

Statistical Mecahcnis in a Nutshell

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1. Introduction

219 Working knowledge of methods for solving interaction-free systems is the foundation needed
to introduce the most important method to, explore the behavior of systems with interaction—
in other words, mean-field theory. ...

290 The microscopic structure of systems examined by statistical mechanics can be described
by means of mechanical models. ... The models to be examined can be, and recently in-
creasingly are, more abstract, however, and exhibit only a faint resemblance to the basic
mechanical description (more specifically, to the quantum nature of matter). The explana-
tion of the success of such abstract models is itself the topic of one of the more interesting
chapters of statistical mechanics: the theory of universality and its foundation in the renor-
malization group.

326 1.2 Statistical Postulates

338 Statistical postulates are for initial conditions. The Maxwell is iintroduced by indepdence
assumtions

415 Marcus and McFee experiment to measure the Maxwell distribution.

[C] Is this really the measurement of the distribution of the gas itself?

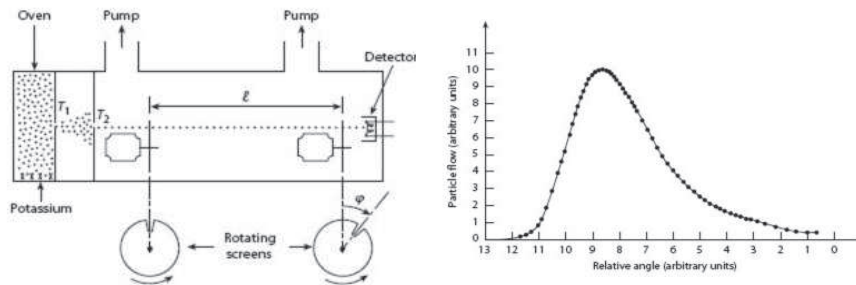


Figure 0.0.1: Marcus and McFee experiment [Fig. 1.2]

2 Thermodynamics

458 A thermodynamic system is a macroscopic system whose behavior is identified thanks to a
small and finite number of quantities- the thermodynamic properties.

Thermodynamics is a “miracle”: the system has $\sim 10^{23}$ degrees of freedom and yet it can
be sell described by a mush smaller number of variables.

[C] Becasue we observes are the product of mircle.

If the state of a thermodynamic system can be fully characterized by the values of the ther-
modynamic variables, and if these values are invariant over time, one says that it is in a

¹The English translation is not good; 5012 fixed pointsare confused, etc.

state of thermodynamic equilibrium. Thermodynamic equilibrium, as R. Feynman [Feyn72] says, occurs when all fast processes have already occurred, while the slow ones have yet to take place. Clearly the distinction between fast and slow processes is dependent on the observation time x that is being considered. This property has been emphasized especially by S.-K. Ma [MaSs, p. 3]:

497 As thermodynamics is usually formulated, the observation time x is not explicitly mentioned; we would, however, do well to remain aware of the fact that the set of thermodynamic variables (and therefore the relations that govern them) is implicitly determined by x . It is the physicist's task (guided each time by the experiment) to determine on each occasion the most appropriate thermodynamic description of the specific system under examination.

2.2 Extensive variable:

510 counter example: microemulsions

The fundamental hypothesis of thermodynamics is that it should be possible to characterize the state of a thermodynamic system by specifying the values of a certain set of extensive variables.

2.3 Central problem of thermodynamics

535 Given the initial state of equilibrium of several thermodynamic systems that are allowed to interact, determine the final thermodynamic state of equilibrium.

2.4 Entropy

574 Callen style characterization: extensivity, convexity and monotonicity.

628 Adiabatic and movable piston: no unique state available.

Then, Lieb-Yngvasson system is introduced.

2.8 Energy scheme

832 Max S is translated into min E . The proof uses the monotone concave fundamental surface. Notice that thanks to max entropy principle, we have

$$\Delta S = S(E, X_{eq} + \Delta X) - S(E, X_{eq}) \leq 0. \quad (0.0.1)$$

Since S is monotone-increasing function of E , there must be $E' \geq E$ such that

$$S(E', X_{eq} + \Delta X) = S(E, X_{eq}). \quad (0.0.2)$$

Therefore, if S is kept constant and X deviates from the equilibrium value, then E increases.

$TdS = \delta Q$ for reversible change. [C] where does this come from? Unclear.

2.9 Intensive variables and thermodynamic potentials

869 This is defined as the derivative.

density is mentioned.

1072 Maxwell's relation is systematized with the aid of the Koenig-Born diagram.

2.16 Magnetic systems

The sample is a thin cylinder inside a solenoid, identified by a number n of coils per unit length with a current I . The magnetic field (magnitude) is $H = nI$ in the solenoid. If the cylinder is homogeneous, it develops a uniform magnetization, with a certain value m of magnetic moment density per unit of volume. As a consequence, the magnetic induction vector \mathbf{B} is uniform, parallel to \mathbf{H} , and takes the form $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{m})$, where $\mu_0 = 4\pi \times 10^{-7}$ Wb/m·A is the magnetic permeability of the vacuum.

Now, let us suppose that we vary the current circulating in the solenoid by δI . The work performed by the system and associated with this variation is given by

$$\delta W = - \int_{t_i}^{t_f} dt I(t) V_{\text{ind}}(t), \quad (0.0.3)$$

where V_{ind} is the induced electromotive force, which can be expressed in terms of the flux Φ of the magnetic induction vector \mathbf{B} in the solenoid as

$$V_{\text{ind}} = \frac{d\Phi}{dt}. \quad (0.0.4)$$

1149 We thus obtain to order δ

$$\delta W = \int_{t_i}^{t_f} dt I(t) \frac{d\Phi(t)}{dt} = I \delta \Phi. \quad (0.0.5)$$

The flux is

$$\Phi = ABn\ell, \quad (0.0.6)$$

where A is the solenoid cross section and ℓ its length. We arrive at

$$\delta \Phi = nV \delta B = nV \mu_0 (\delta H + \delta m) = nV \mu_0 H + \mu_0 \delta M. \quad (0.0.7)$$

As a consequence, the work δW can be expressed as

$$\delta W = nV \mu_0 I \delta H + n \mu_0 I \delta M = \mu_0 V F \delta H + \mu_0 H \delta M. \quad (0.0.8)$$

The first term represents the variation in the energy of the magnetic field due to variations in the magnetic field itself. In fact, this energy is equal to

$$\delta E_{\text{mag}} = d \frac{1}{2} \int d^d \mathbf{r} \mu_0 H^2. \quad (0.0.9)$$

The second term represents the work performed on the sample in order to change its magnetization.

The contribution of the extensive variable \mathbf{M} to “mechanical” work is therefore given by

$$\delta W = \mu_0 \mathbf{H} \cdot \delta \mathbf{M}. \quad (0.0.10)$$

We can see that the variable conjugated to magnetization (in other words, to the total magnetic dipole) is the magnetic field.

1175 Since the dipolar interactions (which occur between regions that are magnetically polarized) are long range, **a certain caution is necessary when dealing with the magnetization M** as an ordinary thermodynamic variable. More specifically, given equal amounts of material and volume, samples with different shapes possess different energies even if immersed in the same magnetic field. One usually accounts for this effect by introducing a demagnetization factor, which is dependent on shapes.

1232 $C_x \geq C_X$.

1415 Planar interface

1467 Theory of elasticity

3. The Fundamental Postulate

1511 The key to the relation between mechanical and thermodynamic properties is the **microscopic expression of entropy**. This expression was found by Ludwig Boltzmann, and it has such an important role that we have decided to call it the fundamental postulate of statistical mechanics. Since we are dealing with a postulate, it cannot be proven- we can, however, make it plausible by showing that the properties of entropy that derive from it agree with the properties that we postulated in thermodynamics.

1521 The book start with CM.

1546 Let us call observables in statistical mechanics those functions, defined on the phase space, that vary smoothly enough when the representative point varies.

1567 The fundamental postulate of statistical mechanics expresses entropy as a function of the accessible volume in phase space— in other words, of the volume $|\Gamma|$ of the phase space in which the thermodynamic observables have values compatible with a specific thermodynamic state. Then the fundamental postulate states that

$$S = k_B \log |\Gamma|. \tag{0.0.11}$$

In this formula, This relation cannot be proven. Also microcanonical expression is possible.

1643 Liouville's theorem tells us $|\Gamma_0| = |\Gamma_t|$. From this Liouville's equation is derived (1691).

1737 The fundamental postulate in its quantum version stipulates that

$$S = k_B \log \mathcal{N}, \tag{0.0.12}$$

where \mathcal{N} is the number of state with eigenvalues compatible with thermodynamic observables.

1792 The variational principle for the entropy states that the equilibrium values ξ^* correspond to

the maximum value of the entropy.

2176 Gibbs formula of entropy.

4. Interaction-free system

2448 Sound wave equation for fluid

Second sound:

Conservation of energy: $\partial_t + \nabla \cdot \mathbf{j}_\epsilon$.

Conservation of momentum: $\partial_t \mathbf{p} + \nabla p$, Newton's equation of motion

Let \mathbf{P} be the total momentum, and regard it as a new extensive variable:

$$S(E_{\text{tot}}, \mathbf{P}) = S(E_{\text{tot}} - P^2/2M, 0). \quad (0.0.13)$$

2492 Then,

$$\left(\frac{\partial S}{\partial \mathbf{P}} \right)_{E_{\text{tot}}} = \frac{\partial S}{\partial E}(-\mathbf{P}/M) = -\mathbf{v}/T. \quad (0.0.14)$$

Having established these premises, it becomes obvious that the average number of phonons characterized by the polarization state a and the wave vector \mathbf{k} in a system endowed with an average velocity \mathbf{v} is given by the Bose factor $f_B = 1/(e^{\beta\epsilon} - 1)$ in terms of the phonon energy at rest, which is given by

$$\epsilon(\mathbf{k}, \mathbf{v}) = \hbar\omega_{\text{tot}} - \hbar\mathbf{k} \cdot \mathbf{v}, \quad (0.0.15)$$

where $\omega_{\text{tot}} = c|\mathbf{k}|$. In what follows, we will assume that the speed of sound does not depend on the polarization. We can now formulate the following expressions for energy density, momentum, and energy flow:

$$\epsilon = \frac{3}{(2\pi)^3} \int d\mathbf{k} f_B(\hbar\omega_{\mathbf{k}} - \hbar\mathbf{k} \cdot \mathbf{v}) \hbar\omega_{\mathbf{k}}, \quad (0.0.16)$$

$$\mathbf{p} = \frac{3}{(2\pi)^3} \int d\mathbf{k} f_B(\hbar\omega_{\mathbf{k}} - \hbar\mathbf{k} \cdot \mathbf{v}) \hbar\mathbf{k}, \quad (0.0.17)$$

$$\mathbf{j}_\epsilon = \frac{3}{(2\pi)^3} \int d\mathbf{k} f_B(\hbar\omega_{\mathbf{k}} - \hbar\mathbf{k} \cdot \mathbf{v}) \hbar\omega_{\mathbf{k}} c \frac{\mathbf{k}}{|\mathbf{k}|}. \quad (0.0.18)$$

The factor 3 in these equations comes from the sum over the three polarization states. Expanding these to first order in \mathbf{v} , we get $\epsilon(\mathbf{v}) = \epsilon$.

$$\mathbf{p} = \frac{3}{(2\pi)^3} \int d\mathbf{k} f_B(\hbar\omega_{\mathbf{k}}) \hbar\mathbf{k} - \frac{3}{(2\pi)^3} \int d\mathbf{k} (-\mathbf{k} \cdot \mathbf{v}) \frac{\partial f_B(\epsilon)}{\partial \epsilon} \hbar\mathbf{k}, \quad (0.0.19)$$

Here, isotropic average of $3(-\mathbf{k} \cdot \mathbf{v})\mathbf{k} = k^2\mathbf{v}$, so

$$\mathbf{p} = \rho\mathbf{v}, \quad (0.0.20)$$

where ρ is the mass density of the phono gas given by

$$\rho = \frac{1}{(2\pi)^3} \int d\mathbf{k} k^2 \frac{\partial f_B}{\partial \omega}. \quad (0.0.21)$$

Similarly, we obtain ($\omega_{\mathbf{k}} = c|\mathbf{k}|$ is used)

$$\mathbf{j}_\epsilon = \frac{3}{(2\pi)^3} \int d\mathbf{k} \left(-\mathbf{k} \cdot \mathbf{v} \frac{\partial f_B}{\partial \epsilon} \right) \hbar \omega_{\mathbf{k}} c \mathbf{k} = c^2 \rho \mathbf{v}. \quad (0.0.22)$$

2527 On the other hand, we have

$$\frac{\partial \epsilon}{\partial t} = \frac{\partial \epsilon}{\partial T} \frac{\partial T}{\partial t}, \quad \nabla P = \frac{1}{3} \nabla \epsilon = \frac{1}{3} \frac{\partial \epsilon}{\partial T} \nabla T. \quad (0.0.23)$$

where $PV = E/3$ has been used. Also

$$\frac{\partial \epsilon}{\partial T} = \frac{3}{(2\pi)^3} \int d\mathbf{k} \frac{\partial f_B}{\partial T} \hbar \omega_{\mathbf{k}} = -\frac{3}{(2\pi)^3} \int d\mathbf{k} \frac{\partial f_B}{\partial E} \frac{(\hbar \omega_{\mathbf{k}})^2}{k_B T} = \frac{3c^2}{k_B T} \rho. \quad (0.0.24)$$

Thus, we have obtained

$$\frac{\partial T}{\partial t} = \frac{1}{3} T \nabla \cdot \mathbf{v}, \quad \frac{\partial \mathbf{v}}{\partial t} = -c^2 \nabla T, \quad (0.0.25)$$

or

$$\frac{\partial^2 T}{\partial t^2} = c_H^2 \Delta T \quad (0.0.26)$$

with $c_H = c/\sqrt{3}$, the speed of the second sound. Such a temperature wave may be obtained if

- 2538 (i) The variation in momentum due to phonons changes only because of pressure gradients.
(ii) The interaction between phonons and between phonons and the lattice is fairly weak, to the extent that one can consider phonon gas to be an ideal gas.

These hypotheses are satisfied if the sample is fairly pure (the interaction with impurities does not conserve momentum) and the temperature is fairly low (low enough that one can disregard those interactions among phonons that do not conserve momentum). **If the temperature is too low**, however, the phonon gas becomes too dilute and will not be able to reach equilibrium.

2607 Polylog function expression of fermi and bose averages. It is interesting to note that the
2671 Fermi energy is inversely proportional to the fermions' mass- and this is the reason that phenomena related to the Fermi distribution are more obvious in electrons.

2718 At high density electrons satisfy $PV \propto V^{2/3}$, so $PV^{5/3} = \text{const}$. Derive $C_P/C_V = 1 + d/g$,
where g is the exponent for the dispersion relation $\epsilon \propto |p|^\gamma$.

2744 Combinatorial derivation of FD and BE.

2769 Einstein condensation.

2835 Langmuir isotherm.

2943 Ortho and para hydrogen: coparison with experiment Fig 4.11 (Wannier Staitical Physics).

5. Phase Transitions

- 3027 The first critical point to be discovered was in carbon dioxide.
- 3252 Group discussion: Order parameter is introduced following the symmetry breaking after Landau and Lifshitz.
- 3289 Peierls argument
The introduction is fairly close to the rigorous version.
- 3393 1D correlation length is obtained. $\xi = a / \log \tanh K$.
Lifson method: JCP 40 3705 (1964). This is based on the block sequence representation of the chain configuration.
- 3418 Simplified Peierls is called Landau argument.
Duality
Mean field
- 3526 Variational principle: Bogolubov ineq etc. are used.
- 3659 Landau theory
The mean field theory requires that we look for the minimum of an effective free energy defined by
- $$\mathcal{F}(h, T, m) = N[f(T, m) - hm]. \quad (0.0.27)$$
- Near CP m is small. so we expand f into series and truncate it.
- 3740 Einstein theory of fluctuations: If, as usually occurs, entropy is a regular function of its arguments around the equilibrium values, then it is possible to deduce a certain number of important relations for the fluctuations.
- 3799 We have so far considered the fluctuations of extensive quantities in a finite region of the system, which are in contact with a much larger system, and therefore characterized by well-defined values of the corresponding intensive quantities (generalized forces and temperature). If we consider an isolated system, we can ask ourselves whether it is possible to observe analogous fluctuations in the intensive quantities. **This problem is still the subject of discussion.** One can formally associate corresponding fluctuations of the intensive variables with the fluctuations of the extensive variables by means of the equations of state. This procedure is fairly arbitrary however and, above all, does not allow one to obtain further physical insights.
Ginzburg criterion:
- 3899 Scaling laws: Relations of this type (known as scaling laws) can be written between any three exponents, and follow from the homogeneity of the free energy and from the fact that only two independent exponents appear in it. They are well satisfied by the experimentally measured exponents, and currently there are few doubts that they are valid for the

asymptotic exponents. Another relation of this type connects β, γ and δ :

$$\gamma = \beta(\delta - 1). \tag{0.0.28}$$

It is enlightening to consider the implication of these relations for the coherence length and for the correlation function. The lines of reasoning we have followed show that the coherence length must itself also satisfy a general homogeneity relation, etc. $\gamma/\nu = 2 - \eta$ is derived.

3926 2D Ising model.

6. Renormalization Group

4102 Kadanoff argument.

4987 Lower and upper critical dimensions: $\epsilon < 0$ case the stability of Gaussian fixed point. Note that all the nonclassical exponents satisfy hyperscaling. $2 - d\nu = \alpha$ is not satisfied by the classical exponents. At the upper critical dimension the nontrivial fixed point agrees with the Gaussian and the classical exponent therefore must satisfy the scaling law: $\alpha_c = 0$, $\nu_c = 1/2$.

$$d_c = \frac{1 - \alpha_c}{\nu_c} = 4. \tag{0.0.29}$$

(This can be applied to ϕ^3 model with $d_c = 6$.)

5012 In this case one would obtain the classical exponents $\alpha = -1$, $\beta = 0$, $\gamma = 1$ and $d_c = 6$. Since strictly speaking these terms are present in the van der Waals equation, we can ask ourselves why the Ising exponents that we obtained for $n = 1$ apply to the liquid-gas transition. The answer is that if the order parameter is a scalar, it is always possible to eliminate these terms by redefining ϕ by means of a translation: $\phi' = \phi - \phi_0$. **When this transformation is forbidden because of the problem's symmetry, however, we are dealing with a new universality class** and we obtain some new exponents, which must be calculated in an expansion in $d - 6$. This is the case of percolation.

Another remarkable value of dimensionality is the one where symmetry breaking occurs at zero temperature. This is called the lower critical dimension. For $n = 1$ (Ising), it is equal to 1, while for $n \geq 2$, it is equal to 2. In this case, it is possible to expand the critical exponents into powers of $d - 2$. For $n = 2$ and $d = 2$, even though there is no symmetry breakig, there is a peculiar phase transition at finite temperature (BKT).

7. Classical Fluids

5131 Pair distribution.

5172 Compressibility equation

5185 Rversible work theorem: how to measure $g(r)$

5256 BBGKY and Kirkwood.

5301 Direct correlation and OZ.

- 5315 Virial expansion; Mayer f . The convergence of the virial expansion and the fugacity expansion of the equation of state can be analyzed by showing that the infinite sequence of reduced densities $\rho = \{\rho^{(i)}(x_1, \dots, x_i)\}$ satisfies a system of linear nonhomogeneous integral equations whose kernel is small if the fugacity (and therefore the density ρ) is small. This allows for an explicit estimate of the convergence radius of the expansions.
- 5570
- 5604 Kirkwood-Salzburg equation is introduced.
- 5649 Convergence of virial expansion.
- 5717 Perturbation around hard core (Zwanzig). However no discussion of hard-core fluid; no PY.

8. Numerical Simulation

- 5976 Verlet algorithm
- 6407 Umbrella sampling: We can sample the canonical distribution with a Hamiltonian H_0 , which is not identical to the one H that we are interested in, if this is to our advantage, as long as we are careful to take the correction into account:

$$\langle A \rangle_H = \frac{\langle A e^{-b(H-H_0)} \rangle_{H_0}}{\langle e^{-b(H-H_0)} \rangle_{H_0}}. \quad (0.0.30)$$

This technique is called umbrella sampling—in addition to being used for the study of perturbations with respect to a given Hamiltonian, it can be used for the study of rare events by enhancing them with H_0 .

- 6443 Discussion
- One of the most interesting aspects of numerical simulation is the way in which it allows one to clarify (not resolve!) the fundamental conceptual problems of statistical mechanics.
- We have actually seen how a suitably defined Markov chain allows us to sample the canonical ensemble, for example. The runs one can actually perform, however, will allow us to evaluate the observables' mean only over a ridiculously small number of configurations. For $N = 100$, for instance, we have about 10^{30} possible configurations. You are therefore not sampling the Boltzmann distribution in the same sense in which, for example, by throwing a die 10,000 times you are checking whether it is “honest,” since the frequencies of the various results are equal to $1/6$ within 1%. The point is that we are not aiming to sample the distribution in phase space, but only to evaluate the observables' averages.

- 6454 We will have to be careful not to squeeze our data too much—in other words, not to base our conclusions on events that, in our run, occurred a small number of times. If we really have to, we can use umbrella sampling to obtain a statistically significant sample.

Last, let us remark that we were able to obtain only the observables' average. There are important thermodynamic quantities that are not observable: first entropy, then free energy, and so on.

So to obtain S integrating specific heat should be more advantageous.

9. Dynamics

6501 Random force: isotropy, no memory and Gaussian noise assumed.

$$\langle \mathbf{f}(t) \mathbf{f}^T(s) \rangle = \Lambda I \delta(t - s). \quad (0.0.31)$$

6538 The noise amplitude is fixed with the aid of the equipartition of energy.

$$M \frac{d\mathbf{v}}{dt} = -\lambda \mathbf{v} + \mathbf{f}, \quad (0.0.32)$$

which can be solved and after a long time

$$\langle v^2 \rangle = \frac{\Lambda}{2M\lambda} \quad (0.0.33)$$

6588 This implies $\Lambda = 2\lambda k_B T$. Diffusion coefficient and Green-Kubo for it are given.

6615 Fractal properties of Brownian trajectories. Covering dimension is introduced.

Onsager reciprocity, regression hypothesis

10. Complex Systems

7561 Percolation

7682 Relation to Potts

7775 Real space RG for Percolation