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# Quantum Thermodynamics and Cramér's Theorem

**Lane P. Hughston**

Department of Computing  
Goldsmiths University of London  
New Cross, London SE14 6NW, United Kingdom

email: [l.hughston@gold.ac.uk](mailto:l.hughston@gold.ac.uk)

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## This presentation is based on the following papers:

D. C. Brody & L. P. Hughston (2016)

Thermodynamics of Quantum Heat Bath, *J. Phys. A* **49**, 452302.

D. C. Brody & L. P. Hughston (2001)

Geometric Quantum Mechanics, *J. Geom. Phys.* **38**, 19-53.

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Geometrisation of Statistical Mechanics. *Proc. Roy. Soc. Lond. A* **455**, 1683-1715.

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The Quantum Canonical Ensemble, *J. Math. Phys.* **39**, 6502-6508.

## Thermodynamics of a “gas” of finite dimensional quantum systems

We consider the thermodynamics of a quantum system consisting of a large number of weakly interacting “molecules,” each of which has finitely many degrees of freedom.

We assume that the molecular interactions are sufficiently weak to ensure that the support of the state space of the system is the topological product of the projective Hilbert spaces of the individual molecules.

It is an essential feature of the notion of a collection of weakly interacting molecules that there should be no appreciable entanglement between the states of the various molecules, and that the energies associated with the interactions between the various molecules can be neglected.

Our goal is to set up the problem in such a way that the thermodynamic properties of the system can be calculated explicitly in the limit as the number of constituents of the system is taken to be large.

## Comments regarding the “molecules”

Three ingredients are required for the development of a statistical model for a finite-dimensional quantum system.

These are: (i) the phase space of the system, denoted  $\Gamma$ , (ii) the Hamiltonian operator of the system  $\hat{H}$ , and (iii) a normalized measure  $\mathbb{P}$  on the phase space that determines how “averages” are taken over it.

We take the system to be modelled by a Hilbert space  $\mathcal{H}$  of finite dimension  $r$ .

The phase space of the system is the complex projective space  $\Gamma = \mathbb{C}\mathbb{P}^{r-1}$  given by the space of rays through the origin in  $\mathcal{H}$ .

The pair  $(\Gamma, \mathcal{F})$  is a measurable space, where  $\mathcal{F}$  denotes the Borel sigma-algebra generated by the open sets of  $\Gamma$ .

The use of the term “phase space” in the present context is justified by the fact that  $\Gamma$  has a natural symplectic structure.

From the operator  $\hat{H}$  we construct an associated Hamiltonian function.

The Hamiltonian function is given for each point  $x \in \Gamma$  by the expectation value of  $\hat{H}$  in the corresponding pure state.

Thus we write  $H(x) = \text{tr}[\hat{H} \hat{\Pi}(x)]$ , where  $\hat{\Pi}(x) = |x\rangle\langle x|/\langle x|x\rangle$  is the projection operator on to the element  $|x\rangle \in \mathcal{H}$  corresponding to the point  $x \in \Gamma$ .

The point is that the symplectic manifold  $\Gamma$ , equipped with the Hamiltonian function  $H(x)$ , has the structure of a classical phase-space.

## Phase-space measure

The choice of measure  $\mathbb{P}$  on  $(\Gamma, \mathcal{F})$  is not fixed in advance, except to the extent that it must be natural to the physical problem under consideration.

For equilibrium this typically means either (a) the uniform distribution (where the measure of a set is the volume of the set under the Fubini-Study metric) or (b) a distribution associated in some way with the Hamiltonian function.

We take the view that the choice of measure is a modelling choice, and that the merits of any particular choice of measure can be judged by its usefulness and naturalness in a specific context.

In the case of a finite dimensional system one further assumption can be made without loss of generality.

This is that the measure can be normalized in such a way that the total measure of the phase space is unity.

Thus if we write  $\mathbb{P}(A)$  for the measure of any measurable set  $A \in \mathcal{F}$ , then we assume that  $\mathbb{P}(\Gamma) = 1$ .

With this convention, the quantum phase space has the structure of a probability space  $(\Gamma, \mathcal{F}, \mathbb{P})$ , upon which  $H : \Gamma \rightarrow \mathbb{R}$  is a random variable.

## **Entropy of a quantum system**

We take the view that the entropy of a quantum system can be expressed as a function of the number of microstates accessible to it.

This suggests the following:

**Definition 1.** *The entropy associated with a measurable subset  $A \subset \Gamma$  of a quantum phase space  $(\Gamma, \mathcal{F}, \mathbb{P})$  with measure  $\mathbb{P}$  is given by*

$$S[A] = k_B \log \mathbb{P}(A). \quad (1)$$

Here  $k_B$  is Boltzmann's constant.

It follows that  $S[\Gamma] = 0$  and that if  $A$  is a proper subset of  $\Gamma$  then  $S[A] < 0$  and that if  $A$  is a set of measure zero, then  $S[A] = -\infty$ .

## Systems consisting of $n$ molecules

Let us consider a quantum system consisting of  $n$  molecules of the same type.

Each molecule will be represented by a finite quantum system for which the Hilbert space is of some dimension  $r$ .

For the total Hamiltonian function of the system let us write

$$H^{(n)}(x) = H_1(x) + H_2(x) + \cdots + H_n(x) \quad (2)$$

where the  $H_j(x)$ ,  $j = 1 : n$ , are the Hamiltonian functions of the molecules.

Here we have written

$$H_j(x) = \frac{\langle x | \hat{H}_j | x \rangle}{\langle x | x \rangle} \quad (3)$$

for the expectation of the Hamiltonian  $\hat{H}_j$  ( $j = 1 : n$ ) of molecule  $j$  in the overall system state  $|x\rangle$ .

It follows from the assumed absence of entanglement among the molecules that the overall state of the system admits a factorization of the form

$$|x\rangle = |x_1\rangle |x_2\rangle \cdots |x_n\rangle. \quad (4)$$

Hence for each  $j$  the Hamiltonian function  $H_j(x)$  depends only on the state space variable  $x_j$  associated with molecule  $j$ .

We assume that the state space of the system as a whole is endowed with a probability measure  $\mathbb{P}$  concentrated on the Segre variety of disentangled states,

$$\mathcal{Q} = \mathbb{C}\mathbb{P}_{(1)}^{r-1} \times \cdots \times \mathbb{C}\mathbb{P}_{(n)}^{r-1} \subset \mathbb{C}\mathbb{P}^{r^n-1}, \quad (5)$$

given by a product measure of the form

$$\mathbb{P}(dx) = \mathbb{P}_1(dx_1) \mathbb{P}_2(dx_2) \cdots \mathbb{P}_n(dx_n). \quad (6)$$



Here the measure on each factor of the product space is assumed to be of the same type.

It follows that the  $H_j(x)$ ,  $j = 1, 2, \dots, n$ , when interpreted as functions on the overall state space, are i.i.d. random variables under  $\mathbb{P}$ .

As a consequence we see that the total Hamiltonian of the system is given by a sum of  $n$  independent, identically distributed random variables.

With this fact in mind, we can abbreviate the notation and omit the arguments of the functions, and for the total Hamiltonian of an  $n$ -particle system we write

$$H^{(n)} = \sum_{j=1}^n H_j. \quad (7)$$

## Specific entropy of an ensemble

To develop a theory of the thermodynamics of such a system we shall take as our starting point a definition of the specific entropy associated with a given value  $E$  of the specific energy.

Thus for a system of  $n$  molecules we have:

$$S^{(n)}(E) = \frac{1}{n} k_B \log \mathbb{P} \left[ \frac{1}{n} \sum_{j=1}^n H_j \leq E \right]. \quad (8)$$

One might object to this definition, arguing that the entropy at energy  $E$  should be defined by confining the range of energy values to a thin band of energies including  $E$ , say the set  $[E - \Delta, E]$  for some choice of  $\Delta > 0$ .

However, the resulting expression for the specific entropy in the thermodynamic limit depends only on the upper boundary of the band.

As we shall see, for large  $n$ , and specific energy  $E$ , “most” of the entropy is concentrated in a very thin shell just below  $E$ .

Our strategy will be to show that for fixed  $E$  the sequence  $S^{(n)}(E)$ ,  $n \in \mathbb{N}$ , converges for large  $n$  to a limit

$$S(E) = \lim_{n \rightarrow \infty} S^{(n)}(E). \quad (9)$$

To show that  $S^{(n)}(E)$  converges we use a variant of Cramér’s theorem in the theory of large deviations.

## Thermodynamic limit

Let us write  $E_-$  and  $E_+$  respectively for the lowest and highest eigenvalues of the Hamiltonian  $\hat{H}$  of a typical molecule, and write  $\bar{E} = \mathbb{E}[H]$  for the mean under  $\mathbb{P}$  of the associated random variable  $H$ .

**Definition 2.** *We say that the measure  $\mathbb{P}$  is  $H$ -complete if for any  $\epsilon > E_-$  it holds that  $\mathbb{P}(H < \epsilon) > 0$ .*

**Proposition 1.** *If  $\mathbb{P}$  is  $H$ -complete, then*

$$\lim_{\beta \rightarrow \infty} \frac{\mathbb{E}[H e^{-\beta H}]}{\mathbb{E}[e^{-\beta H}]} = E_- \quad (10)$$

*and for any  $E \in (E_-, \bar{E}]$  there exists a unique value of  $\beta \geq 0$  such that*

$$E = \frac{\mathbb{E}[H e^{-\beta H}]}{\mathbb{E}[e^{-\beta H}]} \quad (11)$$

For each value of  $E \in (E_-, \bar{E}]$  let us write  $\beta(E)$  for the corresponding value of the parameter  $\beta$ .

Then we have the following:

**Proposition 2.** *The thermodynamic limit*

$$S(E) = \lim_{n \rightarrow \infty} \frac{1}{n} k_B \log \mathbb{P} \left[ \frac{1}{n} \sum_{j=1}^n H_j \leq E \right] \quad (12)$$

*exists and the specific entropy of the system is given as a function of the specific energy by*

$$S(E) = k_B \beta(E) E + k_B \log Z(\beta(E)), \quad (13)$$

*where for each value of  $E \in (E_-, \bar{E}]$  the associated value of  $\beta$  is determined by the relation*

$$E = \frac{\mathbb{E} [H e^{-\beta(E)H}]}{\mathbb{E} [e^{-\beta(E)H}]}, \quad (14)$$

*and  $Z(\beta(E)) = \mathbb{E} [\exp(-\beta(E)H)]$ .*

Setting  $\beta(E) = 1/k_B T(E)$ , we find that the temperature at energy  $E$  is

$$\frac{dS(E)}{dE} = \frac{1}{T(E)}. \quad (15)$$

It is interesting to observe that in the thermodynamic limit the value of the specific entropy is insensitive to the width of the band of energies below the specific energy.

More precisely, let us write

$$S^{(n)}(E - \Delta, E) = \frac{1}{n} k_B \log \mathbb{P} \left[ E - \Delta \leq \frac{1}{n} \sum_{j=1}^n H_j \leq E \right] \quad (16)$$

for the specific entropy of an  $n$ -particle system of weakly interacting molecules when the specific energy of the system lies in the band  $[E - \Delta, E]$  for some choice of  $\Delta > 0$ .

Then we have the following.

**Proposition 3.** *The limit  $S(E - \Delta, E) = \lim_{n \rightarrow \infty} S^{(n)}(E - \Delta, E)$  exists for the entropy associated with the energy band  $[E - \Delta, E]$  and is equal to  $S(E)$ .*

Here  $S(E)$  is the expression obtained without the specification of the lower bound of the energy band.

This result may seem surprising at first glance, but there are many examples of calculations in thermal physics where the device of a band of energies is introduced, only for the physical results later not to depend on it.

The interpretation of the situation in the present context is that in the thermodynamic limit the specific entropy, for a given specific energy, is concentrated almost entirely in a thin shell of the quantum phase space at and immediately below the energy surface corresponding to the specific energy.

The result can be understood as an example of the idea of “concentration of measure”, but is perhaps more easily understood in probabilistic terms.

For the given *a priori* measure it is extremely unlikely that the average of the energies of a large number of independent molecules will be anything other than the *a priori* mean  $\bar{E}$ ; but if we condition on the average being no greater than some specified value  $E$ , then it will be extremely unlikely that the average will be much less than  $E$ .

It will be helpful to look at some examples of thermodynamic systems.

## Example: the Dirac measure

This is the case when the measure  $\mathbb{P}$  on the state space of a representative molecule is concentrated on the energy eigenstates.

The Hilbert space associated with an individual molecule has dimension  $r$ .

In the situation that the Hamiltonian has a nondegenerate spectrum the Dirac measure is given by

$$\mathbb{P}(dx) = \frac{1}{r} \sum_i \delta_i(dx). \quad (17)$$

Here  $\delta_i(dx)$  denotes the usual Dirac measure concentrated at the point  $x_i$  ( $i = 1, 2, \dots, r$ ), where  $x_i$  denotes for each  $i$  the point in  $\Gamma$  corresponding to the energy eigenstate  $|x_i\rangle$  with energy  $E_i$ .

It follows that for  $r = 2$  the partition function is given by

$$Z(\beta) = \frac{1}{2} (e^{-\beta E_1} + e^{-\beta E_2}). \quad (18)$$

Apart from the factor of  $\frac{1}{2}$ , this is the well known formula in standard textbooks.

We find that the expression for the specific energy as a function of  $\beta$  is

$$E(\beta) = \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}}. \quad (19)$$

The mean energy  $\bar{E} = \mathbb{E}[H(x)]$  under  $\mathbb{P}$  is given in this case by

$$\bar{E} = \frac{1}{2}(E_1 + E_2). \quad (20)$$

For each value of  $E \in (E_1, \bar{E}]$  there exists a  $\beta \in \mathbb{R}^+$  such that (19) is satisfied.

In fact, we can invert this relation, to give  $\beta$  as a function of  $E$ , as follows:

$$\beta(E) = \frac{1}{E_2 - E_1} \log \frac{E_2 - E}{E - E_1}. \quad (21)$$

If we set  $\omega = \frac{1}{2}(E_2 - E_1)$ , then we obtain a more compact expression for the energy, namely

$$E(\beta) = \bar{E} - \omega \tanh(\beta\omega). \quad (22)$$

We can use this expression to work out the heat capacity

$$C(\beta) = -k_B \beta^2 \frac{dE(\beta)}{d\beta}, \quad (23)$$



in the case of the Dirac measure and we obtain

$$C(\beta) = k_B \beta^2 \omega^2 \operatorname{sech}^2(\beta\omega). \quad (24)$$

One can check that this goes to zero at low temperature.

We see that the specification of the Hamiltonian of a representative molecule at the microscopic level along with the specification of the relevant measure on the state space of the molecule (in this case, the Dirac measure) is sufficient to determine the equation of state of the system as a whole.

### **Example: the uniform measure**

Now we turn to the uniform measure, or Haar measure, which in the case of a single molecule is given by an expression of the form

$$\mathbb{P}(dx) = \frac{1}{V_\Gamma} dV_x. \quad (25)$$

Here  $dV_x$  denotes the natural volume element associated with the Fubini-Study metric on  $\Gamma$ , and  $V_\Gamma$  is the total volume of  $\Gamma$ .

In the case of  $n$  weakly interacting molecules the uniform measure is defined as in the product (6), with a uniform measure on the phase space of each molecule.

In the case  $r = 2$  we find that under the uniform measure on  $\mathbb{CP}^1$  the Hamiltonian function  $H(x)$ , when viewed as a random variable, has a uniform distribution over the interval  $[E_1, E_2]$ .

That is to say,

$$\mathbb{P}(H \leq E) = \mathbb{1}\{E_1 \leq E \leq E_2\} \frac{E - E_1}{E_2 - E_1} + \mathbb{1}\{E_2 < E\}. \quad (26)$$

As a consequence we find that the energy is given as a function of  $\beta$  by

$$E(\beta) = \frac{1}{\beta} + \frac{E_1 e^{-\beta E_1} - E_2 e^{-\beta E_2}}{e^{-\beta E_1} - e^{-\beta E_2}}, \quad (27)$$

or equivalently

$$E(\beta) = \frac{1}{\beta} + \frac{1}{2}(E_1 + E_2) - \omega \coth(\beta\omega). \quad (28)$$

We can work out the heat capacity and in this case we obtain

$$C(\beta) = k_B (1 - \beta^2 \omega^2 \operatorname{csch}^2(\beta\omega)), \quad (29)$$

which is nonvanishing at zero temperature.

## Concluding remarks

In summary, we have introduced an exact model for the thermodynamics of a quantum system containing a large number of identical “molecules”.

The model depends on the choice of the molecular Hamiltonian and also on the choice of measure on the phase space of a representative constituent.

We have shown that the thermodynamic limit exists and gives rise to an equation of state that determines a canonical relation between the specific entropy and the specific energy of the system.

From the structure of the molecular state space at a microscopic level we are able to infer the macroscopic properties of the system as a whole.

But we can also regard the system as a whole as a Gibbs ensemble and treat any individual molecule within the ensemble as a fully functional large system in its own right in equilibrium with a heat bath at temperature  $T$ .

THANK YOU FOR YOUR ATTENTION!

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