Statistical Mechanics

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Books:

C. Kittel, H. Kroemer, Thermal Physic, Freeman and Company F. Reif, Fundamentals of Statistical and Thermal Physics, Mc Graw Hill L. Landau, E. Lifshitz, Statistical Physics (Volume 5) K. Huang, Statistical mechanics, John Wiley and Sons

0 Introduction

The subject of thermodynamics and statistical mechanics is the description of the macroscopic properties of systems with a large number of degrees of freedom on the basis of the microscopic laws of physics.
A complete description of very large systems is not possible. The number of degrees of freedom is too large. A complete measurement is not possible and in most cases it would bring the system into a completely different state. Instead one uses an incomplete description by only a small number of macroscopic quantities, as for example energy, volume, and particle number.
Originally such systems were described phanomenologically within the framework of thermodynamics. Starting point was the irreversibility of processes (second law of thermodynamics), which allowed to introduce the state variable entropy besides temperature. This allowed to derive thermodynamic relations without recourse to microscopic considerations.
A modern approach which we will follow here has a statistical microscopic basis, which is built upon the laws of mechanics, quantum mechanics, and electrodynamics.
Within this theory one considers ensembles instead of single systems. Questions, which arise, are: How are these ensembles to be described? Are the averages of the ensembles representative? It will turn out, that due to the law of large numbers the relative fluctuations will become very small. Another question is: How does the transition to equilibrium take place?
Statistical mechanics is applied in the physics of condensed matter in its broadest sense. This holds for the solid state, but also for other phases as well as in nuclear physics and elementary particle physics at high energies and in astrophysics.

A Basic Concepts in Statistics

1 Description of quantummechanical ensembles

1.a Statistical operator or density matrix

If we have only incomplete information of a quantum system, then we describe it by a *statistical ensemble*. The system be with probability p_i in the state $|i\rangle$. The probabilities have to obey

$$p_i \geq 0 \quad \text{and} \quad \sum_i p_i = 1. \tag{1.1}$$

The states $|i\rangle$ need not be orthogonal to each other and nedd not be complete, but they are supposed to be normalized. Then the expectation value of an operator A is given by

$$\langle A\rangle = \sum_i p_i \langle i|A|i\rangle. \tag{1.2}$$

We now insert a complete set of orthogonal and normalized states $|\nu\rangle$,

$$\sum_\nu |\nu\rangle\langle\nu| = 1\!\!1. \tag{1.3}$$

Then we obtain for the expectation value of A

$$\langle A\rangle = \sum_{i,\nu} p_i \langle i|A|\nu\rangle\langle\nu|i\rangle = \sum_{i,\nu} \langle\nu|i\rangle p_i \langle i|A|\nu\rangle = \sum_\nu \langle\nu|\rho A|\nu\rangle = \mathrm{tr}(\rho A), \tag{1.4}$$

where

$$\rho = \sum_i |i\rangle p_i \langle i| \tag{1.5}$$

is the statistical operator or density matrix, which describes the statistical ensemble. In general it is not possible to determine the states $|i\rangle$ and their probabilities from ρ.
We consider some properties of ρ: α) ρ is hermitean,

$$\rho^\dagger = \rho, \tag{1.6}$$

since the probabilities p_i are real. β) The trace of ρ equals unity,

$$\mathrm{tr}(\rho) = \sum_{i,\nu} \langle\nu|i\rangle p_i \langle i|\nu\rangle = \sum_i p_i \underbrace{\sum_\nu \langle i|\nu\rangle\langle\nu|i\rangle}_{\langle i|i\rangle=1} = \sum_i p_i = 1, \tag{1.7}$$

since the sum of the probabilities adds up to one. γ) ρ is positive semi-definite, that is for each state $|a\rangle$ one has

$$\langle a|\rho|a\rangle = \sum_i \langle a|i\rangle p_i \langle i|a\rangle = \sum_i p_i |\langle a|i\rangle|^2 \geq 0, \tag{1.8}$$

since $p_i \geq 0$.

Since ρ is hermitean it can be diagonalized, that is there exists an orthonormal basis $\{|n\rangle\}$, for which

$$\rho = \sum_n |n\rangle \rho_n \langle n| \tag{1.9}$$

holds. From β) one concludes $\sum_n \rho_n = 1$ and from γ) that $0 \leq \rho_n \leq 1$ holds.
If the system consists of a pure state only, then one has

$$\rho_n = \begin{cases} 1 & \text{for one } n, \\ 0 & \text{for all other } n\text{s}. \end{cases} \tag{1.10}$$

Example The ensemble consists of neutrons, the spins of which are oriented in $+z$-direction with probability p_1 and in $+x$-direction with probability p_2, $p_1 + p_2 = 1$. With

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.11}$$

one obtains from $\sigma_z|+z\rangle = +|+z\rangle$ and $\sigma_x|+x\rangle = +|+x\rangle$

$$|+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \langle +z| = |+z\rangle^\dagger = \begin{pmatrix} 1 & 0 \end{pmatrix}, \quad |+x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \langle +x| = |+x\rangle^\dagger = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \tag{1.12}$$

and therefore

$$\rho = p_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + p_2 \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \end{pmatrix} = \begin{pmatrix} p_1 + \frac{p_2}{2} & \frac{p_2}{2} \\ \frac{p_2}{2} & \frac{p_2}{2} \end{pmatrix}. \tag{1.13}$$

We observe

$$\mathrm{tr}\rho = p_1 + p_2 = 1 \tag{1.14}$$

and find the eigenvalues

$$\rho_{1,2} = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{1}{2} p_1 p_2}. \tag{1.15}$$

1.b Reduced density matrix

One often deals with the situation, that a system consists of two subsystems, which can be described by complete orthonormal bases $|\nu_1\rangle$, $|\nu_2\rangle$. It may be that both are subsystems of the system we are investigating or subsystem 2 was or still is in contact with subsystem 1. The vectors $|\nu_1, \nu_2\rangle$ (direct product) in Hilbert space constitute a complete orthonormal basis of the total system. Be ρ the density matrix of the total system and A_1 an operator acting only in the first subsystem. Then one has

$$\langle A_1 \rangle = \sum_{\nu_1,\nu_2} \langle \nu_1, \nu_2 | \rho A_1 | \nu_1, \nu_2 \rangle = \sum_{\nu_1,\nu_2,\mu_1,\mu_2} \langle \nu_1, \nu_2 | \rho | \mu_1, \mu_2 \rangle \langle \mu_1, \mu_2 | A_1 | \nu_1, \nu_2 \rangle. \tag{1.16}$$

The operator A_1 acts only in subsystem 1, it leaves subsystem 2 unchanged, thhus acts like the unit-operator $\mathbb{1}_2$,

$$\langle \mu_1, \mu_2 | A_1 | \nu_1, \nu_2 \rangle = \langle \mu_1, \mu_2 | A_1 \mathbb{1}_2 | \nu_1, \nu_2 \rangle = \langle \mu_1 | A_1 | \nu_1 \rangle \langle \mu_2 | \mathbb{1}_2 | \nu_2 \rangle = \langle \mu_1 | A_1 | \nu_1 \rangle \delta_{\mu_2,\nu_2}. \tag{1.17}$$

Thus we may write

$$\langle A_1 \rangle = \sum_{\nu_1,\nu_2,\mu_1} \langle \mu_1 | A_1 | \nu_1 \rangle \langle \nu_1, \nu_2 | \rho | \mu_1, \nu_2 \rangle = \sum_{\nu_1,\mu_1} \langle \nu_1 | \rho_1 | \mu_1 \rangle \langle \mu_1 | A_1 | \nu_1 \rangle = \mathrm{tr}_1(\rho_1 A_1) \tag{1.18}$$

with the reduced density matrix ρ_1, defined by

$$\langle \nu_1 | \rho_1 | \mu_1 \rangle = \sum_{\nu_2} \langle \nu_1, \nu_2 | \rho | \mu_1, \nu_2 \rangle. \tag{1.19}$$

Thus one takes the trace on subsystem 2 and writes

$$\rho_1 = \mathrm{tr}_2 \rho = \sum_{\nu_1,\mu_1} |\nu_1\rangle \sum_{\nu_2} \langle \nu_1, \nu_2|\rho|\mu_1, \nu_2\rangle\langle\mu_1|. \tag{1.20}$$

Even if ρ corresponds to a pure state, then in general ρ_1 will be a mixture. **Example.** Two electrons have total spin 0,

$$|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \tag{1.21}$$

$$\rho = |\chi\rangle\langle\chi| = \frac{1}{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|), \tag{1.22}$$

$$\rho_1 = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow|. \tag{1.23}$$

Both eigenvalues of ρ_1 are 1/2; thus we deal with a mixture.

1.c von Neumann equation

In general ρ is a function of time t. We derive the equation of motion. Starting from the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\mathrm{d}|i\rangle}{\mathrm{d}t} = H|i\rangle \leftrightarrow \mathrm{i}\hbar\frac{\partial\psi_i(x,t)}{\partial t} = H\psi_i(x,t) \tag{1.24}$$

and its hermitean adjoint

$$-\mathrm{i}\hbar\frac{\mathrm{d}\langle i|}{\mathrm{d}t} = \langle i|H. \tag{1.25}$$

we obtain

$$\mathrm{i}\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t} = \mathrm{i}\hbar\sum_i p_i\frac{\mathrm{d}|i\rangle\langle i|}{\mathrm{d}t} = \sum_i p_i(H|i\rangle\langle i| - |i\rangle\langle i|H) = [H,\rho]. \tag{1.26}$$

This is the von-Neumann equation.

Stationary ensembles A stationary ensemble is an ensemble which does not change as a function of time. Thus it obeys the condition

$$\dot{\rho} = 0, \text{ id est } [H,\rho] = 0. \tag{1.27}$$

In the enrgy representation, that is in a basis of states, which are eigenstates of the Hamiltonian, $H|n\rangle = E_n|n\rangle$, one obtains from

$$\langle m|H\rho - \rho H|n\rangle = 0 \tag{1.28}$$

the condition

$$(E_m - E_n)\rho_{m,n} = 0, \tag{1.29}$$

that is $\rho_{m,n}$ vanishes , if $E_m \neq E_n$. If there is no degeneracy then one may write

$$\rho = \sum_n \rho(E_n)|n\rangle\langle n|. \tag{1.30}$$

2 Ensembles of Classical Mechanics

2.a Distribution function

In classical mechanics a system is defined by the momentum and position coordinates of its N particles,

$$(\mathbf{p},\mathbf{x}) = (\mathbf{p}_1,\mathbf{p}_2,...\mathbf{p}_N,\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N). \tag{2.1}$$

These coordinates span the $6N$-dimensional configuration space (phase space Γ-space).

$$\rho(\mathbf{p}_1,...\mathbf{p}_N,\mathbf{x}_1,...\mathbf{x}_N)\mathrm{d}^{3N}p\,\mathrm{d}^{3N}x \tag{2.2}$$

be the probability for the system to be in the volume-element $\mathrm{d}^{3N}p\,\mathrm{d}^{3N}x$ at $(\mathbf{p}_1,...\mathbf{x}_N)$. The expectation value of a function $A(\mathbf{p}_1,...\mathbf{x}_N)$ is then given by

$$\langle A(\mathbf{p},\mathbf{x})\rangle = \int \mathrm{d}^{3N}p\,\mathrm{d}^{3N}x\,\rho(\mathbf{p},\mathbf{x})A(\mathbf{p},\mathbf{x}). \tag{2.3}$$

The distribution function ρ has the properties

$$\rho(\mathbf{p},\mathbf{x}) \geq 0, \qquad \int \mathrm{d}^{3N}p\,\mathrm{d}^{3N}x\,\rho(\mathbf{p},\mathbf{x}) = 1. \tag{2.4}$$

2.b Liouville equation and Liouville theorem

The distribution function is a function of time, $\rho(\mathbf{p},\mathbf{x},t)$. A single system is described by a point in the Γ space, whose coordinates vary as a function of time. Since the number of systems is conserved, an equation of continuity holds in phase space. Equations of continuity have the form $\frac{\partial\rho}{\partial t} + \mathrm{div}\,(\rho\mathbf{v}) = 0$. In phase space both the time derivatives of $\mathbf{x}$ and of $\mathbf{p}$ are "velocities $\mathbf{v}$". Thus the equation of continuity reads

$$\frac{\partial\rho}{\partial t} + \sum_{i,\alpha}\frac{\partial}{\partial x_{i\alpha}}(\rho\dot{x}_{i\alpha}) + \sum_{i,\alpha}\frac{\partial}{\partial p_{i\alpha}}(\rho\dot{p}_{i\alpha}) = 0. \tag{2.5}$$

The particles are numbered by the index i and the cartesian components by α. We consider now the substantial (=total) derivative of ρ, that is, we follow how ρ changes, as we move with the corresponding point in phase space,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\mathrm{d}\rho(\mathbf{p}(t),\mathbf{x}(t),t)}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum_{i,\alpha}\dot{x}_{i\alpha}\frac{\partial\rho}{\partial x_{i\alpha}} + \sum_{i,\alpha}\dot{p}_{i\alpha}\frac{\partial\rho}{\partial p_{i\alpha}}. \tag{2.6}$$

If we express the partial derivative $\frac{\partial\rho}{\partial t}$ by the equation of continuity, then we are left with

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \sum_{i,\alpha}\left(\frac{\partial\dot{x}_{i\alpha}}{\partial x_{i\alpha}} + \frac{\partial\dot{p}_{i\alpha}}{\partial p_{i\alpha}}\right)\rho = 0. \tag{2.7}$$

Now we have

$$\dot{x}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}}, \quad \dot{p}_{i\alpha} = -\frac{\partial H}{\partial x_{i\alpha}}. \tag{2.8}$$

From this we obtain

$$\frac{\partial\dot{x}_{i\alpha}}{\partial x_{i\alpha}} + \frac{\partial\dot{p}_{i\alpha}}{\partial p_{i\alpha}} = \frac{\partial^2 H}{\partial x_{i\alpha}\partial p_{i\alpha}} - \frac{\partial^2 H}{\partial p_{i\alpha}\partial x_{i\alpha}} = 0 \tag{2.9}$$

and thus Liouville's theorem

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0. \tag{2.10}$$

Consequence A system $\mathbf{p}_0$, $\mathbf{x}_0$ at time t_0 changes into the system $\mathbf{p}$, $\mathbf{x}$ at time t. Since the density in phase-space is conserved, the volume element will stay constant,

$$\frac{\partial(\mathbf{p},\mathbf{x})}{\partial(\mathbf{p}_0,\mathbf{x}_0)} = 1. \tag{2.11}$$

We finally determine the partial derivative of ρ,

$$\frac{\partial\rho}{\partial t} = \frac{\mathrm{d}\rho}{\mathrm{d}t} - \sum_{i\alpha}\dot{x}_{i\alpha}\frac{\partial\rho}{\partial x_{i\alpha}} - \sum_{i\alpha}\dot{p}_{i\alpha}\frac{\partial\rho}{\partial p_{i\alpha}} = -\sum_{i\alpha}\frac{\partial H}{\partial p_{i\alpha}}\frac{\partial\rho}{\partial x_{i\alpha}} + \sum_{i\alpha}\frac{\partial H}{\partial x_{i\alpha}}\frac{\partial\rho}{\partial p_{i\alpha}} = -\{\rho,H\}, \tag{2.12}$$

where $\{\rho,H\}$ is the Poisson-bracket between ρ and H.
Stationary Ensembles For them $\dot{\rho}=0$ holds again. If ρ depends only on conserved quantities, then it is stationary, $\rho=\rho(H,\mathbf{P},\mathbf{L},N)$. Since normally the system is not in rotational invariant vessels, $\mathbf{P}$ and $\mathbf{L}$ are normally no conserved quantities, $\rho=\rho(H,N)$.

3 Probabilities, Correlations and Variances

3.a Probability and variance

Apart from the expectation value of an observable A one is also interested in its variance

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2. \tag{3.1}$$

The quantity ΔA indicates, how strongly the measured a of A may deviate from the average $\langle A \rangle$ for a system, $a = \langle A \rangle \pm \Delta A$. This variance ΔA is also called standard deviation. If ΔA is negligible small, then $\langle A \rangle$ is the expected outcome of the measurement.
We now define the probability distribution for A,

$$w_A(a) = \langle \delta(a - A) \rangle = \mathrm{tr}(\rho \delta(a - A)). \tag{3.2}$$

The operator-valued function of an operator is understood in the following way: A be expressed in terms of its eigenstates $|i\rangle$

$$A = \sum_i |i\rangle a_i \langle i|. \tag{3.3}$$

Then the function $f(A)$ is defined as

$$f(A) = \sum_i |i\rangle f(a_i) \langle i|. \tag{3.4}$$

One may convince oneself that the definition is in agreement with the four basic arithmetical operations and the Taylor- and Laurent-expansion. This definition is a generalization, if such an expansion is not possible.

$$\delta(a - A) = \sum_i |i\rangle \delta(a - a_i) \langle i|. \tag{3.5}$$

The probability distribution is then given by

$$w_A(a) = \langle \delta(a - A) \rangle = \mathrm{tr}(\rho \sum_i |i\rangle \delta(a - a_i) \langle i|) = \sum_i \langle i|\rho|i\rangle \delta(a - a_i). \tag{3.6}$$

From this one obtains

$$\begin{aligned} \langle f(A) \rangle &= \sum_i f(a_i) \langle |i\rangle\langle i| \rangle = \sum_i f(a_i) \mathrm{tr}(\rho |i\rangle\langle i|) = \sum_i f(a_i) \langle i|\rho|i\rangle \\ &= \int \mathrm{d}a f(a) \sum_i \delta(a - a_i) \langle i|\rho|i\rangle = \int \mathrm{d}a f(a) w_A(a). \end{aligned} \tag{3.7}$$

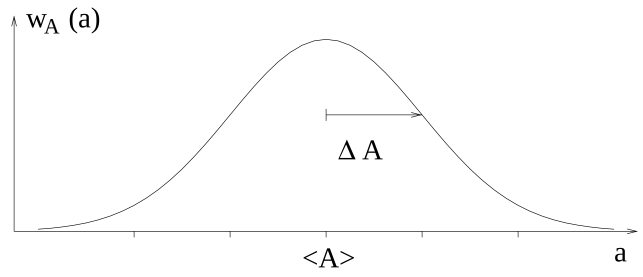
This yields immediately

$$\int \mathrm{d}a\, w_A(a) = 1, \tag{3.8}$$

$$\int \mathrm{d}a\, a w_A(a) = \langle A \rangle, \tag{3.9}$$

$$\int \mathrm{d}a\, (a - \langle A \rangle)^2 w_A(a) = (\Delta A)^2. \tag{3.10}$$

Half the width of the distribution equals approximately ΔA.
Example: Gauss distribution



If the spectrum of A is discrete, then it is useful to replace the distribution $\delta(a-A)$ by the Kronecker-Delta

$$\delta_{a,A} = \sum_i \delta_{a,a_i} |i\rangle\langle i| \tag{3.11}$$

and the integral by the sum

$$\begin{aligned} w_A(a) &= \mathrm{tr}(\rho\delta_{a,A}) = \sum_i \delta_{a,a_i} \langle i|\rho|i\rangle, &(3.12)\\ \langle f(A)\rangle &= \sum_a w_A(a) f(a). &(3.13)\end{aligned}$$

For classical statistical mechanics one has correspondingly

$$w_A(a) = \langle \delta(a-A)\rangle = \int \mathrm{d}^{3N}p\, \mathrm{d}^{3N}x\, \rho(\mathbf{p},\mathbf{x})\delta(a - A(\mathbf{p},\mathbf{x})). \tag{3.14}$$

This corresponds to the integration on the shell given by $a = A(\mathbf{p},\mathbf{x})$.

3.b Correlations

Apart from the fluctuations of one quantity A one is often interested in correlations of several observables A and B. If A and B commutate, then the correltion is defined by

$$K_{A,B} = \langle (A - \langle A\rangle)(B - \langle B\rangle)\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle. \tag{3.15}$$

If $K_{A,B} \neq 0$, then one says, that A and B are correlated.
One can define a probability distribution

$$w_{A,B}(a,b) = \langle \delta(a-A)\delta(b-B)\rangle = \mathrm{tr}(\rho\delta(a-A)\delta(b-B)) = \sum_i \langle i|\rho|i\rangle \delta(a-a_i)\delta(b-b_i) \tag{3.16}$$

for eigenstates $|i\rangle$ of A and B. Then one obtains

$$\langle f(A,B)\rangle = \int \mathrm{d}a\, \mathrm{d}b\, w_{A,B}(a,b) f(a,b), \tag{3.17}$$

e.g.

$$\langle AB\rangle = \int \mathrm{d}a\, \mathrm{d}b\, w_{A,B}(a,b)ab. \tag{3.18}$$

One finds

$$\int \mathrm{d}b\, w_{A,B}(a,b) = w_A(a). \tag{3.19}$$

If $w_{A,B}(a,b) = w_A(a)w_B(b)$, then A and B are called statistically independent. Then one has

$$\langle AB\rangle = \int \mathrm{d}a\, \mathrm{d}b\, ab w_{A,B}(a,b) = \int \mathrm{d}a\, w_A(a) \int \mathrm{d}b\, w_B(b) = \langle A\rangle\langle B\rangle, \tag{3.20}$$

thus $K_{A,B} = 0$. However, from $K_{A,B} = 0$ one cannot conclude statistical independence. For classical systems one introduces analogously the probability distribution

$$w_{A,B}(a,b) = \int \mathrm{d}^{3N}p\, \mathrm{d}^{3N}x\, \rho(\mathbf{p},\mathbf{x})\delta(a - A(\mathbf{p},\mathbf{x}))\delta(b - B(\mathbf{p},\mathbf{x})). \tag{3.21}$$

3.c Fluctuations in the thermodynamic limit

One often deals in statisitical mechanics with densities and volume-integrals of densities

$$A = \int \mathrm{d}^3 r \hat{a}(r), \tag{3.22}$$

as e.g. the particle density, energy density, magnetization etc. The variance of these quantities is

$$\begin{aligned}(\Delta A)^2 &= \int \mathrm{d}^3 r \mathrm{d}^3 r' (\langle \hat{a}(r)\hat{a}(r')\rangle - \langle \hat{a}(r)\rangle\langle \hat{a}(r')\rangle) \\ &= \int \mathrm{d}^3 r \mathrm{d}^3 r' \langle (\hat{a}(r) - \langle \hat{a}(r)\rangle)(\hat{a}(r') - \langle \hat{a}(r')\rangle)\rangle \\ &= \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a}(r),\hat{a}(r')} = \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a}\hat{a}}(r, r'). \end{aligned} \tag{3.23}$$

The correlations of macroscopic quantities have often a finite range. Measurements at loci far apart are statistically independent. The range of the correlations is often of the same order as the range of the microscopic interaction. (Exceptions: Continuous phase transitions, long-range order at broken symmetries). Then $(\Delta A)^2$ is of the order of the volume if we use that K often depends only on the distance, $K_{\hat{a},\hat{a}}(r, r') = K_{\hat{a},\hat{a}}(r - r', 0)$.

$$(\Delta A)^2 = \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a},\hat{a}}(r - r', 0) = V \int \mathrm{d}^3 r K_{\hat{a},\hat{a}}(r, 0). \tag{3.24}$$

Since $\langle A \rangle$ is a volume integral and thus proportional to the volume V one has

$$\frac{\Delta A}{\langle A \rangle} \propto \frac{\sqrt{V}}{V} = \frac{1}{\sqrt{V}}. \tag{3.25}$$

For large systems the fluctuations become negligibly small and $\langle A \rangle$ agrees practically always the measured one.

3.d Example: Magnetic Moments

We consider N magnetic moments μ_i, which are statistically independent. The probability that the moment assumes $\mu_i = +\mu$ be p_1, and that it assumes $\mu_i = -\mu$ be p_2, $p_1 + p_2 = 1$. Then one obtains the total magnetic moment

$$\langle M \rangle = \sum_{i=1} \langle \mu_i \rangle = \sum_i (p_1 - p_2)\mu = N(p_1 - p_2)\mu. \tag{3.26}$$

and the variance

$$(\Delta M)^2 = \langle (M - \langle M \rangle)(M - \langle M \rangle)\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle (\mu_i - \langle \mu_i \rangle)(\mu_j - \langle \mu_j \rangle)\rangle. \tag{3.27}$$

Considering that the moments are statistically independent directed all contributions with $i \neq j$ vanish in the sum and one is left with

$$(\Delta M)^2 = \sum_{i=1}^{N} \langle (\mu_i - \langle \mu_i \rangle)^2 \rangle = \sum_{i=1}^{N} (\langle \mu_i^2 \rangle - \langle \mu_i \rangle^2) = \sum_i (\mu^2 - \mu^2 (p_1 - p_2)^2) = 4N\mu^2 p_1 p_2, \tag{3.28}$$

since $(p_1 - p_2)^2 = (p_1 + p_2)^2 - 4p_1 p_2 = 1 - 4p_1 p_2$. Then one obtains

$$\frac{\Delta M}{\langle M \rangle} = \frac{2\sqrt{p_1 p_2}}{\sqrt{N}(p_1 - p_2)}. \tag{3.29}$$

Probability distribution We now consider the probability distribution. $w_{N_\uparrow}(n)$ be the probability that precisely n of the total N moments are directed upward,

$$w(n) = p_1^n p_2^{N-n} W. \tag{3.30}$$

Here W is the number of sets of n moments out of N moments,

$$W = \binom{N}{n} = \frac{N!}{n!(N-n)!} \tag{3.31}$$

For large N one can apply the Stirling formula (A.5) for n factorial $n! \approx (n/e)^n \sqrt{2\pi n}$. Then one obtains

$$w(n) = \sqrt{\frac{N}{2\pi n(N-n)}} \left(\frac{p_1 N}{n}\right)^n \left(\frac{p_2 N}{N-n}\right)^{N-n}. \tag{3.32}$$

We are interested in $w(n)$ close to its maximum. Thus expand n around its average $p_1 N$ and put $n = p_1 N + \nu$, $N - n = p_2 N - \nu$

$$w(n) = \sqrt{\frac{N}{2\pi n(N-n)}} \underbrace{\left(1 + \frac{\nu}{p_1 N}\right)^{-p_1 N - \nu} \left(1 - \frac{\nu}{p_2 N}\right)^{-p_2 N + \nu}}_{g}. \tag{3.33}$$

and expand $\ln g$ in ν. We obtain

$$\begin{aligned}
\ln g &= (-p_1 N - \nu)\ln(1 + \frac{\nu}{p_1 N}) + (-p_2 N + \nu)\ln(1 - \frac{\nu}{p_2 N}) \\
&= (-p_1 N - \nu)\left(\frac{\nu}{p_1 N} - \frac{\nu^2}{2p_1^2 N^2} + \frac{\nu^3}{3p_1^3 N^3} - ...\right) \\
&+ (-p_2 N + \nu)\left(-\frac{\nu}{p_2 N} - \frac{\nu^2}{2p_2^2 N^2} - \frac{\nu^3}{3p_2^3 N^3} - ...\right) \qquad (3.34) \\
&= 0 \cdot \nu - \frac{1}{2}\left(\frac{1}{p_1 N} + \frac{1}{p_2 N}\right)\nu^2 + \frac{1}{6}\left(\frac{1}{p_1^2 N^2} - \frac{1}{p_2^2 N^2}\right)\nu^3 + ... + \frac{...\nu^k}{N^{k-1}} + ... \qquad (3.35)
\end{aligned}$$

If $\nu = O(N^{1/2})$ then the contribution ν^2/N is of order $O(N^0)$. The next one is $\nu^3/N^2 = O(N^{-1/2})$ and the higher ones $\nu^k/N^{k-1} = O(N^{1-k/2})$ with $k \geq 4$. These become negligibly small for large N and one obtains the Gaussian distribution in this limit

$$w(n) = \frac{1}{\sqrt{2\pi p_1 p_2 N}} \exp\left(-\frac{\nu^2}{2p_1 p_2 N}\right) = \frac{1}{\sqrt{2\pi p_1 p_2 N}} \exp\left(-\frac{(n - Np_1)^2}{2p_1 p_2 N}\right). \tag{3.36}$$