

Statistical Physics - Exam Sheet

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1 Differential forms

- n -form α **exact** $\Leftrightarrow \alpha \in \text{Im}(d) \Leftrightarrow \exists n-1$ -form β s.t. $\alpha = d\beta - \beta$ called **potential** for α ; since $d^2 = 0$, β not unique
- n -form α **closed** $\Leftrightarrow \alpha \in \text{ker}(d) \Leftrightarrow d\alpha = 0$
- since $d^2 = 0$, every exact form is closed; converse, i.e. if every closed form is exact, depends on topology: on contractible domain (such as \mathbb{R}^n), this holds by **Poincaré's lemma**
- some inexact differentials can be made exact by multiplying with **integrating factor** (and can then be integrated to give (path-independent) scalar field; useful in thermodynamics where T is i.f. that exactifies S)

2 Thermodynamics

- $dS = \delta Q/T$ is path-independent total differential and state function (unlike path function δQ)
- ideal gas entropy: $S = S_0 + C_V \ln\left(\frac{T}{T_0}\right) + nR \ln\left(\frac{V}{V_0}\right)$
- **efficiency** $\eta = -\frac{W}{Q}$ defined as work *performed* by system (thus minus sign) divided by heat *added*
 - all reversible engines equally efficient
 - ideal heat engine pumping between reservoirs T_c, T_h : $\eta = 1 - \frac{T_c}{T_h} = 1 - \left(\frac{V_{\min}}{V_{\max}}\right)^{\frac{nR}{C_V}}$, where $\frac{nR}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1$
 - isochoric heat change in ideal gas: $Q_{if} = C_V(T_f - T_i)$
 - by second law, reversible process is isentropic, $\oint dS = 0$
- for **paramagnets** with first law $dU = T dS + H dM$ obeying **Curie's law** $M = \frac{C}{T} H$, internal energy depends only on T
- **potentials**: internal energy $U = TS - pV$, Helmholtz free energy $F = U - TS = -pV$, $H = U + pV = TS$, Gibbs free energy $G = U + pV - TS$ (add $\sum_i \mu_i N_i$ everywhere in presence of chemical potentials)
 - differentials i.t.o. natural variables: $dU = TdS - pdV$, $dF = -SdT - pdV$, $dH = TdS + Vdp$, $dG = -SdT + Vdp$
 - all potentials related via Legendre transformation
 - **principle of minimum energy**: entropy maximizes in equilibrium, all potentials extremize: U minimizes for fixed S, V , (follows from first and second law); F minimizes at fixed T, V ; H at fixed p ; G at fixed T and p
- **Maxwell relations**: $U \rightarrow \left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V$, $F \rightarrow \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$, $H \rightarrow \left.\frac{\partial T}{\partial p}\right|_S = \left.\frac{\partial V}{\partial S}\right|_p$, $G \rightarrow \left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p$
 - related via $\left.\frac{\partial x}{\partial y}\right|_z = \left(\left.\frac{\partial y}{\partial x}\right|_z\right)^{-1}$ and $\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1$
- **intensive quantities**: temperature T , pressure p , density ρ , chemical potential μ , concentration c , magnetic permeability μ_m , melting/boiling point, specific heat capacity c_V , specific volume v ; **extensive**: particle number N , internal energy U , enthalpy H , entropy S , Gibbs energy G , heat capacity C_V , Helmholtz energy F , mass m , volume V
- **real gases**: **van der Waals** $p + \frac{a}{v^2} = \frac{RT}{v-b}$ or $p + \frac{n^2 a}{V^2} = \frac{nRT}{V-nb}$, with $n = \frac{N}{N_A}$, $R = N_A k_B$; **Dieterici** $p = \frac{RT}{v-b} \exp\left(-\frac{a}{vRT}\right)$; **virial expansion** $\frac{pv}{RT} = 1 + \sum_{i=1}^{\infty} \frac{B_i}{v^i}$ for large volume v
- **useful identities**: $p = -\left.\frac{\partial F}{\partial V}\right|_T$, $S = -\left.\frac{\partial F}{\partial T}\right|_V$, $\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_T$, $t\left.\frac{\partial U}{\partial V}\right|_T = T \left.\frac{\partial p}{\partial T}\right|_V - p$; **Helmholtz eq.**: $\left.\frac{\partial U}{\partial V}\right|_T = T^2 \left.\frac{\partial}{\partial T}\right|_V \left.\frac{p}{T}\right|_V$; **thermal expansion coeff.** $\alpha = \frac{1}{V} \left.\frac{\partial V}{\partial T}\right|_{a,N}$; (isothermal)

compressibility $\kappa_T = -\frac{1}{V} \frac{\partial p}{\partial V} = \frac{V^2}{N^2} \frac{\partial^2 p}{\partial^2 \mu}$; **n -ball**: volume $V_n(R) = \frac{\pi^{n/2} R^n}{\Gamma(\frac{n}{2}+1)}$, area $A_{n-1}(R) = \partial_R V_n(R) = \frac{2\pi^{n/2} R^{n-1}}{\Gamma(\frac{n}{2})}$

- **equipartition thm.**: in equilibrium, all microstates compatible with macroscopic conditions equiprobable; energy shared equally amongst all d.o.f.s (i.e. equilibrated systems maximize entropy), each quadratic d.o.f. carries energy $\frac{k_B T}{2}$
- **heat engine**: device that transfers heat from hot to cold reservoir $T_c < T_h$ with aim of converting as much of transferred heat into mechanical work as possible; maximum efficiency attained by *reversible* engine operating idealized Carnot cycle $\eta_C = 1 - \frac{T_c}{T_h}$; **heat pump**: moves heat in other direction from cold to hot, goal now to use as little mechanical work as possible to do so, i.e. heat engine operating in reverse \Rightarrow maximum efficiency of reversible heat pump given by reciprocal of η_C , $\eta_{hp} = \frac{T_h}{T_h - T_c}$
- **black-body radiation**: caloric e.o.s. $U = u(T)V$, thermal e.o.s. $p = \frac{u(T)}{3}$, Stefan-Boltzmann law $u(T) = \sigma T^4$, Gibbs fundamental relation (first law) $dU = TdS - pdV$ yields entropy $S(T, V) = S_0 + \frac{4}{3}\sigma VT^3$, adiabatic e.o.s. $\delta Q = TdS = 0 \Rightarrow S \propto VT^3 = \text{const.}$

3 Statistics

- **ensemble fixed distribution interpretation**

ensemble	fixed	distribution	interpretation
micro	$V N E$	$\frac{1}{Z_m} \delta(H - E)$	isolated system
canonical	$V N T$	$\frac{1}{Z_c} e^{-\beta H}$	system + heat bath
grand	$V T \mu$	$\frac{1}{Z_g} e^{-\beta(H - \mu N)}$	\uparrow + particle reservoir
- entropies: **Boltzmann** $S_m = k_B \ln Z_m$, $S_c = k_B (\ln Z_m + \beta \langle H \rangle_c)$, $S_g = k_B [\ln Z_g + \beta \langle H \rangle_g + \beta \mu \langle N \rangle_g]$ (apply only to equilibrium), **Gibbs** $S_G = -k_B \sum_i p_i \ln(p_i)$ respectively $S_G = -k_B \int \omega \ln \omega d\mu$ on discrete/continuous measure space (valid generally), S_G constant in time due to Liouville's eq. $\frac{d\omega}{dt} = 0$
 - **Liouville thm.** phase space distribution constant along any trajectory in Γ ; viewing motion through phase space as incompressible 'fluid flow' of conserved current of system points implies via Noether's thm. invariance under time evolution generated by Noether charge Hamiltonian
- **equivalence of ensembles**: thermodynamics same for large class of systems (incl. ideal gas), $\frac{S_m}{N} \xrightarrow{N \rightarrow \infty} \frac{S_c}{N}$, $\frac{S_m}{N} \xrightarrow{N \rightarrow \infty} \frac{S_g}{N}$; warning: fails in important cases e.g. phase transitions

$$\begin{array}{ccccc}
 Z_m(E) & \xrightarrow{\text{Laplace in } E} & Z_c(\beta) & \xrightarrow{\text{Laplace in } N} & Z_g(\mu) \\
 \downarrow & & \downarrow & & \downarrow \\
 \sigma = \frac{S_m}{N} & \xrightarrow{\text{Legendre in } \epsilon = \frac{E}{N}} & f = \frac{F}{N} & \xrightarrow{\text{Legendre in } \rho = \frac{N}{V}} & \frac{\Omega}{V}
 \end{array}$$

- **Hamilton's eqs.** $\dot{q}_i = \frac{\partial H}{\partial p_i}$, $\dot{p}_i = -\frac{\partial H}{\partial q_i}$ where $p_i = \frac{\partial L}{\partial \dot{q}_i}$
- **Boltzmann eq.** $\left(\frac{\partial}{\partial t} + \frac{p}{m} \cdot \nabla_x + \mathbf{F} \cdot \nabla_p\right) f(\mathbf{x}, \mathbf{p}, t) = \int d^3 k d^3 p' d^3 k' |\langle \mathbf{p}', \mathbf{k}' | T | \mathbf{p}, \mathbf{k} \rangle|^2 [f_{p'} f_{k'} - f_p f_k]$ describes (non-equilibrium) evolution of phase space densities (for large systems, e.g. gases); incorporates **molecular chaos**, which assumes collision term results solely from two-body collisions between particles uncorrelated prior to scattering (breaks time-reversal invariance since they are obviously correlated after collision), m.c. allows writing collision term as \mathbf{p} -integral in which two-particle correlator $F(\mathbf{x}, \mathbf{p}, \mathbf{k}, t)$ factorizes into one-particle distributions $f(\mathbf{x}, \mathbf{p}, t) f(\mathbf{x}, \mathbf{k}, t)$

– for stationary systems, Boltzmann eq. greatly simplifies to $\frac{p}{m} \cdot \nabla_x f_0(\mathbf{x}, \mathbf{p}) = -\mathbf{F}(\mathbf{x}) \cdot \nabla_p f_0(\mathbf{x}, \mathbf{p})$ since 1. distributions $f(\mathbf{x}, \mathbf{p})$ lose explicit time-dependence 2. H -function becomes stationary, resulting in detailed balance, meaning number of particles leaving any mode due to given scattering process equals number entering that mode by reverse process; stationary solution: **Boltzmann distr.** $f_0(\mathbf{x}, \mathbf{p}) \propto \exp[-\beta(\frac{p^2}{2m} + V(\mathbf{x}))]$

- **Boltzmann H -fct.** $H(t) = \int d^3x d^3p f(\mathbf{x}, \mathbf{p}, t) \ln[f(\mathbf{x}, \mathbf{p}, t)]$
- **Poincaré recurrence thm.** in context of ergodicity (time avr. = phase space avr.), isolated phase-space volume preserving (e.g. Hamiltonian) systems will return arbitrarily close to initial state after finite time

- **Gibbs paradox:** for classical counting of states, entropy not extensive: S increases when gas of identical particles mixed with itself (fixable by adding $\frac{1}{h^{3N} N!}$ to the measure $d\mu_m$); entropy from Boltzmann's H does not have this problem

- **Gibbs variational principle:** microcanonical state has maximal entropy among all states on energy shell \mathcal{E} , holds for other ensembles as well

– useful inequality: $f(\ln f - \ln g) \geq f - g \quad \forall f, g \geq 0$ (= for $f = g$), follows from $x \ln x \geq x - 1$ for $x \geq 0$

- **canonical part. fct.** discrete classical $Z_c = \sum_i e^{-\beta E_i}$, continuous classical $Z_c = \int_{\Gamma} e^{-\beta H} d\mu_c$ with $d\mu_c = \frac{d^{3N} q d^{3N} p}{h^{3N} N!}$; discrete quantum $Z = \text{tr}_{\mathcal{H}}(e^{-\beta \hat{H}})$

– internal energy $U = -\partial_{\beta} \ln(Z_c)$, free energy $F = -\frac{1}{\beta} \ln(Z_c)$

- **grand part. fct.** $Z_c = \sum_{N=0}^{\infty} \int_{\Gamma} g_i e^{-\beta(H - \mu N)} d\mu_c = \sum_{N=0}^{\infty} z^N Z_c(N)$, with fugacity $z = e^{\beta \mu}$ and e.e.v. $\langle H \rangle_g = \frac{1}{Z_g} \sum_{N=0}^{\infty} \int_{\Gamma} H e^{-\beta(H - \mu N)} d\mu_c$, expected particle number $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_g = -\frac{\partial \Omega}{\partial \mu}$

- **fluctuations:** e.g. energy $\sigma_H^2 = \langle (H - \langle H \rangle)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial \langle H \rangle}{\partial \beta}$, where $\langle H \rangle = \frac{1}{Z_c} \int_{\Gamma} H e^{-\beta H} d\mu_c = -\frac{1}{Z_c} \frac{\partial Z_c}{\partial \beta}$

- **uncoupled Ising model/ideal paramagnet** (N uncoupled Ising spins in external field h): $H(s) = -hm \sum_{j=1}^N s_j = -hM(s)$, minus \Rightarrow energy lowered if spins align with external field; $s = (s_1, \dots, s_N) \in \mathcal{S}_N = \{\pm 1\}^N$ is any of 2^N possible spin configurations; energy shell $\mathcal{E} = \{s \in \mathcal{S}_N | H(s) = E\}$ (non-empty only if $E/hm \in \mathbb{Z} \cap [-N, N]$), microcan. part. fct. $Z_m = \binom{N}{N/2}$, entropy $S = Nk_B \ln(2) - \frac{Nk_B}{2} [(1 + \frac{E}{Nmh}) \ln(1 + \frac{E}{Nmh}) + (1 - \frac{E}{Nmh}) \ln(1 - \frac{E}{Nmh})]$; canonical p.f. $Z_c = \sum_{s \in \mathcal{S}_N} e^{-\beta H(s)} = \prod_{j=1}^N \sum_{s_j} e^{\beta h m s_j} = [2 \cosh(\beta h m)]^N$, free energy $F = -\frac{1}{\beta} \ln Z_c = -\frac{N}{\beta} \ln[2 \cosh(\beta h m)]$, magnetization $M = -\frac{\partial F}{\partial h} = Nm \tanh(\beta h m)$, caloric e.o.s. $E = -\frac{\partial \ln Z_c}{\partial \beta} = -Nmh \tanh(\beta h m)$, specific heat $c_h = \frac{C_h}{N} = \frac{1}{N} \frac{\partial U}{\partial T} \Big|_h = k_B \frac{\beta^2 h^2 m^2}{\cosh^2(\beta h m)}$, magnetic susceptibility $\chi = \frac{\partial M}{\partial h} = \frac{\beta N m^2}{\cosh^2(\beta h m)}$, Gibbs fundamental rel. $dS = \frac{1}{T} dE + \frac{M}{T} dh - \frac{\mu}{T} dN$

- **coupled Ising model** $H(s) = J \sum_{\langle s_i, s_j \rangle} (1 - s_i s_j) - h \sum_{i=1}^N s_i$, can. part. fct. $Z_c = \sum_{s \in \mathcal{S}_N} e^{-\beta H(s)}$, **mean-field magnetization** per spin of Ising ferromagnet $m = \tanh(2d\beta J m + \beta h)$ with crit. temp. $T_c = 2dJ/k_B$

- **density operator:** $\rho^\dagger = \rho$, $\text{tr}(\rho) = 1$, $\rho \geq 0$, observable A expectation value $\langle A \rangle = \text{tr}(\rho A)$

– spin- $\frac{1}{2}$: $\rho = \frac{1}{2}(\mathbb{1}_2 + \mathbf{a} \cdot \boldsymbol{\sigma})$ with Bloch vector $\mathbf{a} = \langle \boldsymbol{\sigma} \rangle = \text{tr}(\boldsymbol{\sigma} \rho)$, eigenvalues $\lambda_{\pm} = \frac{1}{2}(1 \pm |\mathbf{a}|)$ where $|\mathbf{a}| \leq 1$; pure state, i.e. $\rho^2 = \rho$ if $|\mathbf{a}| = 1$, mixed else, spin polarization $\pi = \frac{p_+ - p_-}{p_+ + p_-}$

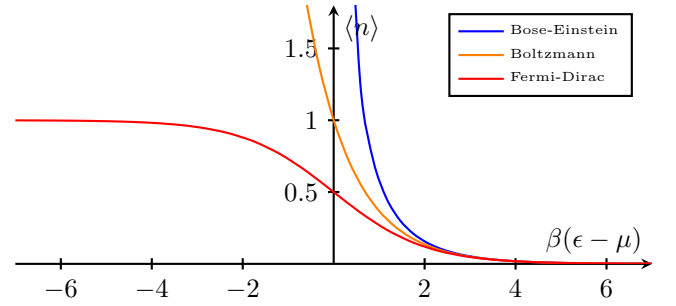
– **von Neumann entropy** $S_N = -k_B \text{tr}_{\mathcal{H}}[\rho \ln(\rho)]$ with $\rho = \sum_n p_n |n\rangle \langle n|$ sum over complete set of states of Hilbert \mathcal{H} , reduces to Boltzmann entropy for microcan. ensemble

– canonical density op. $\rho_c = e^{\beta(F-H)} = \frac{1}{Z_c} e^{-\beta H}$, with normalization $Z_c = \text{tr} e^{-\beta H}$

- (anti-)symmetrized **many-particle states** $\mathcal{P}_{\pm} |\alpha_1\rangle \otimes \dots \otimes |\alpha_n\rangle = \frac{1}{n!} \sum_{\pi \in S_n} (\pm 1)^{\pi} |\alpha_{\pi(1)}\rangle \otimes \dots \otimes |\alpha_{\pi(n)}\rangle$ furnish Fock space $\mathcal{F}_{\pm}(\mathcal{H}) = \bigoplus_{n=0}^{\infty} \mathcal{H}_{\pm}^n$ with $\mathcal{H}_{\pm}^n = \mathcal{P}_{\pm} \mathcal{H}^{\otimes n}$

- **occupation numbers** $\langle n_k^{\pm} \rangle_g = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_k} \ln(Z_g^{\pm}) = \frac{1}{e^{\beta(\epsilon_k - \mu)} \mp 1}$ given by Bose-Einstein/Fermi-Dirac distributions with $Z_g^{\pm} = \text{tr}_{\mathcal{F}_{\pm}}(e^{-\beta(\hat{H} - \mu \hat{N})}) = \prod_{j=0}^{\infty} \sum_{n_j^{\pm}=0}^{\infty} e^{-\beta n_j (\epsilon_j - \mu)} = \prod_{j=0}^{\infty} (1 \mp e^{-\beta(\epsilon_j - \mu)})^{\mp 1}$

– Maxwell-Boltzmann distribution $f(\mathbf{p}) = e^{-\beta \epsilon(\mathbf{p} - \mu)}$, or normalized and spherically sym. $f(v) = (\frac{m}{2\pi k_B T})^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}}$



- total particle fluctuations $\Delta N = \langle N^2 \rangle - \langle N \rangle^2 = \sum_k \langle n_k^2 \rangle - \sum_k \langle n_k \rangle^2$ for non-interacting gases

- **grand potential** $\Omega = -\frac{1}{\beta} \ln Z_g$, $\Omega = -pV$, ideal Bose/Fermi gas $\Omega^{\pm}(T, V, \mu) = -\frac{1}{\beta} \ln(Z_g^{\pm}) = \pm \frac{1}{\beta} \sum_j \ln(1 \mp e^{-\beta(\epsilon_j - \mu)})$ with $p = -\frac{\partial \Omega}{\partial V}$, $S_g = -\frac{\partial \Omega}{\partial T}$

- **ideal Fermi gas:** pressure $\beta p = \frac{4\pi g_s}{h^3} \int_0^{\infty} dp p^2 \ln(1 + e^{\beta(p^2/2m - \mu)}) = \frac{g_s}{\lambda^3} f_{5/2}(z)$, density $\rho = \frac{N}{V} = \frac{4\pi g_s}{h^3} \int_0^{\infty} \frac{p^2 dp}{1 + e^{\beta(p^2/2m - \mu)}} = \frac{g_s}{\lambda^3} f_{3/2}(z)$, where $f_{\nu}^{\pm}(z) = \frac{1}{\Gamma(\nu)} \int_0^{\infty} \frac{x^{\nu-1} dx}{z^{-1} e^x \mp 1}$, $z = e^{\beta \mu}$ and $\lambda = h/\sqrt{2\pi m k_B T}$, low temperature/high density means $\rho \lambda^3 \gg 1 \Rightarrow z \gg 1$, e.o.s. $\frac{pV}{k_B T} = \ln Z_g^{\pm} = \mp g_s \sum_k \ln(1 \mp e^{-\beta(\epsilon_k - \mu)})$, energy $U = \frac{3}{2} pV$

- **ideal Bose gas:** non-interacting (spinless) bosons with disp. rel. $\epsilon_k = \hbar^2 k^2 / 2m$ contained in $V = L^d$; grand part. fct. $Z_g = \sum_{N=0}^{\infty} \sum_{\{n_k\}} e^{-\beta \sum_k n_k (\epsilon_k - \mu)} \delta_{\sum_k n_k, N} = \prod_k \sum_{\{n_k\}} e^{-\beta \sum_k n_k (\epsilon_k - \mu)} = \prod_k \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}$, grand potential $\Omega = -\frac{1}{\beta} \ln(Z_g) = \frac{1}{\beta} \sum_k \ln(1 - e^{-\beta(\epsilon_k - \mu)}) \xrightarrow{V \rightarrow \infty} \frac{V}{\beta} \frac{A_{d-1}(1)}{(2\pi)^d} \int_0^{\infty} \ln(1 - z e^{-\beta \epsilon_k}) k^{d-1} dk$, now subst.

$x = \frac{\beta \hbar^2 k^2}{2m}$ followed by partial integration to get $\Omega = \frac{V}{\beta} \frac{A_{d-1}(1)}{(2\pi)^d} \frac{1}{2} (\frac{2m}{\hbar^2 \beta})^{\frac{d}{2}} \int_0^{\infty} x^{\frac{d}{2}-1} \ln(1 - z e^{-x}) dx = -\frac{V}{\beta} \frac{A_{d-1}(1)}{d} (\frac{2m}{\hbar^2 \beta})^{\frac{d}{2}} \int_0^{\infty} \frac{x^{\frac{d}{2}}}{z^{-1} e^x - 1} dx = -\frac{V}{\beta \lambda^d} f_{\frac{d}{2}+1}^+(z)$, avr.

number of particles $N = \frac{\partial \ln \Omega}{\partial (\beta \mu)} = \frac{V}{\lambda^d} f_{\frac{d}{2}}^+(z) \Rightarrow$ density $n(z) = \frac{1}{\lambda^d} f_{\frac{d}{2}}^+(z)$; pressure $pV = -\Omega$ and $E = -\frac{\partial \ln Z_g}{\partial \beta} = \frac{d}{2} \frac{\ln Z_g}{\beta} = -\frac{d}{2} \Omega$, i.e. $E = \frac{d}{2} pV$; critical temperature obtained by solving $n(1) = \frac{1}{\lambda^d} \zeta(\frac{d}{2})$ for T_c , for $d > 2$, this yields $T_c = \frac{\hbar^2}{2m k_B} (\frac{n}{\zeta(\frac{d}{2})})^{\frac{2}{d}}$; heat capacity at $T < T_c$, $z = 1$ is

$C(T) = \frac{\partial E}{\partial T} \Big|_{z=1} = k_B \frac{d}{2} (\frac{d}{2} + 1) \frac{V}{\lambda^d} \zeta(\frac{d}{2} + 1)$ e.o.s. at high T ($z \rightarrow 0$) is $\frac{pV}{N k_B T} = 1 - \frac{N \lambda^3}{4\sqrt{2}V} + \dots$ has correction to ideal gas that lowers the pressure and is solely due to quantum statistics (not interactions)