case $d = 1$:** + + + + | $\underbrace{- - -}_{L}$ | + + + +

- Probability of one *particular* island: $p = p_0 e^{-\beta \Delta E}$ with $\Delta E = 2J \cdot 2$.
- Prob. of *arbitrary* island of length L : $\# \cdot p$ (with $\# =$ no. of configs $= N - L + 1$). Then $\# \cdot p = p_0 e^{-\beta(\Delta E - T \Delta S)} \equiv p_0 e^{-\beta \Delta F}$.

- $\# \gtrsim N/2$ for $L \lesssim N/2$, thus $\Delta S \sim \log N$ and $\Delta E \sim \text{const.}$, thus $-\beta\Delta F \gg 1$ for arbitrarily small $T > 0$.
- Hence $p_0 \ll \# \cdot p$, no spontan. magn.

• **Case $d = 2$:**

+++++
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- $\Delta E = 2J \cdot L$ (L : boundary length), I'd rather say it is $\Delta E \geq 2J \cdot L$.
- $\# \lesssim N \cdot 3^L$ (\sim "drawing" the boundary step by step) and $L^2 \gtrsim N/2$ for large islands. Hence $k^{-1}\Delta S = \log \# \lesssim L \log 3 + o(L)$.
- Thus $-\beta\Delta F = k^{-1}\Delta S - \beta\Delta E \lesssim L(\log 3 - 2\beta J) \ll -1$ for large β i.e. small T .
- Then: $p_0 \gg \# \cdot p$, spontan. magn.
- Note: Both ΔE and $T\Delta S$ are of same order in L , thus T settles the competition.

Rigorous Argument

Theorem (Griffith) For spin +1 boundary conditions, $\beta > 0$ large enough, and $h = 0$, we have $\liminf_{\Lambda \rightarrow \infty} \langle m(s) \rangle_{\Lambda+} =: m_+(\beta) > 0$ (where $m(s) = \frac{1}{|\Lambda|} \sum_{x \in \Lambda} s_x$, mean spin).

In words: At low T , the boundary condition at the surface leads to a volume effect (magnetization).

Proof

- Configurations s are given by graphs Γ that separate the islands.
- Graphs do not touch boundary because of "+"-rim, thus energy of s is $H_{\Gamma+}(s) = 2J|\Gamma| - J \cdot N_p$.
- Graph decays in cycles γ with occurrence probability $P(\gamma) = \frac{\sum_{\Gamma \supset \gamma} e^{-2\beta J|\Gamma|}}{\sum_{\Gamma'} e^{-2\beta J|\Gamma'|}}$.
- Denominator $\sum_{\Gamma'} e^{-2\beta J|\Gamma'|} \geq \sum_{\substack{\Gamma' = \Gamma \setminus \gamma \\ \Gamma \supset \gamma}} e^{-2\beta J(|\Gamma| - |\gamma|)}$.

Therefore, $P(\gamma) \leq e^{-2\beta J|\gamma|}$.

- $P(s_x = -1) \leq \sum_{\gamma \supset x} P(\gamma)$ because -1 has to be in interior of a cycle, but not the converse.
- Consider cycles of $2n$ horizontal & $2m$ vertical lattice edges and fixed x . Then surface area of one γ bounded by $m \cdot n$, thus $x \in \Gamma$ can be in interior of at most $m \cdot n$ translations of the cycle. There are at most $3^{(2m+2n)}$ cycles that pass through a given point (consider 3 directions

to "step" boundary). Hence, $P(s_x = -1) \leq \sum_{m,n=0}^{\infty} mn \cdot 3^{(2m+2n)} e^{-2\beta J(2m+2n)}$.

- Thus, $P(s_x = -1) \leq \left(\sum_{n=0}^{\infty} n \cdot e^{2n(\log 3 - 2\beta J)} \right)^2 =: f(\beta) \rightarrow 0$ for $\beta \rightarrow \infty$.
- $\langle s_x \rangle_{\Lambda+} = P(s_x = +1) - P(s_x = -1) = 1 - 2P(s_x = -1)$.
- Together the last two points give: $\langle m(s) \rangle_{\Lambda+} = \frac{1}{|\Lambda|} \sum_{x \in \Lambda} \langle s_x \rangle_{\Lambda+} \geq 1 - 2f(\beta) > 0$.

Lemma (consequences for free energy)

- $f(\beta, h) = f_+(\beta, h)$, i.e. free energy independent of boundary condition in thermodynamic limit.
- $-\frac{\partial f_+}{\partial h} \Big|_{0+} \geq m_+(\beta)$ (one-sided derivative), and hence $+\frac{\partial f}{\partial h} \Big|_{0-} = -\frac{\partial f}{\partial h} \Big|_{0+} > 0$ for $\beta > 0$ large enough (from theorem).

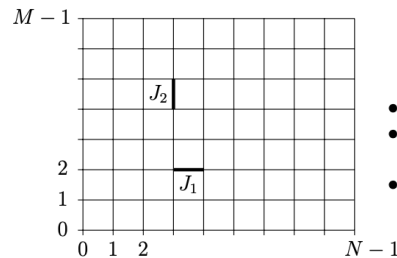
Proof Not done in lecture.

Remarks

- (Generalizations)** to $d \geq 2$, longer range interactions (e.g. next to nearest neighbors), higher spins. But not $d = 1$.
- (Spontaneous symmetry breaking)** happens for Ising model: as $h \rightarrow 0$ it gains discrete spin-flip symmetry $s_x \mapsto -s_x$ (all $x \in \Lambda$), in that $H(s) = H(-s)$ at $h = 0$.

If spin continuous ($\vec{s}_x \in S^{n-1}$, unit sphere & $n \geq 2$), then continuous symmetry $\vec{s}_x \mapsto R\vec{s}_x$ ($x \in \Lambda, R \in \text{SO}(n)$). In $d = 2$, this continuous symmetry does not break spontaneously (theorem of Mermin-Wagner), but it does for $d \geq 3$.

4.4 The exact solution in $d = 2$



- $J_1, J_2 > 0, h = 0$
- periodic boundary conditions in both directions
- β absorbed in J_1, J_2

Setup 2^M configurations $s = (\mu_0, \dots, \mu_{N_1})$ with $\mu = (s_0, \dots, s_{M-1})$. Hamiltonian

$$H(s) = \sum_{i=0}^{N-1} [E(\mu_i) + W(\mu_i, \mu_{i-1})]$$

with $E(\mu) = -J_2 \sum_{m=0}^{M-1} s_m s_{m+1}$, $W(\mu, \mu') = -J_1 \sum_{m=0}^{M-1} s_m s'_m$.

Partition function $Z = Z_{NM}(J_1, J_2)$ & **transfer matrix**

$$Z = \sum_{\mu_0, \dots, \mu_{N-1}} \prod_{i=0}^{N-1} e^{-W(\mu_i, \mu_{i+1}) - \frac{E(\mu_i) + E(\mu_{i+1})}{2}} = \text{tr } T^N$$

$$\langle \mu | T | \mu' \rangle = \exp \left(-W(\mu, \mu') - \frac{E(\mu) + E(\mu_{i+1})}{2} \right)$$

Factorization of $T = V_2^{1/2} V_1 V_2^{1/2}$ with

$$\langle \mu | V_1 | \mu' \rangle = e^{-W(\mu, \mu')}, \quad \langle \mu | V_2 | \mu' \rangle = e^{-E(\mu)} \delta_{\mu\mu'}$$

Largest eigenvalue $\lambda_{\max} \sim$ **partition function** in the thermodynamic limit ($M, N \rightarrow \infty$)

$$-\beta f(J_1, J_2) = \lim_{M \rightarrow \infty} \frac{\lambda_{\max}}{M}$$

In the Onsager solution, it is given by

$$-\beta f(J_1, J_2) = \frac{1}{2} \log(2 \sinh 2J_1) + \frac{1}{2\pi} \int_0^\pi \epsilon(q) dq$$

where $\epsilon(q)$ is the solution of the equation

$$\cosh \epsilon_q = \cosh 2J_1^* \cosh 2J_2$$

$$- \cos q \cdot \sinh 2J_1^* \sinh 2J_2 =: \chi(q).$$

Derivation It holds $\lambda_{\max}^N \leq Z_{MN} \leq 2^N \lambda_{\max}^N$, $\frac{\log \lambda_{\max}}{M} \leq \frac{\log Z_{MN}}{MN} \leq \frac{\log \lambda_{\max}}{M} + \frac{2}{M}$

Phase transitions occur for the condition

$$J_1^* = J_2, q = 0 \quad \text{or} \quad \sinh 2J_1 \cdot \sinh 2J_2 = 1 \quad \text{with}$$

$$J_{\text{critical}} = \frac{1}{2} \sinh^{-1}(1) \approx 0.4406$$

Near the critical point $J \approx J_c$ and $q \approx 0$ the following approximations hold $\chi(q) \approx 1 + 8(J - J_c)^2 + \frac{q^2}{2}$ and $\epsilon(q) \approx [16(J - J_c)^2 + q^2]^{1/2}$.

Derivation

- $\cosh 2(J_1^* - J_2) \leq \chi(q) \leq \cosh 2(J_1^* + J_2)$ for $q \in (0, \pi)$, thus $\chi(q) \geq 1$ and $\chi(1) \iff q = 0 \wedge J_1^* = J_2$, thus $\sinh 2J_1 \cdot \sinh 2J_2 = 1$.
- $[1, \infty) \ni \chi \mapsto \epsilon = \cosh^{-1}(\chi) = \log[\chi + \sqrt{\chi^2 - 1}]$ only singularity at $\chi = 1$, hence ϵ analytic in J_1, J_2 , only $\epsilon(q=0; J_1, J_2)$ singularity for $J_1^* = J_2$, hence critical point.
- $0 = \frac{d}{dJ} |_{J=J^*} \sinh 2J^* \cdot \sinh 2J \implies \frac{dJ^*}{dJ} = -1$
- for $J \approx J_c, q \approx 0$: $J^* - J \approx -2(J - J_c)$
- use $\cosh x(\cos x) \approx 1 \pm \frac{x^2}{2}$, $\sinh x \approx x$ to obtain approximations of $\chi(q), \epsilon(q)$.

Logarithmic divergence manifests in the free energy and the heat capacity, which along the magne-

tization read

$$-\beta f(J) = -\frac{4}{\pi} (J - J_c)^2 \log |J - J_c|$$

$$\frac{c_h}{k} = -\frac{8}{\pi} \log |J - J_c|$$

$$m(J) = \begin{cases} \pm [1 - (\sinh 2J)^{-4}]^{1/8} & J > J_c \\ 0 & J \leq J_c \end{cases}$$

with correct critical exponents $\alpha = 0, \beta = \frac{1}{8}$.

Derivation

- Use approx for $\epsilon(q) \approx |J - J_c| \left(1 + \frac{q^2}{16(J - J_c)^2} \right)^{1/2}$
- $-\beta f(J) = \frac{1}{2\pi} \int_0^\pi \epsilon(q) dq = \frac{4}{\pi} |J - J_c|^2 \int_0^\pi \frac{2 \int_0^\pi (1 + t^2)^{1/2} dt}{4|J - J_c|} = \frac{4}{\pi} (J - J_c)^2 [\log(s + \sqrt{s^2 + 1}) + s\sqrt{s^2 + 1}] \rightarrow -\frac{4}{\pi} (J - J_c)^2 \log |J - J_c|$ as $s = \frac{\pi}{4|J - J_c|} \rightarrow \infty$, use $t = \frac{q}{4(J - J_c)}$
- $\frac{c_h}{k} = \beta^2 \frac{\partial^2}{\partial \beta^2} (\beta f) = -\frac{8}{\pi} \log |J - J_c|$
- $m(J)$: without proof

V_1, V_2 in terms of σ^z, σ^x

$$V_1 = (2 \sinh 2J_1)^{M/2} e^{J_1^* \sum_{m=0}^{M-1} \sigma_m^x} \geq 0$$

$$V_2 = e^{J_2 \sum_{m=0}^{M-1} \sigma_m^z \sigma_{m+1}^z}$$

Derivation **TODO**

V_1, V_2 fermion representation in terms of c_m

$$V_1 = (2 \sinh 2J_1)^{M/2} e^{-2J_1^* \sum_{m=0}^{M-1} (c_m^* c_m - \frac{1}{2})}$$

$$V_2 = e^{-J_2 \sum_{m=0}^{M-1} (c_m^* - c_m)(c_{m+1}^* + c_{m+1})}$$

and V_1, V_2 commute with the parity of N , $(-1)^N$ and thereby with T . This allows to solve the eigenvalue problem separately for subspaces with even (odd) N

Derivation **TODO**

T factorization using Fourier transformation

by transforming $c_m \rightarrow c_q$, T factorizes with commuting factors $T(q)$ as

$$T = (2 \sinh 2J_1)^{M/2} T(0) T(\pi) \prod_{0 < q < \pi} T(q)$$

$$T(q) = V_2(q)^{1/2} V_1(q) V_2(q)^{1/2}$$

with factors for $q = 0, \pi$

$$V_1(q) = e^{-2J_1^* (c_q^* c_q - \frac{1}{2})}$$

$$V_2(q) = e^{2J_2 \cos q (c_q^* c_q - \frac{1}{2})} \quad (\text{for } q = 0, \pi)$$

$$T(q) = e^{-2J_1^* (c_q^* c_q - \frac{1}{2})}$$

and for $0 < q < \pi$

$$V_1(q) = e^{-2J_1^* s_q^z}$$

$$V_2(q) = e^{2J_2 (s_q^z \cos q + s_q^x \sin q)} \quad (\text{for } 0 < q < \pi)$$

with pseudo spin operators

$$s_q^z = c_q^* c_q + c_{-q}^* c_{-q} - 1, \quad s_q^x = c_q c_{-q} + c_{-q}^* c_q^*,$$

$$s_q^y = i(c_q c_{-q} - c_{-q}^* c_q^*), \quad s_q^x s_q^y = -s_q^y s_q^x = i s_q^z \quad (\text{cyclic})$$

that are a representation of the angular momentum algebra (Pauli-matrices) on $\mathbb{C}^2 \otimes \mathbb{C}^2$ (modes $q, -q$).

Derivation TODO

Largest eigenvalue

$$-\beta f(J_1, J_2) = \frac{1}{2} \log(2 \sinh 2J_1) + \frac{1}{2\pi} \int_0^\pi \epsilon(q) dq$$

where $\epsilon(q)$ is the solution of the equation

$$\cosh \epsilon_q = \cosh 2J_1^* \cosh 2J_2$$

$$- \cos q \cdot \sinh 2J_1^* \sinh 2J_2.$$

5 The Renormalization Group

5.1 Scaling hypothesis

Critical exponents characterize singularities of various observables at second order phase transitions.

Example: critical exponents of spin systems (e.g. Ising model) with critical point $J = J_c$ (or $T = T_c$ or $\beta = \beta_c$), $h = 0$ are called:

- Heat capacity

$$c(J) \sim |J - J_c|^{-\alpha} \quad (J \rightarrow J_c)$$

- Spontaneous magnetization

$$m(J, h = 0) \sim |J - J_c|^\beta \quad (J \downarrow J_c)$$

- Susceptibility

$$\chi(J) \sim |J - J_c|^{-\gamma} \quad (J \rightarrow J_c)$$

- Magnetization

$$m(J = J_c, h) \sim h^{1/\delta} \quad (h \downarrow 0)$$

- Correlations (at critical point)

$$\langle s_0 s_x \rangle |_{J=J_c, h=0} \sim |x|^{-(d-2+\eta)} \quad (|x| \rightarrow \infty)$$

η is called the anomalous dimension.

- Correlation length ($h = 0$ but away from crit pt)

$$\langle s_0 s_x \rangle |_{h=0} \sim e^{-|x|/\xi(J)} \quad (|x| \rightarrow \infty, J \neq J_c)$$

$$\xi(J) \sim |J - J_c|^{-\nu} \quad (J \rightarrow J_c)$$

Logarithmic deviations possible. Exponents:

Universality of critical exponents means they

- depend* on dimension d of lattice and symmetry of model (more precisely: of ordered phase), e.g. $\mathbb{Z}_2 = \{\pm 1\}$ (spin flip) for Ising model $\text{SO}(n)$ for n -vector model.

| | Ising | | | Heisenberg |
|----------|---------|---------|---------|------------|
| | $d = 2$ | $d = 3$ | $d = 4$ | $d = 3$ |
| α | 0 | 0.12 | 0 | -0.14 |
| β | 1/8 | 0.31 | 1/2 | 0.3 |
| γ | 7/4 | 1.25 | 1 | 1.4 |
| δ | 15 | 5 | 3 | 4.80 |
| η | 1/4 | 0.05 | 0 | 0.04 |
| ν | 1 | 0.64 | 1/2 | 0.7 |

- are *independent* of type of lattice (quadratic, triangular, etc.) and of spin-couplings (provided they are short-range); and (at $T > 0$) of whether model is classic or quantum.

Remark (direction of limit) Critical exponents are equal on both sides of the critical point (if defined), e.g. $c(T) \approx A_\pm |T - T_c|^{-\alpha_\pm}$ ($T \downarrow \uparrow T_c$) with $\alpha_+ = \alpha_- \equiv \alpha$, but $A_+ \neq A_-$ possible. In case of logarithmic deviations $c(T) = |T - T_c|^{-\alpha} (A_\pm + B_\pm \log |T - T_c|)$, however $B_+ = B_- \equiv B$.

Scaling laws relate critical exponents:

$$\alpha + 2\beta + \gamma = 2, \quad (\text{Rushbrooke})$$

$$\beta(\delta - 1) = \gamma, \quad (\text{Widom})$$

$$\nu(2 - \eta) = \gamma, \quad (\text{Fisher})$$

$$2 - \alpha = \nu d. \quad (\text{Josephson})$$

Change of variables: $t = T - T_c, h = H - H_c$.

Scaling hypothesis Pressure $p(t, h)$ ($= -f$) has a decomposition

$$p(t, h) = p_r(t, h) + p_s(t, h),$$

where p_r regular at $t = h = 0$ & p_s singular with

$$p_s(t, h) = xp(x^s t, x^r h) \quad (\forall x, \text{ some } s, r).$$

Implies:

- $p_s(0, 0) = 0$ (not ∞ because potentials bounded)

- $s, r < 0$ (otherwise $p_s(t, h) = 0$ by $x \rightarrow 0$)

Resulting critical exponents

$$\alpha = \frac{2s + 1}{s}, \beta = -\frac{r + 1}{s}, \gamma = \frac{2r + 1}{s}, \delta = -\frac{r}{r + 1}$$

This confirms Rushbrooke, Widom (scaling laws) and independence of exponents on direction of limit.

Derivation From derivatives (up to regular terms):

$$m(t, h) = \frac{\partial p}{\partial h} = x^{r+1} m(x^s t, x^r h),$$

$$\chi(t, h) = \frac{\partial^2 p}{\partial h^2} = x^{2r+1} \chi(x^s t, x^r h),$$

$$c(t, h) = \frac{\partial^2 p}{\partial t^2} = x^{2s+1} c(x^s t, x^r h).$$

Set $h = 0, x = |t|^{-1/s}$ to obtain

$$m(t, 0) = |t|^{-\frac{r+1}{s}} m(\text{sgn } t = \pm 1, 0),$$

$$\chi(t, 0) = |t|^{-\frac{2r+1}{s}} \chi(\text{sgn } t = \pm 1, 0),$$

$$c(t, 0) = |t|^{-\frac{2s+1}{s}} c(\text{sgn } t = \pm 1, 0),$$

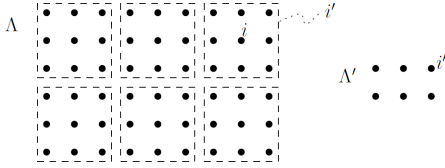
and $t = 0, x = |h|^{-1/r}$ for

$$m(0, h) = |h|^{-\frac{r+1}{r}} m(0, \text{sgn } h = \pm 1).$$

5.2 Renormalization: block spin transformation

Goal Explanation of scaling hypothesis.

Block spin transformation idea Group sites i into blocks i' (size l^d). Decimated lattice with spins $s'_{i'}$.



Possible transformation rules

- i) *majority rule* (Kadanoff): $s'_{i'} = \pm 1$ if $\sum_{i \in i'} s_i \gtrless 0$.
- ii) *linear transformation*: $s'_{i'} = c \sum_{i \in i'} s_i$ ($c > 0$).

c to be chosen s.t. $\{s'_{i'}\}$ and $\{s_i\}$ obey roughly same probability distribution. Extreme examples: all s_i ($i \in i'$) equal: $c = l^{-d}$, all s_i ($i \in i'$) independent: $c = l^{-d/2}$ (by standard deviation for independent spins $\sqrt{l^d} \cdot 1$, which normalizes 70% of outcomes well).

RG transformation Step by step computation of partition function, settling with coarser collection of degrees of freedom (e.g. spin model to block spin model).

First idea Illustrated on Ising model as an example.

- Find renormalization transformation $R : (J, h) \rightarrow (J', h')$ s.t. $e^{-H'(s')} = \sum_{s \rightarrow s'} e^{-H(s)}$ (β

in couplings) with $H(s) = -J \sum_{\langle i, j \rangle} s_i s_j - h \sum_i s_i$ and $H'(s') = -J' \sum_{\langle i', j' \rangle} s'_{i'} s'_{j'} - h' \sum_{i'} s'_{i'}$.

- Then $Z(J', h') = Z(J, h)$. Thermodynamics at (J, h) follow from at (J', h') if RG trafo is known.
- Iterate. $R^n = R^{n-1} \circ R$, ($n = 1, 2, \dots$), $R^0 = \text{id}$ form semi-group (lack inverse).

Failure of that idea $e^{-H'(s')} = \sum_{s \rightarrow s'} e^{-H(s)}$ actually leads to additional couplings (more than nearest neighbors, order k) and constants ($k = 0$) in H' .

Vector space of functions $f : \{\pm 1\}^\Lambda \rightarrow \mathbb{R}$

- $s_X := \prod_{i \in X} s_i$ ($= 1$ if $X = \emptyset$), form orthon. basis
- $2^{|\Lambda|}$ such subsets $X \subset \Lambda$, i.e. $\dim V = 2^{|\Lambda|}$
- $(f, g) := 2^{-|\Lambda|} \sum_s f(s)g(s)$ defines inner product

Derivation Orthonormal by $s^X s^{X'} = s^{X \Delta X'}$ (with Δ symmetric difference) and $\sum_s s^X = 2^{|\Lambda|} \delta_{X, \emptyset}$.

Improved scheme

- Take $H(s) = \sum_{X \subset \Lambda} J_X s^X$ with translation-invariant couplings $\underline{J} = \{J_X\}$. Set additive normalization by $J_\emptyset = 0$.
- J_X found by inverting: $J_X = 2^{-|\Lambda|} \sum_s s^X H(s)$.
- $H'(s') = \sum_{X \subset \Lambda'} J'_X s'^X$ (& thereby J'_X) defined by $e^{-H'(s') - |\Lambda| p_l(\underline{J})} = \sum_{s \rightarrow s'} e^{-H(s)}$ with $p_l(\underline{J})$ chosen as to enforce $J'_\emptyset = 0$.
- Implies $Z_\Lambda(\underline{J}') e^{|\Lambda| p_l(\underline{J})} = Z_\Lambda(\underline{J})$.
- Using $|\Lambda| = |\Lambda'| l^d$, find

$$p(\underline{J}) = p_l(\underline{J}) + l^{-d} p(\underline{J}') \quad \text{with} \quad \underline{J}' = R_l(\underline{J}).$$

Can be viewed as functional for function $p(\underline{J})$ or as recursion relation for $p(\underline{J}^{(n)})$ ($\underline{J}^{(n)} = R_l(\underline{J}^{(n-1)})$).

Assumption made At fixed l , $R_l : \underline{J} \rightarrow \underline{J}'$ & $p_l(\underline{J})$ are regular in \underline{J} (counterexamples exist).

Remarks

- i) (**Λ -dependence of R_l**) Limit $\Lambda \rightarrow \infty$ should exist, thus J'_X independent of $|\Lambda'|$. Exception J'_\emptyset : Extensive (seen from trivial case $H(s) = 0$) if $= 0$ not enforced, hence the form $|\Lambda| p_l(\underline{J})$.
- ii) (**Symmetries**) should be preserved by RG trafo. E.g. spin-flip symmetry $H(s) = H(-s)$: If $J_X = 0$ for $\#(X)$ odd, then need same for J'_X . True if $s \rightarrow s' \iff -s \rightarrow -s'$. Fulfilled by majority rule & linear transformation.

Assumptions on fixed point of R_l

- It exists, i.e. $\exists \underline{J}^* : R_l(\underline{J}^*) = \underline{J}^*$.

- The linearization $DR_l(\underline{J}^*)$ is diagonalizable, eigenvectors $\underline{\phi}^{(i)}$ & positive eigenvalues l^{y_i} .

Motivation for notation l^{y_i} : tangent map $DR_{l^n}(\underline{J}^*) = (DR_l(\underline{J}^*))^n$ of $R_{l^n} = (R_l)^n$ then has eigenvalues $(l^{y_i})^n = (l^n)^{y_i}$ of same form.

Terminology: l^{y_i} with scaling dimension

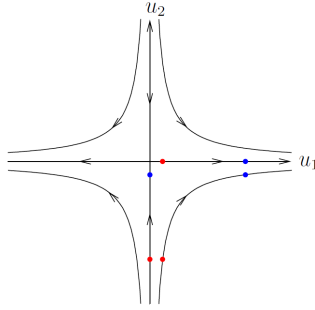
- $y_i > 0$ (expansion) is a relevant eigenvalue
- $y_i = 0$ (neutral) is a marginal eigenvalue
- $y_i < 0$ (contraction) is an irrelevant eigenvalue

Basis transformation to scaling fields $\{\underline{\phi}^{(i)}\}$:

$$\underline{J} - \underline{J}^* = \sum_i u_i \underline{\phi}^{(i)}.$$

R_l acts in linear approximation as $u_i \rightarrow l^{y_i} u_i$.

Example $y_1 > 0$ (relevant), $y_2 < 0$ (irrelevant).



Work in this example now.

p near fixed point found to be

$$p(u_1, u_2) \approx |u_1|^{d/y_1} p(\pm 1, 0) + \sum_{\text{some } \underline{n}} \left(-\frac{h_{\underline{n}}}{y_1} \right) u_{\underline{n}} \log |u_1|$$

with “some $\underline{n} = (n_1, n_2)$ ” given by $d - \sum_{i=1}^n y_i n_i = 0$.

Derivation (important conceptual parts)

$$p(u_1, u_2) - l^{-d} p(l^{y_1} u_1, l^{y_2} u_2) = p_l(u_1, u_2) \quad (\star)$$

is the linear inhomogeneous equation for p to solve:

i) General solution of homogeneous equation.

- $p(0, u_2) = 0$ by letting $l \rightarrow \infty$ (& $y_2 < 0$).
- Take $|u_1| \ll 1$, $l = |u_1|^{-1/y_1}$. Then $p(u_1, u_2) = |u_1|^{d/y_1} p(\pm 1, |u_1|^{y_2/y_1} u_2)$.
- Taylor in u_2 around 0 ($|u_1|^{y_2/y_1} \ll 1$ from $-y_2/y_1 > 0$): $p(u_1, u_2) = |u_1|^{d/y_1} p(\pm 1, 0) + |u_1|^{(d-y_2)/y_1} u_2 p_{,2}(\pm 1, 0) + \dots$
- First part most singular for small u_1, u_2 .

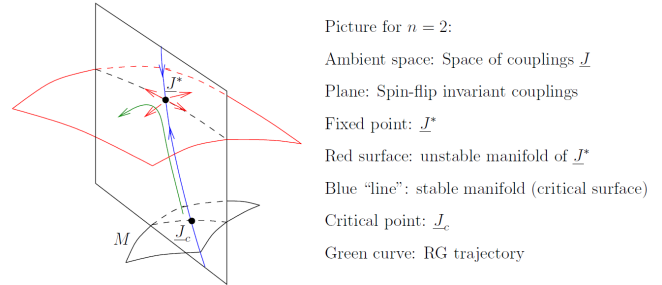
Note: no expansion in u_2 needed in (i), and thus no singularity in u_2 necessary, only in u_1 .

ii) A particular solution of inhomogeneous equ.

- Take $\frac{d}{dl}(\star)|_{l=1}$, define $h(u) = \frac{\partial}{\partial l} p_l(u)|_{l=1}$. Then: $0 = h(u_1, u_2) - d \cdot p(u_1, u_2) + \sum_{i=1}^2 y_i u_i p_{,i}(u_1, u_2)$.

- $h(u)$ regular: $h(u_1, u_2) = \sum_{\underline{n} > 0} h_{\underline{n}} u_{\underline{n}}$ with $\underline{n} = (n_1, n_2)$ and $u_{\underline{n}} = u_1^{n_1} u_2^{n_2}$.
- Ansatz $p(u_1, u_2) = \sum_{\underline{n} > 0} p_{\underline{n}} u_{\underline{n}}$.
- Comparing coefficients yields $p_{\underline{n}} = \frac{h_{\underline{n}}}{d - \sum_i y_i n_i}$.
- If $\frac{h_{\underline{n}}}{y_i}$ rational, denominator can be 0 for some \underline{n} . Then $p_{\underline{n}} u_{\underline{n}}$ is solution to hom. eq. (for that \underline{n}). Hence change corresponding term in Ansatz to $\tilde{p}_{\underline{n}} u_{\underline{n}} \log |u_1|$.
- Comparing coefficients yields $\tilde{p}_{\underline{n}} = -h_{\underline{n}}/y_1$.

Away from fixed point Model with n parameters (e.g. Ising $n = 2$, (J, h)) corresponds to submanifold with $\dim M = n$ in ∞ -dim space of couplings \underline{J} . Let $n = \#$ relevant eigenvalues, then critical surface (stable manifold) has codimension n , hence M will generically intersect it. Intersection corresponds to second-order phase transition at couplings \underline{J}_c .



Picture for $n = 2$:
 Ambient space: Space of couplings \underline{J}
 Plane: Spin-flip invariant couplings
 Fixed point: \underline{J}^*
 Red surface: unstable manifold of \underline{J}^*
 Blue “line”: stable manifold (critical surface)
 Critical point: \underline{J}_c
 Green curve: RG trajectory

By recursion relation & iterations of RG, singular behavior near \underline{J}_c is same as near fixed point \underline{J}^* , where it depends only on relevant variables \Rightarrow scaling hypothesis (see below).

Explanation of scaling hypothesis

- Homogeneous solution for p (i) scales as $p^{(1)}(u_1) = l^{-d} p^{(1)}(l^{y_1} u_1)$, hence explains power law singularity at critical point (with different amplitudes on each side of fixed point).
- Inhomogeneous solution for p (ii) explains logarithmic corrections including their same amplitudes on both sides of fixed point.

Universality Different models intersect critical surface at different critical points, yet have same critical behavior (same fixed point); thus universality.

Models of Ising type Assume RG trafo has fixed point within subspace of spin-flip invariant couplings. Scaling fields at \underline{J}^* are then either even or odd under spin-flip. Just two relevant scaling fields, u_1, u_2 , corresponding to t, h , with even and odd parity, respectively. Then:

$$p_s(t, h) = l^{-d} p_s(t', h'), \quad t' = l^{y_1} t, \quad h' = l^{y_2} h.$$

Comparing to scaling hypothesis with $x = l^{-d}$ gives

$$s = \frac{-y_1}{d}, \quad r = \frac{-y_2}{d}, \quad \text{hence}$$

$$\alpha = 2 - \frac{d}{y_1}, \quad \beta = \frac{d - y_2}{y_1}, \quad \gamma = \frac{2y_2 - d}{y_1}, \quad \delta = \frac{y_2}{d - y_2}.$$

Note For each fixed point \underline{J}^* , spin-flipped couplings $S(\underline{J}^*)$ are one too. Assume it is the same.

Example $d = 2$ From $\alpha = 0$, $\beta = 1/8$ (exact solution) follows $y_1 = 1$, $y_2 = 15/8$. Therefore $d - \sum_{i=1}^2 y_i n_i = 0$ for $n_1 = 2, n_2 = 0$. Hence $p(t, 0)$ has singularity $t^2 \log t$ (indeed in exact solution).

Correlations near critical point

Definition: $\Gamma(x - y; t) := \langle s_x s_y \rangle - \langle s_x \rangle \langle s_y \rangle$.

Recall earlier proposition for correlations at $h = 0$:

$$\Gamma(x - y_i; t) \approx e^{-|x-y|/\xi(t)} \quad \text{for } t \neq 0$$

$$\xi(t) \approx |t|^{-\nu} \quad \text{for } t \rightarrow 0$$

$$\Gamma(x - y_i; t = 0) \approx |x - y|^{-(d-2+\eta)}$$

With RG we can find:

- i) Correlation length $\xi \propto t^{-1/y_1}$, i.e. $\nu = \frac{1}{y_1}$ (since the renormalization step $\xi(t) \mapsto \xi'(t') = \xi(t)/l$, $t \mapsto t' = l^{y_1} t$ motivates $\xi(l^{y_1} t) \stackrel{!}{=} \xi(t)/l$)
- ii) By introducing site-dependent h : confirm $\nu = \frac{1}{y_1}$ and show $\eta = d + 2 - 2y_2$. Fisher & Josephson (remaining scaling laws) follow.

Derivation

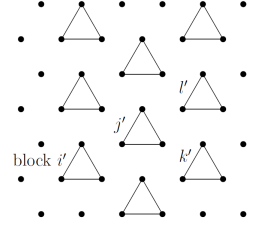
- $e^{-\frac{|x|}{|t|^{-\nu}}} \stackrel{!}{=} e^{-\frac{|x|y_1\nu}{|t|^{-\nu}}}$, hence $|x| \stackrel{!}{=} |x|y_1\nu \Rightarrow \nu = \frac{1}{y_1}$
- Add $-\sum_{x \in \Lambda} h_x s_x$ (site-dependent magnetic field) in Hamiltonian.
- Using $\frac{\partial \log Z}{\partial h_x} = \langle s_x \rangle$ note $\Gamma(x - y; t) = \frac{\partial^2 \log Z(t, h)}{\partial h_x \partial h_y} \Big|_{h=0} = |\Lambda| \frac{\partial^2 p}{\partial h_x \partial h_y} \Big|_{h=0}$.
- Assume generalization $p_s(t, h_x) = l^{-d} p_s(t', h'_{x'})$ with $t' = l^{y_1} t$ and $h'_{x'} = l^{y_2} (l^{-d} \sum_{x \in X'} h_x)$.
- With $\frac{\partial}{\partial h_x} = l^{y_2-d} \frac{\partial}{\partial h'_{x'}}$ and $|\Lambda| l^{-d} = |\Lambda'|$ follows $\Gamma(x - y; t) = l^{2(y_2-d)} \Gamma(x' - y'; l^{y_1} t)$ (here $x' - y' \approx (x - y)/l$).
- Set $y = 0$, pick $l = |x|$, then $\Gamma(x; t) = |x|^{-2(d-y_2)} \Gamma(\frac{x}{|x|}; |x|^{y_1} t)$.
- For $t \neq 0$, exponential decay can only occur with correlation length $\xi(t) = |t|^{-1/y_1}$.
- For $t = 0$, we read $d - 2 + \eta = 2(d - y_2)$, thus $\eta = d + 2 - 2y_2$.
- With coefficients from “models of Ising type”: $\nu(2 - \eta) = \frac{1}{y_1}(2y_2 - d) = \gamma$ and $\nu d = \frac{d}{y_1} = 2 - \alpha$.

5.3 An explicit RG computation

Setting Ising, $d = 2$, triangular lattice.

Choice of block-spin transformation: Majority rule.

Restrict to subspace of even couplings (particularly $h = 0$). Price: lose one relevant eigenvalue.



Order of coupling J_X defined as lowest power J_1^n at which interaction s^X is generated through R . Turns out to be as by mediation.

Correlation of non-nn spins i, k via interaction with a third j : $\langle e^{J_1(s_i s_j + s_j s_k)} \rangle = \langle e^{J_1(s_i s_h)} \rangle \langle e^{J_1(s_j s_k)} \rangle (1 + J_1^2 s_i s_k + \dots)$ (series expansion of the exponentials).

Derivation Use $\langle s_j \rangle = 0$, i.e. $\langle s_i s_j \rangle = s_i \langle s_j \rangle = 0$, $\langle (s_i s_j)^2 \rangle = 1$ and Taylor expansion of exponential.

Truncation of RG map at 2nd order, i.e. $H = -J \sum_{\langle i, j \rangle} s_i s_j - J_2 \sum_{\langle i, k \rangle'} s_i s_k - J_3 \sum_{\langle i, l \rangle''} s_i s_l$, where sums are over 1st, 2nd, 3rd nn.

Decomposition of Hamiltonian $H = H_0 + V$ with $H_0 = \sum_{i'} h((s_i)_{i \in i'})$ (Hamiltonian of a single block) and V all interaction between blocks.

Expectation value after transformation

$$\langle A \rangle_{s'} = Z_0(s')^{-1} \sum_{s: s \rightarrow s'} A(s) e^{-H_0(s)}$$

Partition function after transformation

$$Z_0 := Z_0(s') = \sum_{s \rightarrow s'} e^{-H_0(s)} = \prod_{i'} z(s'_{i'}),$$

$$z(s'_{0'}) = \sum_{(s_i)_{i \in 0'} \rightarrow s'_{0'}} e^{-h(s_i)} = e^{3J_1} + 3e^{-J_1}$$

Derivation For $s'_{0'} = +1$ we have $e^{3J_1} (+ + +)$ and $e^{-J_1} (+ + -, + - +, - + +)$. Same for $s'_{0'} = -1$. Thus $z(s'_{0'})$ independent of $s'_{0'} \Rightarrow Z_0 := Z_0(s')$.

Expectation value of spins For $i, j \in 0'$ we find

$$\langle s_i \rangle_{s'} = z^{-1} ((+1)e^{3J_1} + 2e^{-J_1} + (-1)e^{-J_1}) s'_{0'} = a s'_{0'}$$

$$\langle s_i s_j \rangle_{s'} = z^{-1} ((+1) + (+1)e^{-J_1} + 2(-1)e^{-J_1}) = b$$

$$\text{with } a := \frac{e^{3J_1} + e^{-J_1}}{e^{3J_1} + 3e^{-J_1}} \text{ and } b := \frac{e^{3J_1} - e^{-J_1}}{e^{J_1} + 3e^{-J_1}}.$$

Block-spin Hamiltonian $H'(s')$ given by

$$e^{-(H'(s') - |\Lambda| p_l(\underline{J}))} = \sum_{s \rightarrow s'} e^{-H_0(s) - V(s)} = Z_0(s') \langle e^{-V} \rangle_{s'},$$

hence

$$H'(s') = |\Lambda| p_l(\underline{J}) - \log Z_0 - \log \langle e^{-V} \rangle_{s'}.$$

Cumulant expansion of $-\log \langle e^{-V} \rangle$:

$$-\log \langle e^{-V} \rangle = -\langle V \rangle + \frac{1}{2}(\langle V^2 \rangle - \langle V \rangle^2) + \dots$$

Derivation Use Taylor expansions $\langle e^{-V} \rangle = 1 - \langle V \rangle + \frac{1}{2} \langle V^2 \rangle + \dots$ and $-\log(1-x) = x + x^2/2 + \dots$

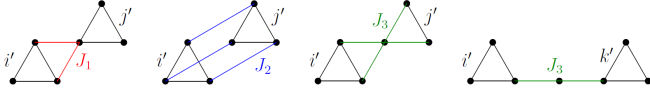
Mean of V is given by the couplings after RG:

| coupling | contribution |
|----------|---------------------------|
| J'_1 | $(2J_1 + 3J_2 + 2J_3)a^2$ |
| J'_2 | J_3a^2 |
| J'_3 | 0 |

Derivation For i, j in blocks $i' \neq j'$ we have

$$\langle s_i s_j \rangle_{s'} = \langle s_i \rangle_{s'} \langle s_j \rangle_{s'} = a^2 s'_{i'} s'_{j'}$$

Count contributions illustrated in figure below:



Variance of V , i.e. $\frac{1}{2}(\langle V^2 \rangle_{s'} - \langle V \rangle_{s'}^2)$:

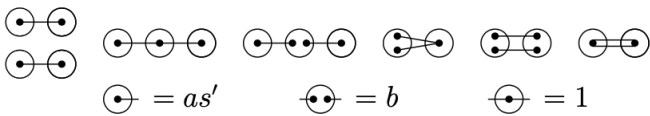
| coupling | contribution |
|----------|--|
| J'_1 | $4J_1^2(a^2 - a^4) + 4J_1^2(a^2b - a^4)$ |
| J'_2 | $J_1^2(a^2 - a^4) + 7J_1^2(a^2b - a^4)$ |
| J'_3 | $4J_1^2(a^2b - a^4)$ |

Derivation Computation of order 2 in total: keep only $V = -J_1 \sum_{[i,j]} s_i s_j$ with $[i, j]$ nn in different blocks. Then

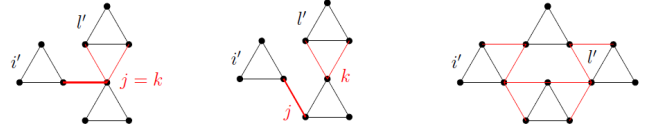
$$\begin{aligned} \langle V^2 \rangle_{s'} - \langle V \rangle_{s'}^2 &= J_1^2 \sum_{[i,j],[k,l]} \langle s_i s_j s_k s_l \rangle - \langle s_i s_j \rangle \langle s_k s_l \rangle \\ &\equiv J_1^2 \sum_{[i,j],[k,l]} \langle s_i s_j, s_k s_l \rangle_{s'} \end{aligned}$$

(omit 1/2 by counting pairs only once). Calculate several cases

$$\langle s_i s_j, s_k s_l \rangle_{s'} = \begin{cases} 0 & i', j', k', l' \text{ pairwise disjoint} \\ (a^2 - a^4) s'_{i'} s'_{l'} & i' \neq l' \text{ and } j = k \\ (a^2b - a^4) s'_{i'} s'_{l'} & i' \neq l', j' = k' \text{ but } j \neq k \\ \text{const} & \text{else.} \end{cases}$$



Alternatively calculate diagrammatically. Then count as before, see figure below.



Result: RG transformation Putting all the above together gives

$$\begin{aligned} J'_1 &= 2J_1a^2 + 4J_1^2(a^2 + a^2b - 2a^4) + 3J_2a^2 + 2J_3a^2 \\ J'_2 &= J_1^2(7a^2b + a^2 - 8a^4) + J_3a^2 \\ J'_3 &= 4J_1^2(a^2b - a^4) \end{aligned}$$

Fixed points of map Trivial one $\underline{J} = 0$ (high temperature) and one at (Newton's method)

$$J_1^* = 0.27887 \quad J_2^* = -0.01425 \quad J_3^* = -0.01523$$

Eigenvalues at fixed point $\lambda_1 = 1.7728$ (relevant) & $\lambda_{2,3}$ (irrelevant). Rewrite $\lambda_1 = l^{y_1}$ with $l = \sqrt{3}$ (s.t. decimation factor $l^2 = 3$) and $y_1 = 1.042$ (1 in exact computation).

Derivation Calculate linearization at fixed point.

$$M = \begin{pmatrix} 1.8313 & 1.3446 & 0.8964 \\ 0.0052 & 0 & 0.4482 \\ 0.0781 & 0 & 0 \end{pmatrix}$$

Critical point J_c can be found from this as $J_c = 0.2574$ (exact result: 0.27465).

Derivation Write $u_i = \underline{\psi}^{(i)} \cdot (\underline{J} - \underline{J}^*)$ with $\underline{\psi}^{(i)}$ dual basis to eigenvectors. Critical surface given by $u_i = 0$. Critical coupling of Ising fulfills $J_1 = J_c$, $J_2 = J_3 = 0$. Thus $\underline{\psi}^{(i)} \cdot J_c = \underline{\psi}^{(i)} \cdot \underline{J}^*$. Enter $\underline{\psi}^{(i)}$.

6 Second Quantization

Single particle definitions states ϕ from single particle Hilbert space \mathcal{H} with ONB $\{\phi_1, \dots, \phi_n\}$. Observable $b : \mathcal{H} \rightarrow \mathcal{H}$. For states as wavefunctions $\psi(x) = \langle x|\psi \rangle$

From one to many particles n identical particles

$$\mathcal{H} \longrightarrow \mathcal{H}^{(n)} = \bigotimes_n \mathcal{H} \quad (\text{Hilbert space})$$

$$|\psi\rangle \in \mathcal{H} \longrightarrow |\psi^n\rangle \in \mathcal{H}^{(n)} \quad (\text{States})$$

$$b : \mathcal{H} \rightarrow \mathbb{C} \longrightarrow B : \mathcal{H}^{(n)} \rightarrow \mathbb{C}^{(n)} \quad (\text{Observables})$$

$$B = \sum_{k=1}^n b_k$$

$$B = \sum_{i < k}^n b_{ik}$$

$$|\psi\rangle \stackrel{!}{=} e^{i\phi} |\psi\rangle \longrightarrow P_\sigma |\psi^n\rangle \stackrel{!}{=} \chi(\sigma) |\psi^n\rangle \quad (\text{Admissibility})$$

with $b_k = \mathbb{1} \otimes \dots \otimes \mathbb{1} \otimes \underbrace{a}_{k\text{-th position}} \otimes \mathbb{1} \otimes \dots \otimes \mathbb{1}$ and

$\mathcal{H}^{(0)} = \mathbb{C}$. Symmetric group S_n acts on $\mathcal{H}^{(n)}$ by $P_\sigma : \psi_1 \otimes \dots \otimes \psi_n \mapsto \psi_{\sigma^{-1}(1)} \otimes \dots \otimes \psi_{\sigma^{-1}(n)}$.

Identical particles Labeling is arbitrary, no observable must be able to tell particles apart $\langle P_\sigma \psi^n | B | P_\sigma \psi^n \rangle = \langle \psi^n | B | \psi^n \rangle$ for $\sigma \in S^n$, which is equivalent to $[P_\sigma, B] = 0$.

Symmetric/antisymmetric states From the admissibility requirement, it follows that $\chi(\sigma\tau) = \chi(\sigma)\chi(\tau)$ and hence $\chi(\sigma) = 1$ or $\chi(\sigma) = \text{sgn}(\sigma)$. This decomposes the Hilbert space into symmetric and antisymmetric subspaces:

$$\mathcal{H}_s^{(n)} = \{|\psi^n\rangle \mid P_\sigma |\psi^n\rangle = |\psi^n\rangle\} \quad (\text{Bosons})$$

$$\mathcal{H}_a^{(n)} = \{|\psi^n\rangle \mid P_\sigma |\psi^n\rangle = \text{sgn}(\sigma) |\psi^n\rangle\} \quad (\text{Fermions})$$

Bosons take integer spins, fermions half-integer values. Single permutation criterion: $P_{(i,i+1)} |\psi\rangle = \pm |\psi\rangle \implies |\psi\rangle \in \mathcal{H}_{s/a}^{(n)}$ for $i = 1, \dots, n-1$.

Creation and annihilation operators Define operators $a(\phi) : \mathcal{H}^{(n)} \rightarrow \mathcal{H}^{(n-1)}$, $a^\dagger(\phi) : \mathcal{H}^{(n-1)} \rightarrow \mathcal{H}^{(n)}$ for $n \geq 1$ by

$$a^\dagger(\phi) \psi^n(x_1, \dots, x_n) :=$$

$$\frac{1}{\sqrt{n}} \sum_{k=1}^n (\pm 1)^{k-1} \phi(x_k) \Psi(x_1, \dots, \hat{x}_k, \dots, x_n)$$

$$a(\phi) \psi^{n-1}(x_2, \dots, x_n) = \sqrt{n} \int dx_1 \overline{\phi(x_1)} \Psi(x_1, \dots, x_n)$$

where $\psi^n \in \mathcal{H}^{(n)}$ and the hat $\hat{}$ denotes omission of

the argument. $a^\dagger(\phi)$ ($a(\phi)$) is (anti-)linear in ϕ . The annihilation operator $a(\phi)$ follows from the creation operator.

Commutation relations

$$[a(\phi), a(\phi')]_\pm = 0, \quad [a^\dagger(\phi), a^\dagger(\phi')]_\pm = 0, \\ [a(\phi), a^\dagger(\phi')]_\pm = \langle \phi | \phi' \rangle$$

Occupation number basis For ONB $\{\phi_1, \dots, \phi_k\}$ define $a_k := a(\phi_k)$, then relations become

$$[a_i, a_k]_\pm = 0, \quad [a_i^\dagger, a_k^\dagger]_\pm = 0, \quad [a_i, a_i^\dagger] = \delta_{ik}.$$

Vacuum $a_k |0\rangle = 0$ for $k = 1, 2, \dots$. Change of basis $|\tilde{\phi}_i\rangle = \sum_j \langle \phi_j | \tilde{\phi}_i \rangle |\phi_j\rangle$. N -particle states are

$$|n_1, n_2, \dots\rangle = (n_1! n_2! \dots)^{-1/2} (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} \dots |0\rangle$$

with $\sum_{i=1}^\infty n_i = N$. The action of the annihilation/creation operators for bosons are

$$a_k^\dagger |n_1, \dots\rangle = \sqrt{n_k + 1} |n_1, \dots, n_k + 1, \dots\rangle$$

$$a_k |n_1, \dots\rangle = \sqrt{n_k} |n_1, \dots, n_k - 1, \dots\rangle$$

and for fermions

$$a_k^\dagger |n_1, \dots\rangle = (-1)^{S_k} (1 - n_k) |n_1, \dots, n_k + 1, \dots\rangle$$

$$a_k |n_1, \dots\rangle = (-1)^{S_k} n_k |n_1, \dots, n_k - 1, \dots\rangle$$

with $S_k = n_1 + \dots + n_{k-1}$.

Fock space $\mathcal{F} = \bigoplus_{n=0}^\infty \mathcal{H}^{(n)}$. States $\Psi \in \mathcal{F}$ are sequences $\Psi = (\psi^0, \psi^1, \psi^2, \dots)$ with $\psi^n \in \mathcal{H}^{(n)}$ and $\|\Psi\|^2 = \langle \Psi | \Psi \rangle = \sum_{n=0}^\infty \langle \psi^n | \psi^n \rangle_{\mathcal{H}^{(n)}} < +\infty$.

States through creation operators

$$\Psi = a^\dagger(\phi_1) a^\dagger(\phi_2) \dots a^\dagger(\phi_n) |0\rangle$$

$$\psi^n(x) = \frac{1}{\sqrt{n!}} \sum_{\sigma \in S_n} \left\{ \begin{array}{c} 1 \\ \text{sgn}(\sigma) \end{array} \right\} \phi_1(x_{\sigma(1)}) \dots \phi_n(x_{\sigma(n)})$$

Number operator $N : \mathcal{F} \rightarrow \mathcal{F}$ with $(N\Psi)^n = n \cdot \psi^n$. Then $N = N^\dagger$ has eigenspaces $\mathcal{H}^{(n)}$ of eigenvalues $n = 0, 1, \dots$. Define eigenvector $|0\rangle = (1, 0, \dots)$ of eigenvalue 0 to be the vacuum.

$$Na(\phi) = a(\phi)(N-1) \implies [N, a(\phi)] = -a(\phi)$$

$$Na^\dagger(\phi) = a^\dagger(\phi)(N+1) \implies [N, a^\dagger(\phi)] = +a^\dagger(\phi)$$

Observables Promote 1-particle operator o on \mathcal{H} to $O := d\Gamma(o)$ on \mathcal{F} by setting $O\psi^n = \sum_{i=1}^n o_i \psi^n$, where o_i acts on the i -th particle. This is equivalent to the Fock representation

$$O = d\Gamma(o) = \sum_{kl} a_k^\dagger \langle \phi_k | o | \phi_l \rangle a_l.$$

For 2-particle operators $O = \sum_{1 \leq i < j \leq n} o_{ij}$ and Fock

representation

$$\frac{1}{2} \sum_{k_1, k_2, l_1, l_2} a_{k_2}^\dagger a_{k_1}^\dagger \langle \phi_{k_1} \otimes \phi_{k_2} | o | \phi_{l_1} \otimes \phi_{l_2} \rangle a_{l_1} a_{l_2}.$$

Derivation of equivalence. **TODO**

Number of particles For $o = 1$ we obtain $O = \sum_k a_k^\dagger a_k$ since $\langle \phi_k | 1 | \phi_l \rangle = \delta_{kl}$. It count particles since $O\psi^n = \sum_{i=1}^n 1 \cdot \psi^n = n\psi^n$.

7 Ideal Quantum Gases

7.1 Formalism

States on Hilbert space \mathcal{H}

- Mixed state: density matrix on \mathcal{H} , i.e. operator $P : \mathcal{H} \rightarrow \mathcal{H}$ with $P = p^* \geq 0$, $\text{tr}P = 1$.
- Pure state: $\psi \in \mathcal{H}$, $\|\psi\| = 1$, i.e. $P = |\psi\rangle\langle\psi|$.

Convex combinations of density matrices If P_1, P_2 are density matrices, then so is $P = p_1 P_1 + p_2 P_2$ where $p_1 + p_2 = 1$, $p_i \geq 0$ (probability of state being drawn from P_i).

Spectral decomposition $P = \sum_k p_k P_k$ with $P_k = |\phi_k\rangle\langle\phi_k|$ and p_k & ϕ_k eigenvalues & -vectors of P . They fulfill $p_k = \bar{p}_k \geq 0$, $\sum_k p_k = 1$, $\langle \phi_k | \phi_l \rangle = \delta_{kl}$. Hence interpretation of P : Statistical mixture of pure states $|\phi_k\rangle$ with probabilities p_k .

Expectation value of observable: $\langle A \rangle = \text{tr}(AP)$. Compatible with $\langle A \rangle_\psi = \langle \psi | A | \psi \rangle$ for pure state.

Entropy $S(P) = -k \text{tr}(P \log P)$. No additive ambiguity. Similar properties as classically.

Systems under consideration N identical particles in a fixed box Λ with Hamiltonian H_N acting on Hilbert space \mathcal{H}_N .

Microcanonical ensemble Besides N , E fixed within small tolerance $\Delta > 0$. then ensemble:

$$P = \Sigma_\Delta(E)^{-1} P_\Delta(E), \quad \Sigma_\Delta(E) = \text{tr}P_\Delta(E)$$

with $P_\Delta(E)$ projection onto eigenvectors of H_N with eigenvalues within $[E - \Delta, E]$, $\Sigma_\Delta(E)$ their number.

Entropy from microcanonical ensemble

$$S(P) = k \log \Sigma_\Delta(E)$$

From $S(P) = -k(x \log x) \text{tr}P_\Delta(E)$ for $x = \Sigma_\Delta(E)^{-1}$.

Canonical ensemble T fixed instead of E .

$$P = Z(\beta)^{-1} e^{-\beta H_N}, \quad Z(\beta) = \text{tr}e^{-\beta H_N}.$$

Fock space

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_N; \quad H = \bigoplus_{N=0}^{\infty} H_N.$$

Grand canonical ensemble μ fixed instead of N .

Classically: sum over $\{\Gamma_N\}_{N \geq 0}$. Now: Fock space.

$$P = \Xi(\beta, \mu)^{-1} e^{-\beta(H - \mu N)}, \quad \Xi(\beta, \mu) = \text{tr}e^{-\beta(H - \mu N)},$$

where N is particle operator, commutes with H .

Resulting quantities (replace μ with $e^{\beta\mu}$)

- Grand canonical potential $\Omega(\beta, \mu) = -pV = -\frac{1}{\beta} \log \Xi(\beta, \mu)$.
- Expectation value particle number: $N \equiv \langle N \rangle = z \left(\frac{\partial}{\partial z} \log \Xi \right)_\beta = Vz \left(\frac{\partial(\beta p)}{\partial z} \right)_\beta$.
- Expectation value energy: $U \equiv \langle H \rangle = - \left(\frac{\partial}{\partial \beta} \log \Xi \right)_z = -V \left(\frac{\partial(\beta p)}{\partial \beta} \right)_z$.

Derivation By $e^{A+B} = e^A e^B$ for $[A, B] = 0$, have $\langle N \rangle = \text{tr}(NP) = \frac{\text{tr}(N e^{-\beta H} z^N)}{\text{tr}(e^{-\beta H} z^N)} = \frac{z(\partial \Xi / \partial z)_\beta}{\Xi}$.

7.2 Independent particles

Define $\eta = \begin{cases} +1 & \text{for bosons,} \\ -1 & \text{for fermions.} \end{cases}$

System Either fermions (F) or bosons (B) with single-particle energy spectrum $\epsilon_0 \leq \epsilon_1 \leq \epsilon_2 \leq \dots \leq \epsilon_\alpha \leq \dots$, $\epsilon_\alpha \xrightarrow{\alpha \rightarrow \infty} \infty$.

Occupation-number basis $|n_0, n_1, n_2, \dots\rangle$ of Fock space where

$$n_\alpha = \begin{cases} 0, 1 & (F) \\ 0, 1, 2, 3, \dots & (B) \end{cases}; \quad \sum_\alpha n_\alpha < \infty$$

N, H are diagonal w.r.t. this basis:

$$N |n_0, n_1, n_2, \dots\rangle = \left(\sum_\alpha n_\alpha \right) |n_0, n_1, n_2, \dots\rangle$$

$$H |n_0, n_1, n_2, \dots\rangle = \left(\sum_\alpha \epsilon_\alpha n_\alpha \right) |n_0, n_1, n_2, \dots\rangle$$

Grand canonical partition function follows as

$$\Xi = \sum_{n_0, n_1, \dots} \prod_\alpha e^{\beta(\mu - \epsilon_\alpha)n_\alpha} = \prod_\alpha (1 \pm e^{\beta(\mu - \epsilon_\alpha)})^{\pm 1}$$

with $\pm \leftrightarrow (F)/(B)$. Need $\mu < \epsilon_0$ for (B) so that geometric series converges. Thus,

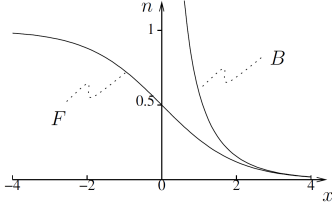
$$\log \Xi = \pm \sum_\alpha \log(1 \pm e^{\beta(\mu - \epsilon_\alpha)}).$$

- Thus $\langle N \rangle = \sum_{\alpha} \langle n_{\alpha} \rangle = V \int_0^{\infty} \frac{dN(\epsilon)}{z^{-1}e^{\beta\epsilon} - 1} + o(V)$.

$$\log \Xi = \mp \sum_{\alpha} \log(1 \mp e^{\beta(\mu - \epsilon_{\alpha})})$$

$$\langle n_{\alpha} \rangle = \frac{1}{e^{\beta(\epsilon_{\alpha} - \mu)} \pm 1}$$

Universal Fermi/Bose distribution is $n(x) = (e^x \pm 1)^{-1}$. See plot below.



Occupation number expectation value is given by Fermi/Bose distribution as $\langle n_{\alpha} \rangle = n(\frac{\epsilon_{\alpha} - \mu}{kT})$. For $T \rightarrow 0$: step function for fermions, peaked at 0 for bosons.

Derivation $\langle n_{\alpha} \rangle = \frac{\sum_{\{n_k\}} n_{\alpha} e^{\beta \sum_{\gamma} (\mu - \epsilon_{\gamma}) n_{\gamma}}}{\sum_{\{n_k\}} e^{\beta \sum_{\gamma} (\mu - \epsilon_{\gamma}) n_{\gamma}}} = -\frac{1}{\beta} \left(\frac{\partial \log \Xi}{\partial \epsilon_{\alpha}} \right)_{\mu, \beta} = \frac{1}{e^{\beta(\epsilon_{\alpha} - \mu)} \pm 1}$.

Remark (modes) Underlying idea: particles occupying modes α (single-particle states) independently (no constraint on N). $\Xi = \prod_{\alpha} \Xi_{\alpha}$ makes sense then.

7.3 Bose-Einstein condensation

Setting Restrict to bosons. Assume $\epsilon_0 = 0$ by shifting μ , hence $\mu < 0$ & $0 < z < 1$.

Condensation At $T = 0$, N -particle state has all in single-particle groundstate $\alpha = 0$. Condensation means that property being stable at $T > 0$.

Counting states for large V : Extensive asymptotics

$$\#\{\alpha | \epsilon_{\alpha} \leq \epsilon\} = N(\epsilon)V + o(V), \quad (V \rightarrow \infty)$$

with $N(\epsilon)$ integrated density of states. Hence,

$$\#\{\alpha | \epsilon \leq \epsilon_{\alpha} \leq \epsilon + \Delta\epsilon\} = \Delta N(\epsilon)V + o(V)$$

Occupation number $\langle n_{\alpha} \rangle = \frac{1}{z^{-1}e^{\beta\epsilon} - 1}$.

Particle density in thermodynamic limit

$$\rho(z) = \lim_{V \rightarrow \infty} \frac{\langle N \rangle}{V} = \int_0^{\infty} \frac{dN(\epsilon)}{z^{-1}e^{\beta\epsilon} - 1}$$

Derivation

- Occupation number is bounded uniformly in V , α (not in z): $\langle n_{\alpha} \rangle \leq \frac{1}{z^{-1} - 1}$.

Critical density is maximum achievable $\rho \in (0, \rho^*)$.

$$\rho^*(z) = \sup_z \rho(z) = \lim_{z \uparrow 1} \rho(z) = \int_0^{\infty} \frac{dN(\epsilon)}{e^{\beta\epsilon} - 1}$$

$\rho \geq \rho^*$ can happen in canonical ensemble. Explore by adjusting $z = e^{-1/\xi V}$ with $0 < \xi < \infty$ fixed, s.t. $0 < z < 1$ but $z \rightarrow 1$ as $V \rightarrow \infty$.

Bose-Einstein condensation With $z = e^{-1/\xi V}$:

$$\langle n_0 \rangle = \frac{1}{z^{-1} - 1} = \xi V + o(V),$$

i.e. lowest mode $\alpha = 0$ has macroscopic occupation.

Other states ($\alpha \neq 0$) $\langle n_{\alpha} \rangle$ diverges as $V \rightarrow \infty$, but occupation is macroscopic only if ϵ_{α} grows slower than V^{-1} , i.e. if $\epsilon_{\alpha} = O(V^{-1})$.

Derivation Consider $\langle n_{\alpha} \rangle = \frac{1}{z^{-1}e^{\beta\epsilon} - 1}$ with $\epsilon_{\alpha} \rightarrow 0$, $z \rightarrow 1$. Denominator vanishes as $(\xi V)^{-1} + \beta\epsilon_{\alpha}$. Alternative: take $z = 1 - \epsilon$, then $|\beta\mu| = |\log z| \ll 1$, then $\mathcal{O}(V) = N - N^* = N_0 = \langle n_0 \rangle = \frac{1}{e^{-\beta\mu} - 1} \approx \frac{1}{-\beta\mu}$, so $\mu \stackrel{!}{=} \mathcal{O}(V^{-1})$.

Example: ideal gas. Free, spinless particles in cube $0 \leq x_i \leq L$, periodic boundary cond. Then

- $\rho^* = +\infty$ for $d \geq 2$.
- Bose-Einstein condensation (“in momentum space”) occurs for $d > 2$, i.e. only the mode $\vec{k} = 0$ is macroscopically occupied. In fact,

$$n(\vec{k}) = \underbrace{\frac{(2\pi)^{-d}}{e^{\beta\hbar^2 k^2/2m} - 1}}_{n^*} + \underbrace{\xi \delta^{(d)}(\vec{k})}_{n_0}$$

in the limit $L \rightarrow \infty$, then $z \uparrow 1$.

Derivation

- Particle in a box: single-particle states are $\psi_{\vec{k}}(\vec{x}) = i^{\vec{k} \cdot \vec{x}}$, quantized momenta $k_i = \frac{2\pi}{L} \nu_i$ ($\nu_i \in \mathbb{Z}$, i_1, \dots, d), corresponding energies $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$.
- Count modes in terms of momenta: $\#\{\vec{k} | \vec{k} \in \Delta^d k\} = \left(\frac{L}{2\pi}\right)^d \Delta^d k + o(L^d)$ (indeed $\propto V = L^d$ at leading order).

Qualitatively:

- Critical density $\rho^* = (2\pi)^{-d} \int d^d k \frac{1}{e^{\beta\hbar^2 k^2/2m} - 1}$.
- Integrand $\sim k^{-2}$ as $k \rightarrow 0$, i.e. $\rho^* = +\infty$ for $d \geq 2$ and condensation otherwise.
- For $d > 2$, spectrum has gap above groundstate $\propto L^{-2} \gg L^{-d}$, thus only $\vec{k} = 0$ macroscopically occupied.

7.4 Thermodynamics of ideal gas

Setting $d = 3$, either F/B, particles have spin s ($q = 2s + 1$ spin orientations), otherwise same model as in previous example. Thus single-particle states are $|\psi_{\vec{k}}\rangle \otimes |m\rangle$ with $m = -s, -s + 1, \dots + s$.

Thermal & caloric equation of state

$$\begin{cases} \beta p &= \frac{q}{\lambda^3} f_{5/2}^{-\eta}(z) \\ n &= \frac{q}{\lambda^3} f_{3/2}^{-\eta}(z) \\ u &= \frac{3}{2} p v \end{cases}$$

with $n = \frac{1}{v} = \frac{V}{V}$, $u = \frac{U}{V}$ and thermal wavelength $\lambda = \frac{h}{\sqrt{2\pi m k T}}$. For $\beta p v = \frac{f_{5/2}^{\pm}(z)}{f_{3/2}^{\pm}(z)} = 1$ obtain classical equations of state $u = \frac{3}{2} k T$, $p v = k T$.

Function f (note that f^- bosons, f^+ fermions)

$$\begin{aligned} f_m^{-\eta}(z) &= \frac{1}{(m-1)!} \int_0^{\infty} dx \frac{x^m}{z^{-1} e^x + \eta} \\ f_{5/2}^{-\eta}(z) &= -\eta \frac{2}{\sqrt{\pi}} \int_0^{\infty} dx \sqrt{x} \log(1 - \eta z e^{-x}) \\ z \frac{d f_m^{\pm}(z)}{dz} &= f_{m-1}^{\pm}(z) \end{aligned}$$

Derivation

- From eq. for $\log \Xi$ for independent particles obtain $\frac{1}{V} \log \Xi = \frac{q}{(2\pi)^3} \frac{(2\pi)^3}{L^3} \sum_{\vec{k}} \pm \log(1 \pm z e^{-\beta \frac{h^2 \vec{k}^2}{2m}})$.
- For $L \rightarrow \infty$: Riemann sum. $\sum_{\vec{k}} \rightarrow qV \int \frac{d^3 k}{(2\pi)^3}$. Hence in thermodynamic limit (using result for grand canonical potential): $\frac{p}{kT} = \pm \frac{q}{(2\pi)^3} \int d^3 k \log(1 \pm z e^{-\beta \frac{h^2 \vec{k}^2}{2m}})$.
- With substitution $x = \beta \frac{h^2 \vec{k}^2}{2m}$, $d^3 k = 4\pi k dk = \dots dx$ get $\frac{p}{kT} = \frac{1}{\lambda^3} f_{5/2}^{\pm}(z)$. Here, "thermal wavelength" $\lambda = \frac{h}{\sqrt{2\pi m k T}}$, note analogy to de Broglie h/p of particle with energy $p^2/2m = kT$.
- Have $\frac{p}{kT} = \frac{q}{\lambda^3} f_{5/2}^{\pm}(z)$. Use $N = V z \left(\frac{\partial(\beta p)}{\partial z} \right)_{\beta}$ to get $\frac{1}{v} = \frac{q}{\lambda^3} f_{3/2}^{\pm}(z)$.
- $\frac{U}{V} = -\frac{\partial}{\partial \beta}(\beta p)_z = \frac{3}{2} p$ ($\beta p \propto \beta^{-3/2}$ for fixed z).

7.5 Non-degenerate Bose/Fermi gases (Classical limit)

Degeneracy $d = \frac{n\lambda^3}{q} = \frac{\lambda^3}{vq}$ distinguishes classical/qm behavior: $d \ll 1$ ($n \ll 1, T \gg 1$) is classical. In this limit $T \rightarrow \infty$, $\mu \rightarrow -\infty$.

Power series for $f_{5/2}^{-\eta}(z)$ with approximation

$f_{5/2}^{-\eta}(z) = \sum_{l=1}^{\infty} \eta^{l+1} \frac{(z)^l}{l^{5/2}}$ for $|z| < 1$ one obtains:

$$\begin{cases} \frac{\beta p \lambda^3}{q} = f_{5/2}^{-\eta}(z) = z - \eta \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots \\ \frac{n \lambda^3}{q} = f_{3/2}^{-\eta}(z) = z - \eta \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots \end{cases}$$

Hence, $d \ll 1 \implies f_{5/2}^{-\eta}(z) \ll 1 \implies z \ll 1$.

Derivation $f_{5/2}^{\pm}(z) = \pm \frac{2}{\sqrt{\pi}} \int_0^{\infty} dx \sqrt{x} \log(1 - z e^{-x})$. $\log(1 - z e^{-x}) = -\sum_{n=1}^{\infty} \frac{(z e^{-x})^n}{n}$ and $\frac{2}{\sqrt{\pi}} \int_0^{\infty} dx \sqrt{x} e^{-x n} = n^{-3/2}$. Hence $f_{5/2}^{\pm}(z) = \mp \sum_{n=1}^{\infty} \frac{(\mp z)^n}{n} n^{-3/2}$.

Comparison to classical gas Entering power series into equation of state gives same form as Ursell-Mayer expansion. Hence, thermodynamics of non-interacting quantum particles at small z resembles interacting classical particles.

Classical limit is $z \ll 1$, then $l = 1$ term suffices and classical ideal gas emerges. Corresponds to condition $v \gg \lambda^3$ (i.e. mean inter-particle distance $\sim v^{1/3}$ large compared to quantum length scale λ).

Entropy (per particle)

$$s = k \left(\frac{5}{2} + \log \left(q v \left(\frac{4\pi m u}{3h^2} \right)^{3/2} \right) \right) + \mathcal{O}\left(\frac{\lambda^3}{v}\right)$$

Note similarity to classical real gas for $q = 1$.

Derivation $s = \frac{1}{T}(u + p v - \mu) = k \left(\frac{5}{2} \frac{p v}{k T} - \frac{\mu}{k T} \right) = k \left(\frac{5}{2} - \log z \right) + \mathcal{O}(z)$. Use $z = \frac{1}{q} \frac{\lambda^3}{v}$ with $\lambda \approx \sqrt{\frac{3h^2}{4\pi m u}}$ (from $l = 1$, i.e. $f_{5/2}^{\pm}(z) \approx z$).

Pressure of Fermi/Bose gas to next order in z

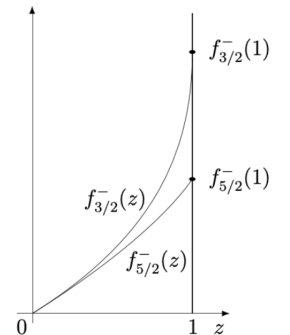
$$p_{\eta} v = k T \left(1 - \eta \frac{1}{2^{5/2} q} \frac{\lambda^3}{v} + \mathcal{O}\left(\left(\frac{\lambda^3}{v}\right)^2\right) \right)$$

(from $\frac{p v}{k T} = \frac{f_{5/2}^{\pm}(z)}{f_{3/2}^{\pm}(z)}$). Meaning: Fermi gas ($\eta = -1$) has higher pressure than classical gas (Pauli exclusion principle), and Bose ($\eta = +1$) has smaller pressure.

7.6 Degenerate Bose gas

Degeneracy $d = \frac{n\lambda^3}{q} =$

$\frac{\lambda^3}{vq}$ In the degenerate limit $d \gg 1$ we have as $T \rightarrow 0$, μ approaches 0 from below (required to ensure $\langle n_k \rangle \geq 0$: $\mu < \min_k \epsilon_k = \epsilon_0 = 0$). There, $\lim_{z \rightarrow 1} f_{5/2}^{-\eta}(z) \approx 1.341$ and $\lim_{z \rightarrow 1} f_{3/2}^{-\eta}(z) \approx 2.612$.



Notation of states Label modes $\vec{k} \neq 0$ with (*), $\vec{k} = 0$ with (0). Recall from example on ideal gas, states are either in mode $k = 0$ or in modes $k > 0$: $\rho(T) = \rho^*(T) + \rho^0$ ($\rho^0 = \xi$).

Density of excited states ρ_\times is bounded by

$$\rho_\times = \frac{q}{\lambda^3} f_{3/2}^-(z) \leq \rho^* = \lim_{z \nearrow 1} \rho = \frac{q}{\lambda^3} f_{3/2}^-(1)$$

$$\beta p = \frac{q}{\lambda^3} f_{5/2}^-(z) \leq \beta p^* = \lim_{z \nearrow 1} \beta p = \frac{q}{\lambda^3} f_{5/2}^-(1)$$

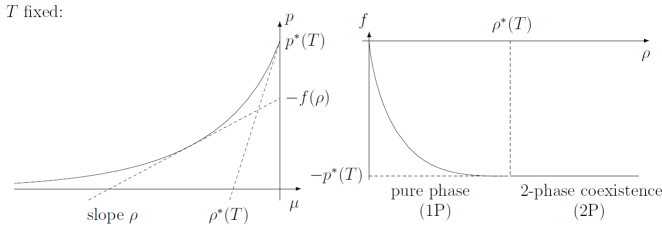
Critical temperature $T_c = \frac{\hbar^2}{2\pi m k} \left(\frac{\rho^*}{q f_{3/2}^-(1)} \right)^{2/3}$

- for $T > T_c$: excited states ρ_\times make up total density of states $\rho_\times = \rho$
- for $T < T_c$: z stuck in 1 ($\mu = 0$), limiting density of excited states is less than the total particle density $\rho_\times = \rho^* < \rho$. The remaining particles $\xi = \rho - \rho^*$ occupy lowest energy state with $k = 0$. This is Bose-Einstein condensation.

Range $\rho \geq \rho^*$ obtained via Legendre transform. Constant ρ, μ correspond to constant f , i.e. phase coexistence.

$$f(T, \rho) = \sup_{\mu} (\mu \rho - p(T, \mu))$$

$$df = -s dT + \mu d\rho$$



Phase coexistence in the segment 2P.

Fraction of particles in condensate given by

$$\frac{\xi}{\rho} = \frac{\rho - \rho^*}{\rho} = 1 - \frac{v}{v^*}$$

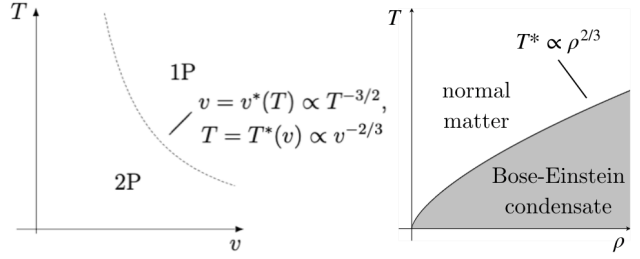
Energy $U = \sum_{\vec{k}} \epsilon_{\vec{k}} \langle n_{\vec{k}} \rangle$. 0 for $\vec{k} = 0$ (from $\epsilon_0 = 0$). Write $U = U^* + U^0$ with $U^0 = 0$.

Entropy Write $S = S^* + S^0$ with $S^0 = 0$ since $\frac{S}{k} = \sum_{\vec{k}} ((1 + \langle n_{\vec{k}} \rangle) \log(1 + \langle n_{\vec{k}} \rangle) - \langle n_{\vec{k}} \rangle \log \langle n_{\vec{k}} \rangle)$ is $\mathcal{O}(\log V)$ for $\vec{k} = 0$ (as $\approx \log \langle n_{\vec{k}} \rangle$).

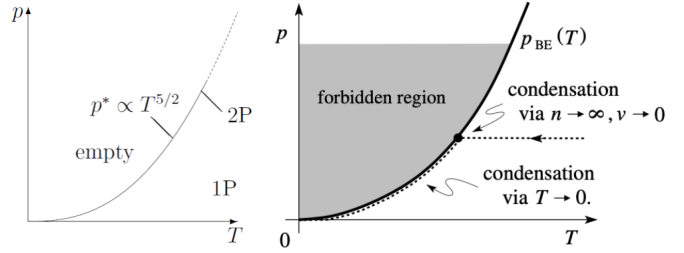
Volume of condensate It is as if $V^0 = 0$:

Then, $(u, s, v) = \frac{v}{v^*} (u^*, s^*, v^*) + (1 - \frac{v}{v^*}) (0, 0, 0)$ with the per-particle quantities $u := \frac{U}{N} = \frac{U^*}{N^*} \cdot \frac{N^*}{N} = \frac{v}{v^*} \cdot u^*$, $s = \frac{v}{v^*} s^*$, $v = \frac{v}{v^*} v^*$.

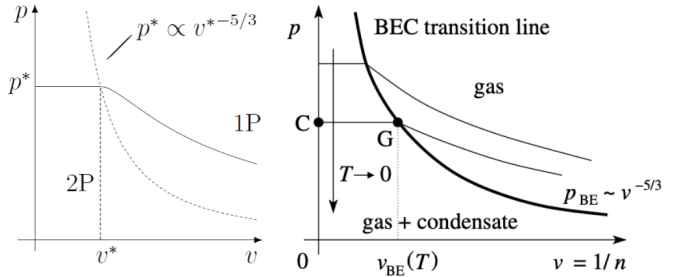
T-dependence Use $T_c \propto (\rho^*)^{2/3} = (v^*)^{-2/3}$. Line shows phase coexistence curve.



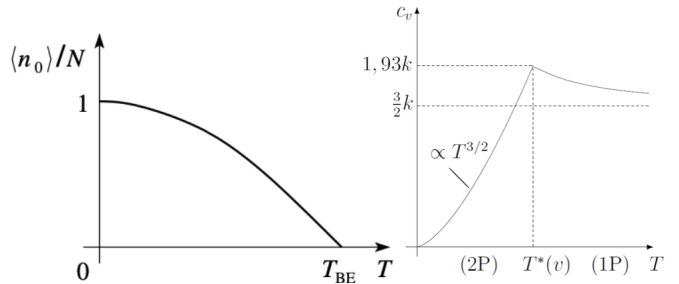
Phase diagram Crit pressure $p^*(T) \propto T \lambda^{-3} = T^{5/2}$



Isotherms Use $p^*(T) \propto T^{5/2}$, $T_c \propto (v^*)^{-2/3}$ to obtain transition line $p^* \propto (v^*)^{-5/3}$.



Occupation & heat capacity shows a cusp (2nd order transition), not a delta function.



Derivation

- For $T < T_c$ ($\rho > \rho^*$): $\rho^* \propto T^{5/2}$, hence $s = -\frac{\partial f}{\partial T} = \frac{dp^*}{dT} = \frac{5}{2} \frac{p^*}{T} \propto T^{3/2}$ for $T < T_c$. Heat capacity from $c_v = v \cdot T \frac{ds}{dT}$. At T^* : $c_v = k \frac{15}{4} \frac{f_{5/2}^-(1)}{f_{3/2}^-(1)}$.
- For $T > T_c$: use ideal gas entropy $s = \frac{1}{T} (u + pv - \mu) = k \left(\frac{5}{2} \frac{pv}{kT} - \frac{\mu}{kT} \right)$. Then $s \propto \text{const.} - \frac{3}{2} \log T$.