

# Microcanonical Ensemble [tsc10]

Distribution functions are at the center of both kinetic theory and statistical mechanics – very different distribution functions.

- Kinetic theory begins with one-particle distribution functions. Interactions are accounted for in non-factorizing pair-distributions, 3-point distributions etc.
- Statistical mechanics, by contrast, employs distributions of microstates of macroscopic systems. Interactions are accounted for in the energies of microstates, for example.

## Classical Hamiltonian system:

Consider an autonomous classical dynamical system with  $3N$  degrees of freedom (e.g.  $N$  particles moving in 3D space).

Canonical coordinates ( $6N$  in number):  $q_1, \dots, q_{3N}; p_1, \dots, p_{3N}$ .

Hamiltonian function:  $H(q_1, \dots, q_{3N}; p_1, \dots, p_{3N})$ .

Canonical equations:  $\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}; \quad i = 1, \dots, 3N$ .

Dynamical variable:  $f(q_1, \dots, q_{3N}; p_1, \dots, p_{3N})$ .

Hamilton's equation of motion (expressed with a Poisson bracket):

$$\frac{df}{dt} = \sum_{i=1}^{3N} \left( \frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right) = \sum_{i=1}^{3N} \left( \frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \doteq \{f, H\}.$$

Conserved quantity:  $\frac{df}{dt} = 0 \Leftrightarrow \{f, H\} = 0$ .

Energy conservation is guaranteed:  $\{H, H\} = 0 \Rightarrow \frac{dH}{dt} = 0$ .

## Points and trajectories in phase space:

The microstate of a classical system is specified by one point in the  $6N$ -dimensional phase space ( $\Gamma$ -space):

$$\mathbf{X} \doteq (q_1, \dots, q_{3N}; p_1, \dots, p_{3N}).$$

As time evolves, this point traces a trajectory through  $\Gamma$ -space. Cauchy's theorem dictates that phase-space trajectories do not intersect themselves or each other. There are no collisions between phase points.

In kinetic theory, microstates are described by  $N$  points in the 6D space spanned by the position coordinates  $x, y, z$  and velocity coordinates  $v_x, v_y, v_z$  of a single particle. Particles do collide.

- In kinetic theory, two points in  $(x, y, z; v_x, v_y, v_z)$  represent different particles of the same macroscopic system.
- In statistical mechanics, two phase points may either represent the same macroscopic system or different macroscopic systems:

Physical ensemble: each phase point represents the same system in different microstates.

Statistical ensemble: each phase point represents a different but equivalent system.

The conservation law,

$$H(q_1, \dots, q_{3N}; p_1, \dots, p_{3N}) = \text{const},$$

confines the motion of any phase point to a  $6N - 1$ -dimensional hypersurface in  $\Gamma$ -space. The microcanonical ensemble will take this restriction into account, as we shall see.

Additional conservation laws, if they exist, will further reduce the dimensionality of the manifold to which phase-space trajectories are confined.

### **Probability density in phase space:**

Knowledge of the microstate of a macroscopic system is almost always limited to a probability distribution.

Probability density (in  $\Gamma$ -space):  $\rho(\mathbf{X}, t)$ .

Normalization: 
$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}, t) = 1.$$

Expectation value of a dynamical variable  $f$ :

$$\langle f \rangle = \int_{\Gamma} d^{6N} X f(\mathbf{X}) \rho(\mathbf{X}, t).$$

Solution of canonical equations expressed as probability density:

$$\rho(\mathbf{X}, t) = \delta(\mathbf{X} - \mathbf{X}(t)).$$

### Probability flow in phase space:

Consider the probability density  $\rho(\mathbf{X}, t)$  inside a volume  $V_0$  with surface  $S_0$  in  $\Gamma$ -space. Probability is conserved.

- (a) If probability changes inside  $V_0$ , it must flow through  $S_0$ .
- (b) Gauss's theorem converts the surface integral into a volume integral.

$$\frac{\partial}{\partial t} \int_{V_0} d^{6N} X \rho(\mathbf{X}, t) \stackrel{(a)}{=} - \oint_{S_0} d\mathbf{a} \cdot \dot{\mathbf{X}} \rho(\mathbf{X}, t) \stackrel{(b)}{=} - \int_{V_0} d^{6N} X \nabla_{\mathbf{X}} \cdot [\dot{\mathbf{X}} \rho(\mathbf{X}, t)].$$

Probability current:  $\mathbf{J}(\mathbf{X}, t) \doteq \dot{\mathbf{X}} \rho(\mathbf{X}, t)$ .

$$\text{Continuity equation: } \frac{\partial}{\partial t} \rho(\mathbf{X}, t) + \nabla_{\mathbf{X}} \cdot \mathbf{J}(\mathbf{X}, t) = 0.$$

In the context of a kinetic theory, a second equation between  $\rho$  and  $\mathbf{J}$  is provided by a constitutive law. This is not a legitimate option here.

Instead we must use  $\nabla_{\mathbf{X}} \cdot \mathbf{J} = \nabla_{\mathbf{X}} \cdot [\dot{\mathbf{X}} \rho] = \rho \underbrace{\nabla_{\mathbf{X}} \cdot \dot{\mathbf{X}}}_0 + \dot{\mathbf{X}} \cdot \nabla_{\mathbf{X}} \rho$ .

$$\text{Vanishing term: } \nabla_{\mathbf{X}} \cdot \dot{\mathbf{X}} = \sum_{i=1}^{3N} \left[ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] = \sum_{i=1}^{3N} \left[ \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right] = 0.$$

Equation of motion for probability density:

$$\Rightarrow \frac{\partial}{\partial t} \rho(\mathbf{X}, t) + \dot{\mathbf{X}} \cdot \nabla_{\mathbf{X}} \rho(\mathbf{X}, t) = 0.$$

$$\text{Convective derivative: } \frac{d}{dt} \doteq \frac{\partial}{\partial t} + \dot{\mathbf{X}} \cdot \nabla_{\mathbf{X}}.$$

$$\text{Classical Liouville theorem: } \frac{d}{dt} \rho(\mathbf{X}, t) = 0.$$

### Classical Liouville operator:

$$\text{Use } \dot{\mathbf{X}} \cdot \nabla_{\mathbf{X}} \rho = \sum_{i=1}^{3N} \left( \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right) = \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \{\rho, H\}.$$

$$\text{Liouville operator: } L \equiv \iota\{H, \} = \iota \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} \right).$$

$$\text{Classical Liouville equation: } \iota \frac{\partial \rho}{\partial t} = \iota\{H, \rho\} = L\rho.$$

Formal solution of classical Liouville equation:  $\rho(\mathbf{X}, t) = e^{-iLt}\rho(\mathbf{X}, 0)$ .

$L$  is a Hermitian operator.<sup>1</sup> Hence all its eigenvalues are real. The time evolution encoded in  $e^{-iLt}$  is oscillatory in nature.

The phase-space density  $\rho(\mathbf{X}, t)$  cannot relax to equilibrium in any obvious way. The Liouville equation reflects the time reversal symmetry of the underlying microscopic dynamics.

Obtaining the broken time reversal symmetry of irreversible processes from the Liouville equation is a central problem in statistical mechanics (topic of ergodic theory).

### **Stationarity condition for phase-space probability density:**

In spite of the difficulties in understanding how thermal equilibrium is reached at the microscopic level of description, the condition of the classical phase-space density is straightforward:

$$\frac{\partial \rho}{\partial t} = 0 \Rightarrow L\rho = 0 \Rightarrow \{H, \rho\} = 0.$$

If  $\rho = \rho(H)$  then  $\{H, \rho\} = 0$ . A probability density which only varies in direction perpendicular to the energy hypersurfaces in phase space is necessarily time-independent.

Stationarity is a necessary condition for thermal equilibrium. Thermal equilibrium hinges on a further criterion as we shall see, which will determine the functional dependence of  $\rho(H)$ .

### **Density operator:**

Pure states of a quantum system are described by state vectors  $|\pi(t)\rangle$ . Generically, the instantaneous state of a quantum system is a mixed system, which is described by the density operator  $\rho(t)$ .

Diagonal representation:  $\rho(t) = \sum_i p_i |\pi_i(t)\rangle \langle \pi_i(t)|$ ,  $\sum_i p_i = 1$ .

The system is with probability  $p_i$  in pure state  $|\pi_i(t)\rangle$ . In this representation, the Liouville operator is readily shown to be Hermitian, to be positive semi-definite and to have unit trace.

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<sup>1</sup>The classical Liouville operator, which acts on phase-space densities, can be shown to be Hermitian (self-adjoint) if those densities are conceived as vectors in a complex space with an inner product.

Expectation value of an observable  $A$ :  $\langle A(t) \rangle = \text{Tr}[A\rho(t)]$ .

$$\Rightarrow \langle A(t) \rangle = \sum_i p_i \langle \pi_i(t) | A | \pi_i(t) \rangle = \sum_{nn'} \langle n | A | n' \rangle \langle n' | \rho(t) | n \rangle.$$

The last expression uses the orthonormal basis  $\{|n\rangle\}$ . The expectation value is then the trace of a matrix product, one of which is the density matrix.

### Quantum time evolution:

Schrödinger equation:  $H|\pi_i(t)\rangle = i\hbar \frac{\partial}{\partial t} |\pi_i(t)\rangle$ .

$$\Rightarrow i\hbar \frac{\partial \rho}{\partial t} = \sum_i p_i [H|\pi_i(t)\rangle \langle \pi_i(t)| - |\pi_i(t)\rangle \langle \pi_i(t)| H] = H\rho - \rho H = [H, \rho].$$

Liouville operator:<sup>2</sup>  $L \doteq \frac{1}{\hbar} [H, \ ]$ .

Liouville equation:  $i \frac{\partial \rho}{\partial t} = \frac{1}{\hbar} [H, \rho] = L\rho$ .

Formal solution:  $\rho(t) = e^{-iLt} \rho(0) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}$ .

The time evolution of an expectation value can be carried by the density operator  $\rho$  or by the dynamical variable  $A$ :

$$\langle A(t) \rangle = \text{Tr}[A e^{-iHt/\hbar} \rho e^{iHt/\hbar}] = \text{Tr}[e^{iHt/\hbar} A e^{-iHt/\hbar} \rho].$$

von Neumann equation with formal solution:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \quad \Rightarrow \quad \rho(t) = e^{-iHt/\hbar} \rho(0) e^{iHt/\hbar}.$$

Heisenberg equation with formal solution:

$$i\hbar \frac{\partial A}{\partial t} = -[H, A] \quad \Rightarrow \quad A(t) = e^{iHt/\hbar} A(0) e^{-iHt/\hbar}.$$

Density matrix in energy representation  $H|\lambda\rangle = E_\lambda|\lambda\rangle$ :

$$\rho_{\lambda\lambda'}(t) = \sum_{\lambda\lambda'} \langle \lambda | \rho | \lambda' \rangle e^{-i(E_\lambda - E_{\lambda'})t/\hbar}.$$

The oscillatory time evolution reminds us again of the problem associated with the approach to equilibrium (to be tackled elsewhere).

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<sup>2</sup>The Liouville operator is not an operator at the same level as the density operator and the Hamiltonian. It is a super-operator of sorts. Demonstrating its Hermitian nature requires a reinterpretation of the quantum mechanical operators  $H$ ,  $\rho$  as vectors in a space with an inner product.

### Stationarity condition for density operator:

As in the classical case, the condition for stationarity of the density operator is straightforward:

$$i\hbar \frac{\partial \rho}{\partial t} = 0 \quad \Rightarrow \quad [H, \rho] = 0.$$

If the density operator is expressible as  $\rho(H)$  it commutes with  $H$ . Commutability makes it diagonal in the energy representation:

$$\rho = \sum_{\lambda} p_{\lambda} |\lambda\rangle \langle \lambda|.$$

The oscillatory off-diagonal elements of  $\rho_{\lambda\lambda'}(t)$  have disappeared. Not all stationary probability distributions  $\{p_{\lambda}\}$  describe thermal equilibrium. The further criterion is an extremum principle.

### Gibbs entropy:

Q What criterion determines the functional dependence of  $\rho$  on  $H$ ?

A  $\rho(H)$  must maximize the entropy functional  $S[\rho]$  subject to the constraints related to whether the system is isolated, closed, or open.

Q What is the functional dependence of  $S$  on  $\rho$ ?

A It's the Gibbs entropy, motivated by Boltzmann's  $H$ -function and by Shannon's concept of uncertainty (discussed earlier):

- classical system:  $S[\rho] = -k_B \int d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$ ,
- quantum system:  $S[\rho] = -k_B \text{Tr}[\rho \ln \rho]$ .

The constant  $C_N$  in the classical expression allocates a specific phase-space volume element to every microstate:<sup>3</sup>

- distinguishable particles:  $C_N = h^{3N}$ ,  $h \simeq 6.62 \times 10^{-34} \text{Js}$ ,
- indistinguishable particles:  $C_N = h^{3N} N!$ .

The factor  $N!$  compensates for overcounting indistinguishable permutations of identical particles. No correction is necessary in quantum mechanics, where microstates have a definite permutation symmetry.

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<sup>3</sup>The constant  $C_N$ , which is additive for a normalized  $\rho$ , makes the square-bracket dimensionless. Its numerical value, dictated by Heisenberg's uncertainty principle, establishes consistency between quantum and classical statistics.

### Phase space allocated per quantum state:

The number of microstates that can be accommodated in a phase-space volume element  $d^{6N}X$  is

$$\frac{d^{6N}X}{h^{3N}} = \prod_{i=1}^{3N} \left[ \frac{1}{h} dq_i dp_i \right].$$

Illustration of phase-space allocation for the harmonic oscillator ( $N = 1$ ).

$$\text{Hamiltonian: } H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = \frac{h\omega}{2\pi} \left( n + \frac{1}{2} \right).$$

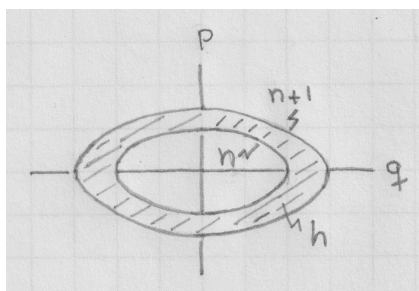
Classical trajectories are concentric ellipses with axes  $2q_{max}, 2p_{max}$ .

Quantized amplitudes inferred from quantized energy:

$$q_{max} = \sqrt{\frac{h}{\pi m \omega} \left( n + \frac{1}{2} \right)}, \quad p_{max} = \sqrt{\frac{h m \omega}{\pi} \left( n + \frac{1}{2} \right)}.$$

Area of ellipse:  $A(n) = \pi q_{max} p_{max} = h(n + 1/2)$ .

Area per quantum state:  $A(n + 1) - A(n) = h$ .



### Microcanonical ensemble:

Thermodynamic systems in isolation have constant energy:  $H = \text{const}$ . We use this fact in the evaluation of the Gibbs entropy,  $S = S[\rho]$ , with the stationarity condition,  $\rho = \rho(H)$ , enforced.

Consider a classical system of  $N$  interacting particles confined to a volume  $V$  at (conserved) internal energy  $U$ .

- The phase-space density  $\rho(\mathbf{X})$  is constant on an infinitesimally thin energy shell,  $U \leq H(\mathbf{X}) \leq U + \Delta$ , and zero elsewhere.

– Volume of energy shell:  $\Omega_{\Delta}(U, V, N) = \int_{U \leq H(\mathbf{x}) \leq U + \Delta} d^{6N} X.$

$$\Rightarrow \rho(\mathbf{X}) = \begin{cases} \Omega_{\Delta}^{-1} & : U \leq H(\mathbf{X}) \leq U + \Delta \\ 0 & : \text{otherwise,} \end{cases}$$

– Entropy:  $S = -k_B \int_{U \leq H(\mathbf{x}) \leq U + \Delta} d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})]$

$$\Rightarrow S(U, V, N) = k_B \ln \left[ \frac{\Omega_{\Delta}(U, V, N)}{C_N} \right].$$

The dependence of  $S$  on the energy width  $\Delta$  is undesirable and can, in fact, be avoided. In a high-dimensional space, most of the volume of a compact object is contained in a thin surface skin.

Example: sphere in  $d$ -dimensional space

– Volume of sphere;  $V(r) = C_d r^d$ ,  $C_d \doteq \frac{\pi^{d/2}}{\Gamma(d/2 + 1)}.$

– Volume of skin with width  $\Delta$ :  $V_{\Delta}(r) = V(r) - V(r - \Delta).$

$$\Rightarrow \frac{V_{\Delta}(r)}{V(r)} = \frac{[r^d - (r - \Delta)^d]}{r^d} = \left[ 1 - \left( 1 - \frac{\Delta}{r} \right)^d \right] = [1 - e^{-d|\ln(1 - \Delta/r)|}].$$

– The deviation between  $V(r)$  and  $V_{\Delta}(r)$  vanishes exponentially with increasing  $d$ . In the phase space of a macroscopic system  $d = 6N$  is of the order of Avogadro's number.

If we replace the shell volume  $\Omega_{\Delta}(U, V, N)$  by the entire volume inside the shell,  $\Omega(U, V, N)$ , the resulting entropy expression differs only by a term  $\propto \ln N$ , which is negligible in macroscopic systems.

$$\Rightarrow S(U, V, N) = k_B \ln \left[ \frac{\Omega(U, V, N)}{C_N} \right], \quad \Omega(U, V, N) = \int_{H(\mathbf{x}) \leq U} d^{6N} X.$$

For an isolated quantum system,  $H|n\rangle = E_n|n\rangle$ , transcribing the conclusions reached means counting energy levels with  $E_n < U$ :

Maximize  $S = -k_B \sum_{E_n < U} p_n \ln p_n$  subject to the constraint  $\sum_{E_n < U} p_n = 1.$

$$\Rightarrow p_n = \frac{1}{N_{<}(U)} \text{ where } N_{<}(U) = \sum_{E_n < U} 1. \quad \Rightarrow S = k_B \ln[N_{<}(U)].$$



### Aspects of significance:

- Of the two constraints,  $N = \text{const}$  and  $U = \text{const}$ , the *microcanonical* ensemble observes both, the *canonical* ensemble only the first, and the *grandcanonical* ensemble neither.
- For macroscopic systems with short-range interactions, the results of all three ensembles are equivalent.
- Each ensemble naturally leads to a thermodynamic potential:
  - ▷ microcanonical ens.: internal energy  $U$  or the entropy  $S$ ;
  - ▷ canonical ens.: Helmholtz potential  $A$  or Gibbs potential  $G$ ;
  - ▷ grandcanonical ens.: grand potential  $\Omega$ .

Thermodynamic potentials are interrelated via Legendre transforms.

- Constraints tend to make the path toward the solution harder. The microcanonical ensemble with its two constraints is rarely the first choice.
- The microcanonical ensemble is often employed in astrophysics, where entities of interest tend to be thermally isolated.

### Simple applications:

▷ Classical ideal gas [tex73]

▷ Array of classical harmonic oscillators [tex74]

In these two applications, it is straightforward to calculate the phase-space volume enclosed by an energy hypersurface.

▷ Array of quantum harmonic oscillators I [tex75]

Here we employ a combinatorial method to count the degeneracy of energy levels.

▷ Array of quantum harmonic oscillators II [tex126]

▷ Quantum paramagnet [tex127]

Here we Fourier transform the sum  $\sum_{\lambda} \delta(U - E_{\lambda})$  into an integral  $\int dk e^{Nf(k)}$  for  $N$  noninteracting degrees of freedom. For large  $N$  that integral is amenable to evaluation by the saddle-point method.

## Entropy of mixing revisited:

Here we resolve the Gibbs paradox encountered earlier (in [tsc4]).

Consider two dilute gases in a rigid and insulating box separated by a mobile conducting wall:  $N_1$  atoms on the left and  $N_2$  atoms on the right.

$p$ $T$	$p$ $T$
$N_1$ $V_1$	$N_2$ $V_2$

At thermal equilibrium:  $p_1 = p_2 \doteq p$ ,  $T_1 = T_2 \doteq T \Rightarrow N_1/V_1 = N_2/V_2$ .

The removal of the internal wall initiates the mixing of particles 1 and 2 without any change in pressure or temperature.

Does the entropy increase or stay the same? The answer depends on whether particles 1 and 2 are of the same kind (indistinguishable) or of a different kind (distinguishable).

Mixing occurs without changes in any of the following quantities:

- total internal energy:  $U = U_1 + U_2$ ,
- total volume:  $V = V_1 + V_2$ ,
- total number of particles:  $N = N_1 + N_2$ .

Consider the Sackur-Tetrode formula for the entropy of an ideal gas [tex73]:

$$S(U, V, N) = \frac{5}{2} N k_B + N k_B \ln \left[ \frac{V}{N h^3} \left( \frac{4\pi m U}{3N} \right)^{3/2} \right].$$

Distinguishable particles:

- Initial entropy:  $S_{init} = S(U_1, V_1, N_1) + S(U_2, V_2, N_2)$
- Final entropy:  $S_{fin} = S(U_1, V_1 + V_2, N_1) + S(U_2, V_1 + V_2, N_2)$
- Entropy change:  $\Delta S = N_1 k_B \ln \frac{V_1 + V_2}{V_1} + N_2 k_B \ln \frac{V_1 + V_2}{V_2} > 0$ .

Indistinguishable particles:

- Initial entropy:  $S_{init} = S(U_1, V_1, N_1) + S(U_2, V_2, N_2)$
- Final entropy:  $S_{fin} = S(U_1 + U_2, V_1 + V_2, N_1 + N_2)$
- Entropy change:  $\Delta S = 0$ .

### Negative temperatures:

Macrostates with negative (absolute temperature) can be realized in isolated systems with a finite range of energy levels. Level-occupancy inversion can be caused by laser pumping, for example.

Consider  $N$  noninteracting 2-level systems.

- Energy levels:  $\pm\epsilon$ .
- Occupancies,  $N_{\pm}$  with  $N_+ + N_- = N$ .
- Internal energy:  $U = (N_+ - N_-)\epsilon$ .

$$\Rightarrow N_+ = \frac{1}{2} \left[ N + \frac{U}{\epsilon} \right], \quad N_- = \frac{1}{2} \left[ N - \frac{U}{\epsilon} \right].$$

Degeneracy of state with energy  $U$ :  $N_U(U, N) = \frac{N!}{N_+!N_-!}$ .

Configurational entropy:

$$S(U, N) = k_B \ln N_U(U, N) = k_B N \ln N - \frac{1}{2} k_B \left[ N + \frac{U}{\epsilon} \right] \ln \left( \frac{1}{2} \left[ N + \frac{U}{\epsilon} \right] \right) - \frac{1}{2} k_B \left[ N - \frac{U}{\epsilon} \right] \ln \left( \frac{1}{2} \left[ N - \frac{U}{\epsilon} \right] \right)$$

$$\Rightarrow \frac{S}{Nk_B} = \ln 2 - \frac{1}{2} \left[ 1 + \frac{U}{N\epsilon} \right] \ln \left( 1 + \frac{U}{N\epsilon} \right) - \frac{1}{2} \left[ 1 - \frac{U}{N\epsilon} \right] \ln \left( 1 - \frac{U}{N\epsilon} \right).$$

Inverse temperature:  $\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_N = \frac{k_B}{2\epsilon} \ln \left( \frac{1 - U/N\epsilon}{1 + U/N\epsilon} \right)$ .

