An Introduction to Statistical Mechanics and Thermodynamics

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Thermodynamics is taught first for the dubious reason that it is older than statistical mechanics.

Guiding principles:

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Problems are designed to enhance conceptual understanding

Advanced Graduate and graduate levels make no distinction.

Pedagogical Principles:

Start with classical statistical mechanics

Statistical mechanics is based on the definition of entropy by Boltzmann in 1877. This is one of the key features of the book

Self-contained probability theory is given.

Feynman: If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or atomic fact, or whatever you wish to call it) that all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence you will see an enormous amount of information about the world, if just a little imagination and thinking are applied.

- Due to our lack of detailed knowledge of te microscopic state of an object, we need to use probability theory.
 - [C] Is this a logically valid statement?
- The intention of this book is to present thermal physics as a consequence of the molecular nature of matter.

Part I Entropy

2. The classical ideal gas

- The most important feature that is missing from a classical ideal gas is that it does not exhibit any phase transitions.
- Distinguishability: To be specific, particles are distinguishable when the exchange of two particles results in a different microscopic state. In classical mechanics, this is equivalent

to saying that every point in phase space represents a different microscopic state. Distinguishability does not necessarily mean that the particles have different properties; classically, particles were always regarded as distinguishable because their trajectories could, at least in a thought experiment, be followed and the identity of individual particles determined.

13 $S = k_B \log W$, where W is Wahrscheinlichkeit. This should not be confused with the phase volume.

[C] Road Map for Part I is given on p15. Even the flow chart is given.

3. Discrete Probability theory

What is probability? Frequentist definition contradicts the finiteness of our life; Bayes rescues this: Bayesian define probability as a description of a person's knowledge of the outcome of a trial, based on whatever evidence is at that person's disposal.

Bayesian probability is accepted by most statisticians. However, it is in disrepute among some physicists because they regard it as subjective, in the sense that it describes what an individual knows, rather than being absolute truth. However, none of us has access to absolute truth, and Bayesian statistics provides an appropriate way to describe what we learn from experiments.

[C] Observability must be guaranteed. The above argument is too crude.

- Joint probability introduced
- 21 Random numbers

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- 29 Log sum derivation of Stirling.
- 31 Gosper's approximation

$$N! \sim e^{-N} N^N \sqrt{(2N+1/3)\pi}$$
 (0.0.1)

Wolfram math site cites this. Stirring's approximation is one of the most accurate approximation in physics.

4. The classical ideal gas: configuration entropy

- $S_{\text{total}}(E, V, N) = S_p(E, N) + S_q(V, N).$
- Partition into two parts $V = V_A + V_B$. Spatial even distribution assumed, then

$$P(N_A, N_B) = \frac{N!}{N_A! N_B!} \left(\frac{V_A}{V}\right)^{N_A} \left(\frac{V_B}{V}\right)^{N_B}.$$
 (0.0.2)

- From this $\langle N_A \rangle = NV_A/V$. The standard deviation is $\sqrt{NV_AV_B}/V$, thus the actual number is very close to the average.
- Thermodynamic limit: asymptotically exact.

Defining $\Omega_q(N, V) = V^N/N!$

$$\log P(N_A, N_B) = \log Q_q(N_A, V_A) + \log Q_q(N_B, V_B) - \log Q_q(N, V). \tag{0.0.3}$$

¹yielding $\sqrt{\pi/3} \sim 1.02333$ instead of 0 obtained with the conventional Stirling approximation for 0!. Mortici, JMI 5 611 (2011) ON GOSPERS FORMULA FOR THE GAMMA FUNCTION

It will be convenient to define

$$S_q(N, V) = k_B \log \Omega = k_B X N, \tag{0.0.4}$$

where X is an arbitrary constant. (0.0.3) reads

$$\log P(N_A, N_B) = S_q(N_A, V_A) + S_q(N_B, V_B) - S_q(N, V). \tag{0.0.5}$$

Near equilibrium, note that $\log P$ is negligible, and

$$S_q(N, V) = S_q(N_A, V_A) + S_q(N_B, V_B).$$
(0.0.6)

Analytically,

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$$S_q(N, V) = k_B N[\log(V/N) + X]$$
 (0.0.7)

 k_B and X will be determined in 8.

5. Continuous random number

- Dirac delta. This is defined as the weak limit. Note that the width of the function $\delta_{\epsilon}(cx)$ os a factor of 1/|c| times that of $\delta_{\epsilon}(x)$.
- Bayes' theorem; also log likelihood calculation is illustrated (p56).

6. The classical ideal gas: energy dependence of entropy

With the assumption of uniform probability density in momentum space, we can calculate the probability distribution for the energy from that of the momenta, using the methods from Section 5-4 with the aid of δ -function.

$$P(E_A, E_B) = \frac{\int dp_A \,\delta(E_A - H_A) \int dp_A \,\delta(E_B - H_B)}{\int dp \,\delta(E - H)}.$$
 (0.0.8)

Introduce

$$\Omega_E(E, N) = \int dp_A \, \delta(E - H), \qquad (0.0.9)$$

and we have

$$P(E_A, E_B) = \frac{\Omega_E(E_A, N_A)\Omega_E(E_B, N_B)}{\Omega_E(E, N)}.$$
 (0.0.10)

Then, spherical evaluation of Ω_E is honestly done (p64-5). The result asymptotically reads

$$P(E_A, E_B) = (E_A/E)^{3N_A/2} (E_B/E)^{3N_B/2}$$
(0.0.11)

Again, the sharpness of the distribution is demonstrated. Ω_E is introduced analogically ([C] not logically clear) and

$$S_E(E, N) = k_B N \left[\frac{3}{2} \log(E/N) + X \right]$$
 (0.0.12)

is written. ([C] X need not be identical.) [C] As a whole the argument is sloppy.

7. Classical gases: ideal and otherwise

The full S is given with X arbitrariness comment.

Equilibrium conditions are worked out with the max entropy principle (\sim p76).

- Indistinguishable particles: what is particles are distinguishable?
- Indistinguishable case is calculated with the x-coordinate ordering. This naturally produces the 1/N! factor.

"The result is the same as the distinguishable case (p41)." The result assumes the binomial factor due to the free particle exchange between two subparts A and B.

The author claims:

The result that the entropy is exactly the same for classical systems with distinguishable and indistinguishable particles might be surprising to some readers, since most of the literature for the past century has claimed that they were different. My claim that the two models have the same entropy depends crucially on the definition of entropy that I have used. However, I think we might take as a general principle that two models with identical properties should have the same entropy. Since the probability distributions are the same, their properties are the same. It is hard to see how any definition that results in different entropies for two models with identical properties can be defended.

[C] However this must be due to a logical error.

- Second law: entropy max \Rightarrow equilibrium: this is an extremely important result ([C] the argument sounds circular.) Any constraint means lower entropy: this is the second law of thermodynamics.
- 85 Zeroth Law

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8. T, P, μ and all that

What do we mean by temperature? Standard: ideal gas law

To derive the ideal gas law, we need MB distribution. It is obtained as a marginal:

$$P(\mathbf{r}_1, \mathbf{p}_1) = \frac{\Omega(E - p_1^2/2m, V, N - 1)}{Nh^3\Omega(E, V, N)}$$
(0.0.13)

From this

$$P(\mathbf{r}_1) = \frac{V\Omega(E - p_1^2/2m, V, N - 1)}{Nh^3\Omega(E, V, N)}$$
(0.0.14)

Expanding this, we get

$$P(\mathbf{r}_1) = -\beta p_1^2 / 2m + \cdots {(0.0.15)}$$

- Using this, the pressure on the wall is calculated.
- Temperature scale. Thus, the derivatives of S are discussed one by one.

Part II Thermodynamics

9. The postulates of laws of thermodynamics

- The point of view taken in this book is that statistical mechanics is the more fundamental theory. Thermodynamics is based on assumptions that can be understood in the context of statistical mechanics. What we will call the 'Postulates of Thermodynamics' and the 'Laws of Thermodynamics' are, if not theorems, at least plausible consequences of the theory of statistical mechanics.
- Thermodynamics can give different insights, and is often more efficient.
- A macroscopic state is not a property of a thermodynamic system; it is a description of a thermodynamic system based on macroscopic. Due to the experimental uncertainty of macroscopic measurements, a macroscopic state is consistent with an infinity of microscopic states.

Formally, this might seem to be a rather loose definition of what we mean by 'macroscopic state'. In practice, however, there is rarely a problem. Because microscopic fluctuations are so much smaller than experimental uncertainties, it is relatively easy to specify which microscopic states are consistent with macroscopic measurements. measurements.

104 Postulates

1. Existence of equilibrium states

There exist equilibrium states of a macroscopic system that are characterized uniquely by a small number of extensive variables.

2. Entropic maximization

The values assumed by the extensive parameters of an isolated composite system in the absence of an internal constraint are those that maximize the entropy over the set of all constrained macroscopic states.

whenever we release a constraint on a composite system, the entropy will increase: $\Delta S \geq$

- 0. Thus, equilibrium may be obtained by maximization of entropy.
- 3. Additivity

The entropy of a composite system is additive over the constituent subsystems.

4. Monotonicity

The entropy is a monotonically increasing function of the energy for equilibrium value of the energy.

5. Analyticity

The entropy is a C1 function of extensive parameters.

6. Extensivity

Entropy is an extensive function of the extensive variables

$$S(\lambda...) = \lambda S(...). \tag{0.0.16}$$

However, this is not true for all systems. For example, gas with absorbing wall (Problem on p233).

The laws of thermodynamics are stated next. Only the third law cannot be understood classically.

10. Perturbation of thermodynamic state functions

- 110 Exact and inexact differential $d\omega = 0$ is discussed.
- 113 Conservation of energy revisited.

11. Thermodynamic processes

- The concept of a quasi-static process is an idealization. [C] but is realistic enough because dissipation is proportional to δx^2 .
- Heat engine. Max efficiency is obtained from Clausius.

12. Thermodynamic Potential

- Legendre transformation is discussed as the relation between the point and the line representation, but not quite convex analytic.
- 130 Massieu functions.

13. Consequence of extensivity

Euler's theorem; Gibbs-Duhem

An important consequence of the Gibbs-Duhem relation is that for extensive systems we only need r + 1 equations of state for an r-component system to recover the fundamental relation and with it access to all thermodynamic information.

[C] Here, eq of states mean the formula for extensive quantified in terms of intensive quantities and N. The fundamental equation of state is a hyperplane in r + 2-space (r + 1 and E). Therefore, trivially, we need r + 1 extensive variables.

14 Thermodynamic identities

- in thermodynamics it is rarely obvious what the 'other' variables are. Consequently, it is extremely important to specify explicitly which variables are being held constant when taking a partial derivative.
- Maxwell relations; Jacobian used.
- 148 Examples: Joule-Thomson coefficient.
- 151 General strategy
 - 1. Express the partial derivative as a Jacobian.

2. If there are any thermodynamic potentials in the partial derivative, bring them to the numerator. Unless you have a good reason to do something else, insert $\partial(T, P)$ in this step. 3? Eliminate thermodynamic potentials if you know the derivative. For example:

$$\left(\frac{\partial F}{\partial T}\right)_{VN} = -S. \tag{0.0.17}$$

4. Eliminate thermodynamic potentials by using the differential form of the fundamental relation. For example: if you want to evaluate

$$\left(\frac{\partial F}{\partial P}\right)_{T.N} \tag{0.0.18}$$

use Gibbs to guess the useful Maxwell. etc.

[C] Not so practical.

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15. Extremum Principles

Energy minimum principle from entropy maximum principle. Let the system be S = S(U, X). Then, for an isolated system near equilibrium

$$\delta S = \left(\frac{\partial^2 S}{\partial X^2}\right)_U \delta X^2 + \left(\frac{\partial S}{\partial U}\right)_X \delta U = \left(\frac{\partial^2 S}{\partial X^2}\right)_U \delta X^2 + \frac{1}{T}\delta U \tag{0.0.19}$$

Now comes the subtle part. Up to this point the system is isolated, so the total energy is fixed.

If we wish to change the system under constant S, the heat exchange is killed, and the process must be reversible, so changing X must be 'slowed down by applying force. Thus the internal energy changes (spontaneously is reduced \Rightarrow Energy minimum principle)

For the analysis of the entropy maximum principle, we isolated a composite system and released an internal constraint. Since the composite system was isolated, its total energy remained constant. The composite system went to the most probable macroscopic state after release of the internal constraint, and the total entropy went to its maximum. Because of the increase in entropy, the process was irreversible.

Now we are considering a quasi-static process without heat exchange with the rest of the universe, so that the entropy of the composite system is constant. However, for the process to be quasi-static we cannot simply release the constraint, as this would initiate an irreversible process, and the total entropy would increase. Outside forces are required to change the constraints slowly to maintain equilibrium conditions. This means that the energy of the composite system for this process is not constant.

The piston-Gas illustration is a good one. We can turn (0.0.19) around:

$$\delta U = -T \left(\frac{\partial^2 S}{\partial X^2} \right)_U \delta X^2 + T \delta S \tag{0.0.20}$$

Since $\delta S =$, this implies energy minimum.

Min principle for Helmholtz. Max or min work is discussed (p161).

16. Stability Conditions

Intrinsic stability: In this chapter we look inside a composite system to see what conditions a subsystem must satisfy as a consequence of the extremum principles in 15. These are called the 'intrinsic' stability conditions.

Since any thermodynamic system could become a subsystem of some composite system, the stability conditions we derive will be valid for all thermodynamic systems.

[C] This book strictly uses compartmentalized system to derive the stability criteria. That is, 'fluctuations' are considered as compartmentalized systems. Energy minimum principle implies

$$U(S, X + \Delta X, N) + U(S, X - \Delta X, N) - 2U(S, X, N) \ge 0$$
 (0.0.21)

Or

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$$\left(\frac{\partial U}{\partial X}\right)_{S,N} \ge 0 \tag{0.0.22}$$

This is the stability condition.

Stability criterion wrt other potentials are discussed similarly.

17. Phase Transitions

- 178 VdW eq is derived from A.
- 180 Reduced form.
- Maxwell construction.

Meta and unstable states are mentioned. A-V plot and tangential construction (convex hull) is discussed.

Latent heat, Clapeyron and phase rule are discussed

18. Nernst postulate

The entropy of a thermodynamic system goes to a constant as the temperature goes to zero. Planck's stronger version is that the constant is 0.

It reveals the pervasive influence of quantum mechanics on macroscopic phenomena.

Ideal gas contradicts this.

195 Consequences of the third law:

Specific heats vanish in the $T \to 0$ limit.

Thermal expansion coefficient must vanish (use Maxwell).

Part III Classical Statistical Mechanics

19. Ensembles in classical statistical mechanics

- 202 Microcanonical and MD.
- The standard derivation of the canonical distribution is given.

$$P(E) = \frac{1}{Z}\Omega(E)e^{-\beta E}$$
(0.0.23)

Liouville's theorem: The canonical distribution is invariant in time. This is shown with the aid of Liouville's theorem. The probability must satisfy a continuity equation

$$\frac{\partial P}{\partial t} + \Delta(vP) = 0, \tag{0.0.24}$$

On the other hand

$$\frac{dP}{dt} = \frac{\partial P}{\partial t} + v\Delta P. \tag{0.0.25}$$

If the canonical equation of motion is used, we can see v is incompressible, so (0.0.24) implies that (0.0.25) vanishes:

$$\frac{dP}{dt} = 0\tag{0.0.26}$$

The interpretation of (0.0.26) is that the probability density in the neighborhood of a moving point remains constant throughout the trajectory.

- 209 Canonical peak position, and fluctuation discussed.
- 212 Gibbs-Helmholtz equation.
- 214 Configuration space. Master equation; detailed balance
- One particle factorization approximation:
- This trick is used repeatedly in statistical mechanics. Even when it is not possible to make an exact factorization of the partition function, it is often possible to make a good approximation that does allow factorization.

Factorization of the partition function is the most important trick you need for success in statistical mechanics. Do not forget it!

Classical harmonic oscillators

- 220 $H = K + \sum |q|^r$ system.
- $224 H = \sum c|p_i| + mg \sum z_i.$

Classical rubber band defined by conformational angles only.

20. Classical Ensembles: grand and otherwise

21. Irreversibility

234 Trivial irreversibility:

Consider a particle moving in empty space. At some initial time it is observed to be located in some finite region of space. Since the particle is moving, it will eventually leave this region. If space is infinite, it will not return. This is, technically, irreversible behavior, but of a trivial kind.

This trivial form of irreversibility is real, and occurs in the radiation of light from a star. It is quite general in infinite systems, whether classical or quantum. An open system also displays this trivial form of irreversibility, since it is really just a piece of an infinite system.

However, we would like to separate this trivial irreversibility from the non-trivial irreversibility that we experience every day.

[C] However, is there any ultimate difference?

- 236 Loschmidt, Zermelo
- If a system is subdivided into semimacroscopic cells for which ordinary equilibrium thermodynamics applies, then the entropy increase can be mimicked.

Part IV Quantum Statistical Mechanics

22 Quantum ensemble

- 248 Basic quantum mechanics
- 253 Random phase approximation
- The decomposition of a density operator into ket-bra sum is not unique, but usually we decompose it into eigenspace projections:

It is usual to express the density matrix operator in terms of the eigenstates of a system, which gives the impression that the ensemble also consists entirely of eigenstates. Even though we know that this is not the case, the demonstration above shows that all predictions based on the (erroneous) assumption that a macroscopic system is in an eigenstate will be consistent with experiment.

23. Quantum canonical ensemble

The derivation is quite parallel to the classic case. The logic is applied to the subsystem eigenenergies:

$$P_n = \frac{1}{Z} e^{-\beta E_n}. (0.0.27)$$

Quantum mechanical entropy; the origin of the third law.

The discrete entropy (the original Shannon) cannot be negative. Before taking the thermodynamic limit $T \to 0$ implies obviously, the ground state probability reads $P_0 = 1/\Omega_G$, the ground state degeneracy. Therefore,

$$\lim_{T \to 0} S(T) = -k_B \Omega_G \frac{1}{\Omega_G} \log \frac{1}{\Omega_G} = k_B \log \Omega_G. \tag{0.0.28}$$

- What Nernst said is that the entropy density vanishes, so if Ω_G is sub-exponential as a function of N. However, $W_G = a^N$ can occur for disordered systems.
- Factorization $\sum \prod = \prod \sum$. A warning is also given. simple harmonic; Einstein model

24. Black-body radiation

In physics, the expression 'black body' refers to an object that absorbs all radiation incident on it and reflects nothing. It is, of course, an idealization, but one that can be approximated very well in the laboratory.

A black body is not really-black Although it does not reflect light, it can and does radiate light arising from its thermal energy. This is, of course, necessary if the black body is ever to be in thermal equilibrium with another object.

- [C] The explanation is not recommended.
- Low frequency agrees with equipartition.
- 289 Background radiation

25. Harmonic solid

301 Debye approximation

306

Debye-blackbody correspondence is mentioned. Harmonic crystal with alternating masses.

26 Ideal quantum gases

Single particle quantum state, and density of single-particle states. To derive the density δ is used as

$$D(\epsilon) = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \, \delta(\epsilon - \epsilon_n). \tag{0.0.29}$$

Many-particle quantum state = microstate.

- 314 number representation
- With distinguishable particles, we can derive the ideal gas law. This derivation requires only: distinguishability, extensivity and wave function factorization.
- U = (2/3)PV discussed.

27 Bose-Einstein distribution

- Perhaps the most startling property of systems governed by Bose- Einstein statistics is that they can exhibit a phase transition in the absence of interactions between the particles. In this chapter we will explore the behavior of an ideal gas of bosons and show how this unusual phase transition arises.
- 329 Bose-intein condensation

We can trace the strange behavior of bosons at low temperatures to the form of the boson

occupation number

$$\langle n_0 \rangle = \frac{1}{e^{-\beta\mu} - 1} \tag{0.0.30}$$

If we were to set $\mu = 0$, the occupation number would be infinite. This means that for very small but non-zero values of μ , the occupation number of the ground state can be arbitrarily large. In fact, it can even contain all the bosons in the system!

From the equation

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$$\langle n_0 \rangle = N(1 - (T/T_c)^{2/3}),$$
 (0.0.31)

we can obtain the low temperature behavior of the chemical potential:

$$\mu \sim -\frac{k_B T}{N} (1 - (T/Tc)^{3/2})^{-1}.$$
 (0.0.32)

- For macroscopic system this is extremely small. The occupation of the second level is discussed as well.
- 333 The isothermal compressibility of ideal Bose gas below T_c is infinite.

Fermi-Dirac statistics

- The chemical potential is a rather weak function of temperature, so that its zero-temperature limit usually provides a very good approximation to its value at non-zero temperatures. This limit is so important that it has a name, the Fermi energy, ϵ_F .
- 338 Particle-hole symmetry

$$\frac{1}{e^{\beta(\epsilon-\mu)}+1} = 1 - \frac{1}{e^{-\beta(\epsilon-\mu)}+1}. (0.0.33)$$

341 Compressibility of metals: the bulk modulus $B = -V(\partial P/\partial)_T$ is given by

$$B = \frac{\hbar^2}{3m} \pi^{4/3} \left(\frac{N}{V}\right)^{5/3}.$$
 (0.0.34)

Therefore,

$$B = \frac{2N}{3V}\epsilon_F. \tag{0.0.35}$$

The numerical predictions of eq. (0.0.35) turn out to be within roughly a factor of 2 of the experimental results for metals, even though the model ignores the lattice structure entirely. This is remarkably good agreement for a very simple model of a metal. It shows that the quantum effects of Fermi-Einstein statistics are responsible for a major part of the bulk modulus of metals.

- 344 Sommerfeld expansion.
- 348 Fermions with internal levels.
- 349 A model system with energy gaps.

Consider a system with the following density of states:

$$D(\epsilon) = \begin{cases} 0 & 0 > \epsilon \\ A(\epsilon_1 - \epsilon) & e_1 > \epsilon > 0 \\ 0 & \epsilon_2 > \epsilon > \epsilon_1 \\ A(\epsilon - \epsilon_2) & \epsilon > \epsilon_2 \end{cases}$$
(0.0.36)

where A is a constant, and $\epsilon_2 > \epsilon_1 > 0$. The number of particles is given by $N = A\epsilon_1^2/2$, so the Fermi energy is $\epsilon_F = (\epsilon_1 + \epsilon_2)/2$.

In the last assignment we found that the Sommerfeld expansion gives incorrect results for this model. In this assignment we will calculate the low-temperature behavior correctly.

- 1. Show that if $\epsilon_1 \gg k_B T$, $\mu = \epsilon_F$ is a very good approximation, even if $k_B T \simeq \epsilon_2 \epsilon_1$.
- 2. Calculate the energy of this model as a function of temperature for low temperatures. Assume that $\epsilon_1 \gg \epsilon_2 \epsilon_1 \gg k_B T$.
- 3. Calculate the heat capacity of this model as a function of temperature for low temperatures from your answer to the previous question. Assume that $\epsilon_1 \gg \epsilon_2 \epsilon_1 \gg k_B T$.

2.9 Insulators and Semiconductors

- 361 Gap and fermi energy are explained.
- 365 Semiconductor statistics

30. Phase transitions and the Ising Model

Ising chain by factorization: Let $\tau_j = \sigma_{j-1}\sigma_j$. Then, all τ are independent and take ± 1 .

$$Z = \sum_{\{\tau\}} \prod_{j=1}^{N} e^{\beta J \tau_j} = 2 \prod_{j=2}^{N} \sum_{\tau} e^{\beta J \tau} = 2(2 \cosh \beta J)^{N-1}.$$
 (0.0.37)

If j and h are nonzero, we need the transfer matrix technique.

rmp375The result of the transfer matrix calculation. It is analytic.

- 376 Mean field approximation, graphical solution
- 380 Critical exponent
- 382 Landau theory