

A. Einstein

"The Theory of Opalescence
of Homogeneous Fluids
and Liquid Mixtures
near the Critical State"

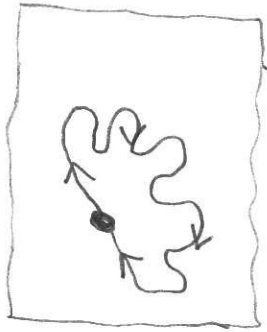
Annalen der Physik

33 (1910), pp. 1275-1298

Notes: John D. Norton

Synopsis

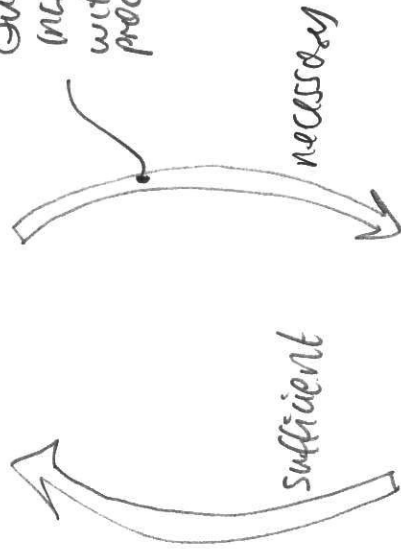
$$S = k \log W + \text{constant}$$



state space

Posit irreversibility is only apparent

quantity = $\phi(S, E)$
increases with processes



$$S = k \log W$$

must be $\log 50$

$$W = W_1 W_2 \Rightarrow S = S_1 + S_2$$

Probability away fluctuation, from equilibrium state to nearby λ_i to $\lambda_i + d\lambda_i$

$$dW = e^{-\frac{1}{k}(S-S_0)} d\lambda_1 \dots d\lambda_n$$

If some transformation effected by external means reversibly, it would require work

$$-A = (S-S_0) \frac{A}{T_0}$$

Einstein does not have -

$$dW = \text{const.} e^{-\frac{1}{k} \frac{A}{T_0}} d\lambda_1 \dots d\lambda_n$$

Expand A as power series

$$dW = \text{const.} e^{-\frac{1}{2k} \sum \lambda_i^2} d\lambda_1 \dots d\lambda_n$$

Gaussian!

$$\text{mean work for one variable } \lambda_i = \frac{kT_0}{2}$$

Background

M. Smolachowski,
 "molecular-kinetic theory
 of opalescence of gases in the
 critical state, and some
 related phenomena."
Annalen der Physik
 25 (1908), pp. 205-226

Rayleigh

"on the Transmission of
 light through an
 atmosphere containing
 small particles in
 suspension, and on the
 origin of the blue of
 the sky"
 Philosophical Magazine, 1899

distinct projects

joined

Further investigation
 of how molecular
 fluctuation phenomena
 yield observable
 consequences.
 Especially
 density
 fluctuations near
 criticality \Rightarrow observable
 opalescence

Energy
 scattered $\sim \frac{1}{\lambda^4}$ wave
 length
 \therefore blue in visible light
 more strongly scattered



Einstein's
 overt purpose

Fully analyse the
 scattering of electro-
 magnetic waves using
 Maxwell's theory
 for this phenomenon

Density fluctuations
 in air explain
 the sky's blueness
 without overt
 molecular hypotheses

Supported
 by

- Fullest explanation of " $S = k \ln W$ "
- Careful computation of
 general law of fluctuations

FOUNDATIONALY
 VERY
 INTERESTING!
 DEVELOPED
 HERE ONLY

Editor
of Annalen
der Physik

226. To Wilhelm Wien

Zurich [7 October 1910]

Highly esteemed Colleague:

Simultaneously with this postcard I am sending you a manuscript of a paper I just finished.^[1] Please accept it for the *Annalen*.^[2] The first part of the paper, which deals with Boltzmann's principle, is perhaps too lengthy. But please do not take this amiss; I have been wanting to expound on my opinion about this topic, and this was an opportunity to do so.^[3]

Respectfully yours,

A. Einstein

Doc. 9

**The Theory of the Opalescence
of Homogeneous Fluids and Liquid
Mixtures near the Critical State**

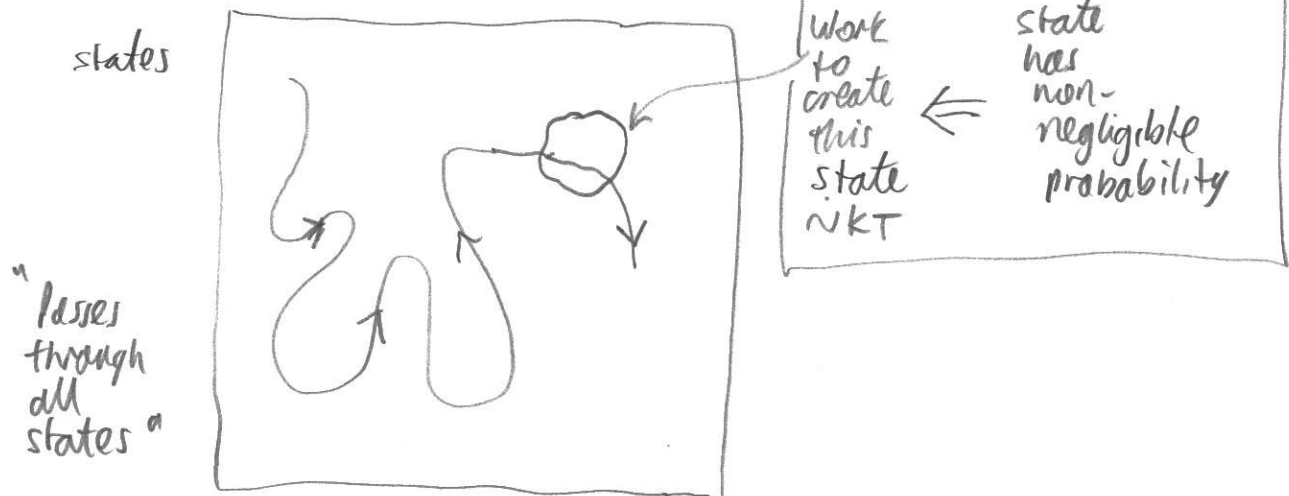
by A. Einstein.

[*Annalen der Physik* 33 (1910): 1275-1298]

In an important theoretical paper,¹ Smoluchowski has shown that the opalescence of fluids near the critical state as well as the opalescence of liquid mixtures near the critical mixing ratio and the critical temperature can be explained in a simple way from the point of view of the molecular theory of heat. This explanation is based on the following general implication of Boltzmann's entropy-probability principle: In the course of an infinitely long period of time, an externally closed system passes through all the states that are compatible with the (constant) value of its energy. However, the statistical probability of a state is noticeably different from zero only when the work that would have to be expended according to thermodynamics to produce the state in question from the state of ideal thermodynamic equilibrium is of the same order of magnitude as the kinetic energy of a monatomic gas molecule at the temperature under consideration.

Basic supposition of statistical analysis

Main result for fluctuations



Boltzmann's ergodic hypothesis (or just Poincaré recurrence?)

Apply fluctuation result to fluids

↓
opalescence

If such a small amount of work suffices to bring about, in volumes of fluid of the order of magnitude of the cube of a wavelength, a density that deviates markedly from the average density of the fluid or a mixing ratio that deviates markedly from the average, then, obviously, the phenomenon of opalescence (the Tyndall phenomenon) must take place. Smoluchowski has shown that this condition is actually fulfilled near the critical state; however, he did not provide an exact calculation of the quantity of light given off laterally through opalescence. This gap shall be filled in the following.

↑
Novel result
promised

The basic relation that
drives Einstein's approach to
thermodynamics & statistical physics

§1. General Remarks about the Boltzmann Principle

Boltzmann's principle can be expressed by the equation

$$(1) \quad S = \frac{R}{N} \lg W + \text{const.},$$

where

R is the gas constant,

N is the number of molecules in one gram-molecule,

S is the entropy,

W is the quantity customarily designated as the "probability"
of the state with which the entropy value S is associated.

$$\frac{R}{N} = k \quad \text{now}$$

problem deriving Boltzmann's principle

$W \sim$ number ways the state can be realized (= Boltzmann's complexions)

Need a complete theory to find W



We do not have a complete theory



Boltzmann's principle "devoid of content"

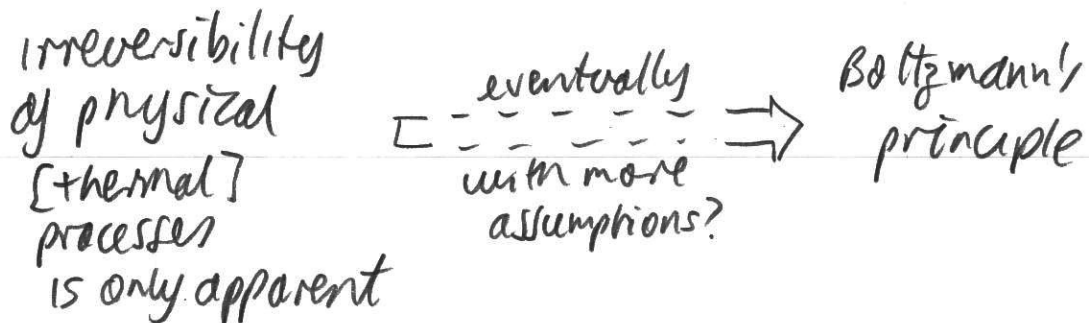
W is commonly equated with the number of different possible ways (complexions) in which the state considered—which is incompletely defined in the sense of a molecular theory by observable parameters of a system—can conceivably be realized. In order to be able to calculate W , one needs a complete theory (perhaps a complete molecular-mechanical theory) of the system under consideration. Given this kind of approach, it therefore seems questionable whether Boltzmann's principle by itself has any meaning whatsoever, i.e., without a complete molecular-mechanical or other theory that completely represents the elementary processes (elementary theory). If not supplemented by an elementary theory or—to put it differently—considered from a phenomenological point of view, equation (1) appears devoid of content.

?? the worry : $S = k \log W$
↑ measurable ↑ introduced here as a definition since we have no independent access

Why "no complete theory" ? → Full character of quantum systems obscure.

How to rescue Boltzmann's principle:

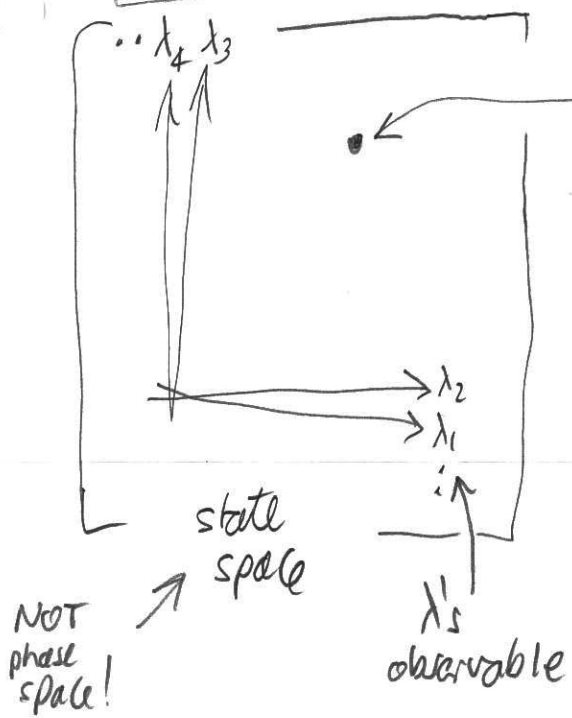
However, Boltzmann's principle does acquire some content independent of any elementary theory if one assumes and generalizes from molecular kinetics the proposition that the irreversibility of physical processes is only apparent.



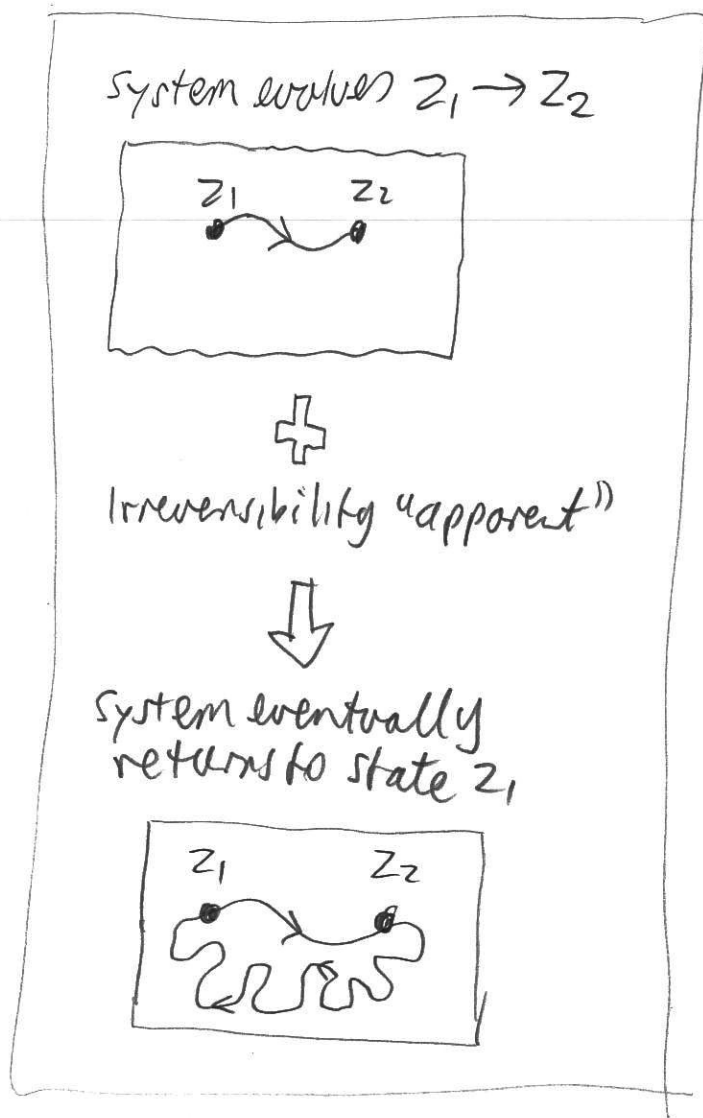
The setup assumed ↴

For let the state of a system be determined in the phenomenological sense by the variables $\lambda_1, \dots, \lambda_n$, that are observable in principle. To each state Z there corresponds a combination of values of these variables. If the system is externally closed, then the energy—and, indeed, in general, no other function of the variables—is constant. Let us think of all the states of the system that are compatible with the energy value of the system, and let us denote them by Z_1, \dots, Z_r . If the irreversibility of the process is not one of principle, then, in the course of time, the system will pass through these states Z_1, \dots, Z_r again and again. On this assumption, one can speak of the probability of the individual states in the following sense: Suppose we observe the system for an immensely long period of time θ and determine the fraction τ_i of the time θ during which the system is in the state Z_i ; then τ_i/θ represents the probability of the state Z_i . The same holds for the probability of the other states Z . According to Boltzmann, the apparent irreversibility must be attributed to the fact that the states differ in their probabilities, and that the system is probably going to assume states of higher probability, if it happens to find itself in a state of relatively low probability. That which appears to be completely law governed in irreversible processes is to be attributed to the fact that the probabilities of the individual states Z are of *different orders of magnitude*, so that a given state Z will practically always be followed by *one* state, from among all the states bordering on Z , because of this one state's enormous probability as compared with the probabilities of the other states.

Set up



Individual Z (= "Zustand") state is a point.

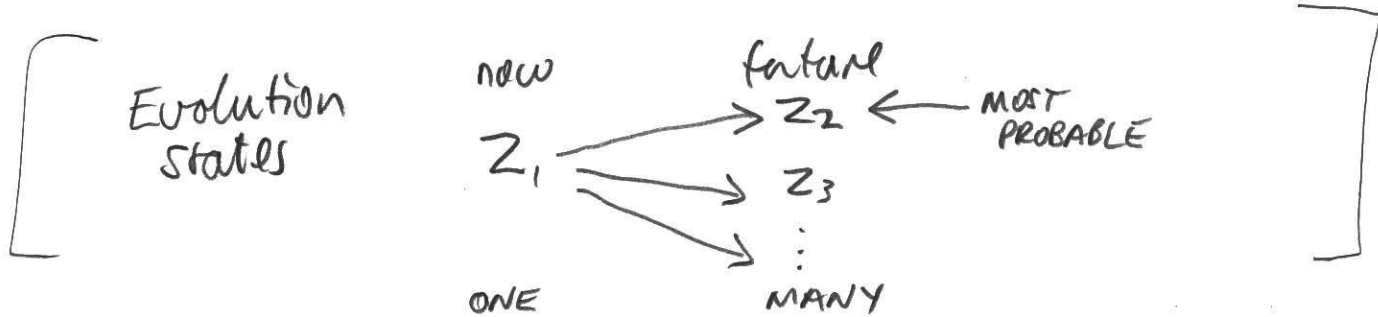


Probability of state Z

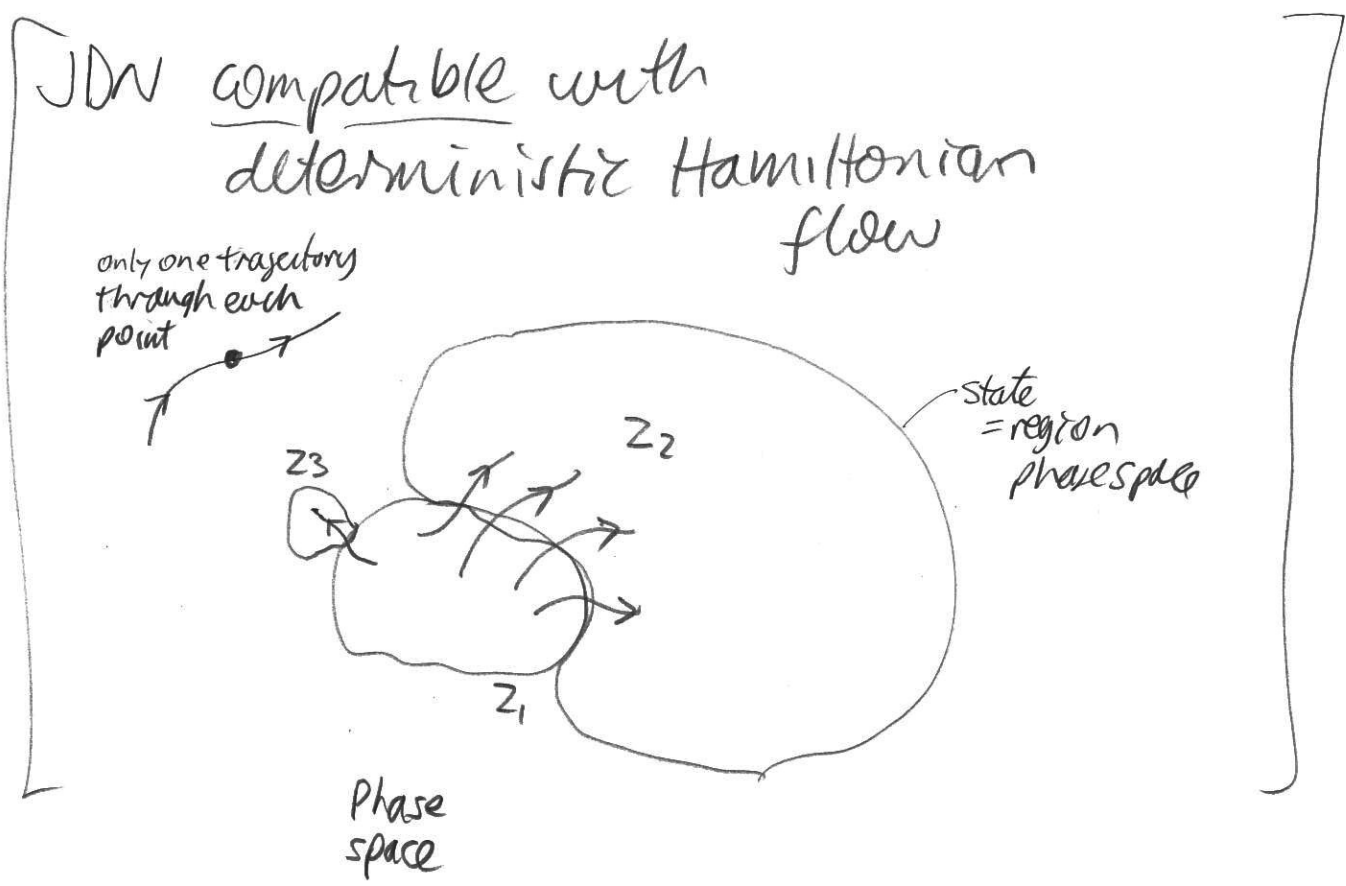
= $\frac{\tau \leftarrow \text{time spent in Z}}{\Theta \leftarrow \text{immensely long time we observed}}$

$Z_1 \xrightarrow[\text{irreversible}]{\text{apparent}} Z_2$ really $\text{Prob } Z_2 \gg \text{Prob } Z_1$

"Different orders of magnitude"

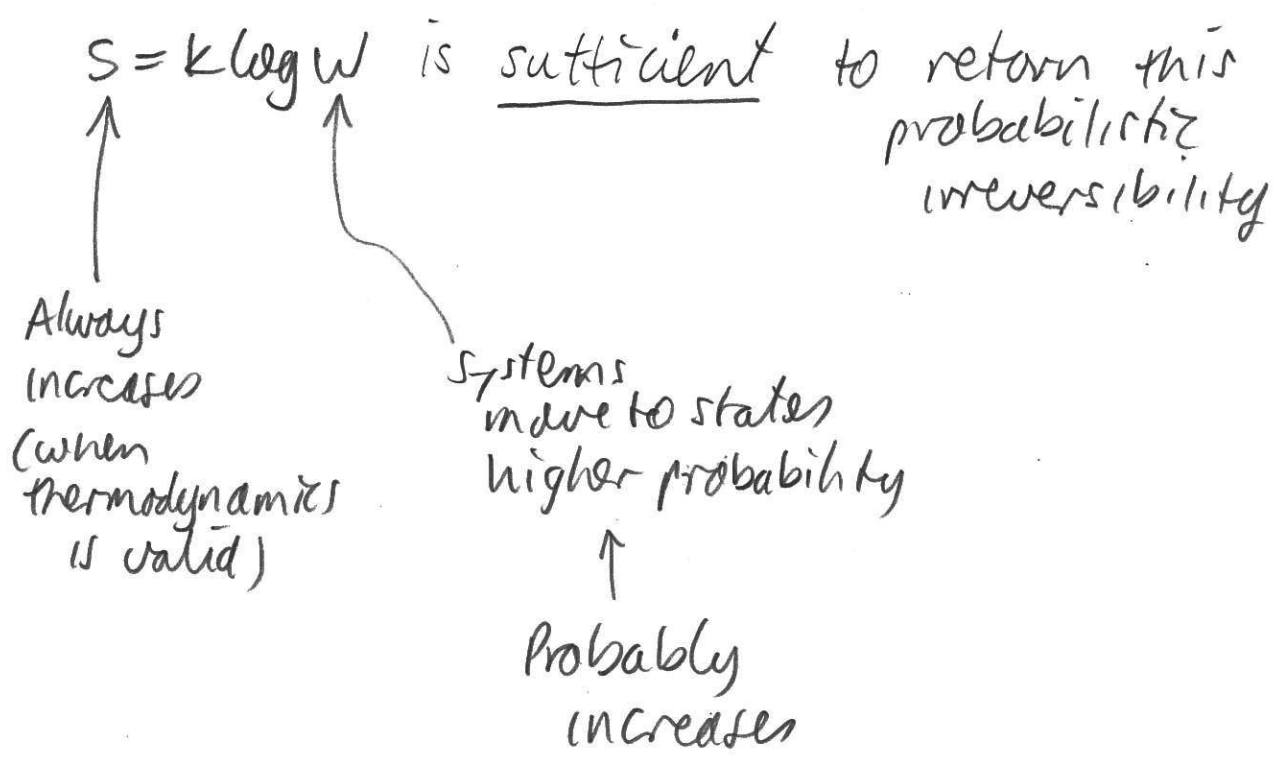


the probabilities of the individual states Z are of different orders of magnitude, so that a given state Z will practically always be followed by *one* state, from among all the states bordering on Z , because of this one state's enormous probability as compared with the probabilities of the other states.



New the main argument for Boltzmann's Principle

It is this probability we have just described, for the definition of which no elementary theory is needed, which is related to the entropy in the way expressed by equation (1). It can easily be recognized that equation (1) must really be valid for the probability so defined. For entropy is a function that does not decrease in any process in which the system is isolated (within the range of validity of thermodynamics). There are other



... but is it necessary?

Now show necessity:

system is isolated (within the range of validity of thermodynamics). There are other functions, too, that have this property; however, if the energy E is the only function of the system that does not vary with time, then all of these functions are of the form $\varphi(S, E)$, where $\partial\varphi/\partial S$ is always positive. Since the probability W is, as well, a function that does not decrease in any process, then W is also a function of S and E alone, or—if only states of the same energy are being compared—a function of S alone. That

Any quantity
that always
increases
(when thermodyn-
amics is valid)

$$= \varphi(S, E)$$

some
increasing
function
in S

HOW IS
THIS
JUSTIFIED?

Probability W
has this property

Therefore, $W = \varphi(S, E)$

Justification ?

10a

IF (a) there is a space of states

parameterized by $\lambda = (\lambda_1, \dots, \lambda_n)$

(b) every state λ_1 and λ_2 are related by an order

$\lambda_1 \rightsquigarrow \lambda_2$ $\lambda_1 \approx \lambda_2$ $\lambda_1 \lesssim \lambda_2$ (exactly one holds)

λ_2 can spontaneously move to λ_1

λ_1 & λ_2 are connected by a reversible process

λ_1 can spontaneously move to λ_2

Weakness
Are there states not related by the order?
OVER

(c) A function S on λ is adapted to the order iff

$$S(\lambda_1) \begin{matrix} > \\ = \\ < \end{matrix} S(\lambda_2) \iff \lambda_1 \begin{matrix} \rightsquigarrow \\ \approx \\ \lesssim \end{matrix} \lambda_2$$

(d) S is defined for all λ .

THEN

if S and S^* satisfy (c), S^* is a function of S .

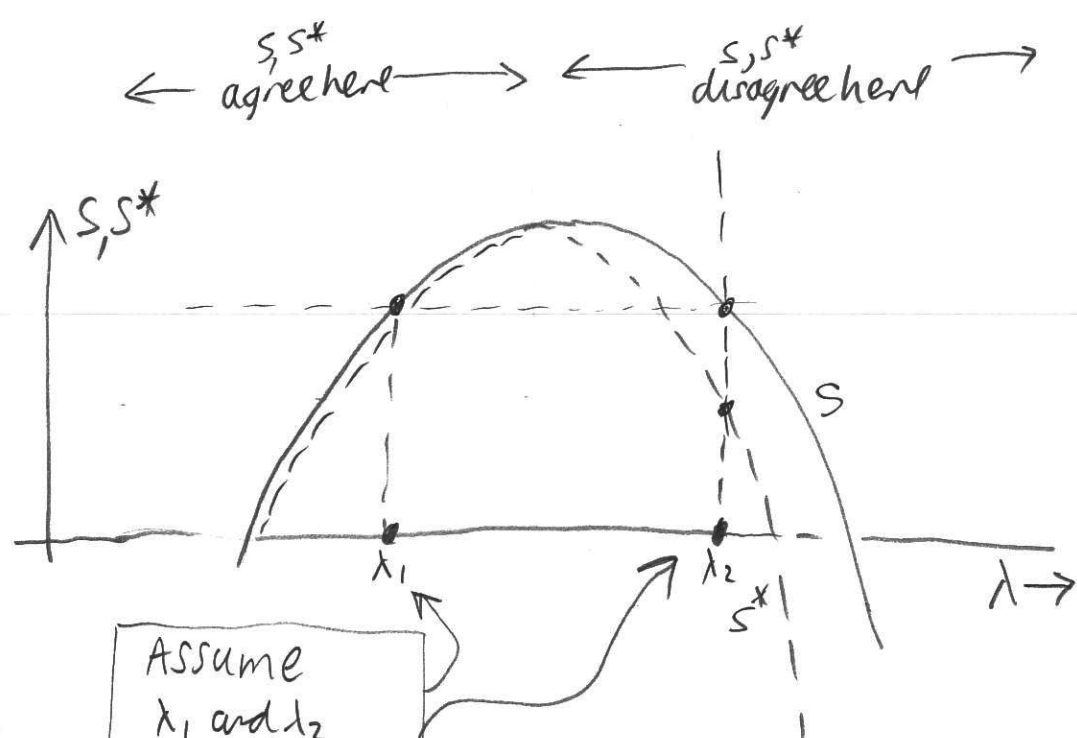
Proof: S^* can fail to be a function of S if

(i) $\exists \lambda$ such that either $S(\lambda)$ or $S(\lambda^*)$ are undefined \rightarrow violates (a)

(ii) $\exists \lambda, \lambda'$ such that $S(\lambda) = S(\lambda')$ but $S^*(\lambda) \neq S^*(\lambda')$ \rightarrow violates (b) since then $\lambda \approx \lambda'$ and $\lambda \not\lesssim \lambda'$

\therefore value $S(\lambda)$ fixes value $S^*(\lambda)$

when there are states not related by the order relation...



Assume λ_1 and λ_2 NOT related by order relation.

By construction
 $S(\lambda_1) = S(\lambda_2) = S$
 but
 $S^*(\lambda_1) \neq S^*(\lambda_2)$

$\therefore S^*$ cannot be a function of S since the one value $S = S(\lambda_1) = S(\lambda_2)$ is associated with two values of S^*

$$W = \phi(S, E) \rightarrow S = f(W, E)$$

↑
invertible
in S

↑
For fixed E,
 $f \sim \log$

or—if only states of the same energy are being compared—a function of S alone. That the relation between S and W given in equation (1) is the only possible one can be deduced, as we know, from the theorem that the entropy of a total system that is composed of subsystems equals the sum of the entropies of the subsystems. Equation (1) can thus be proved for all of the states Z that belong to the same value of energy.

The 1905 argument

Independent subsystems

$$\begin{aligned} \text{System} &= \text{Sys}_1 \oplus \text{Sys}_2 \oplus \dots \\ \text{Prob } W &= W_1 \times W_2 \times \dots \\ \text{Entropy } S &= S_1 + S_2 + \dots \end{aligned}$$

How has E dropped out of the relation?

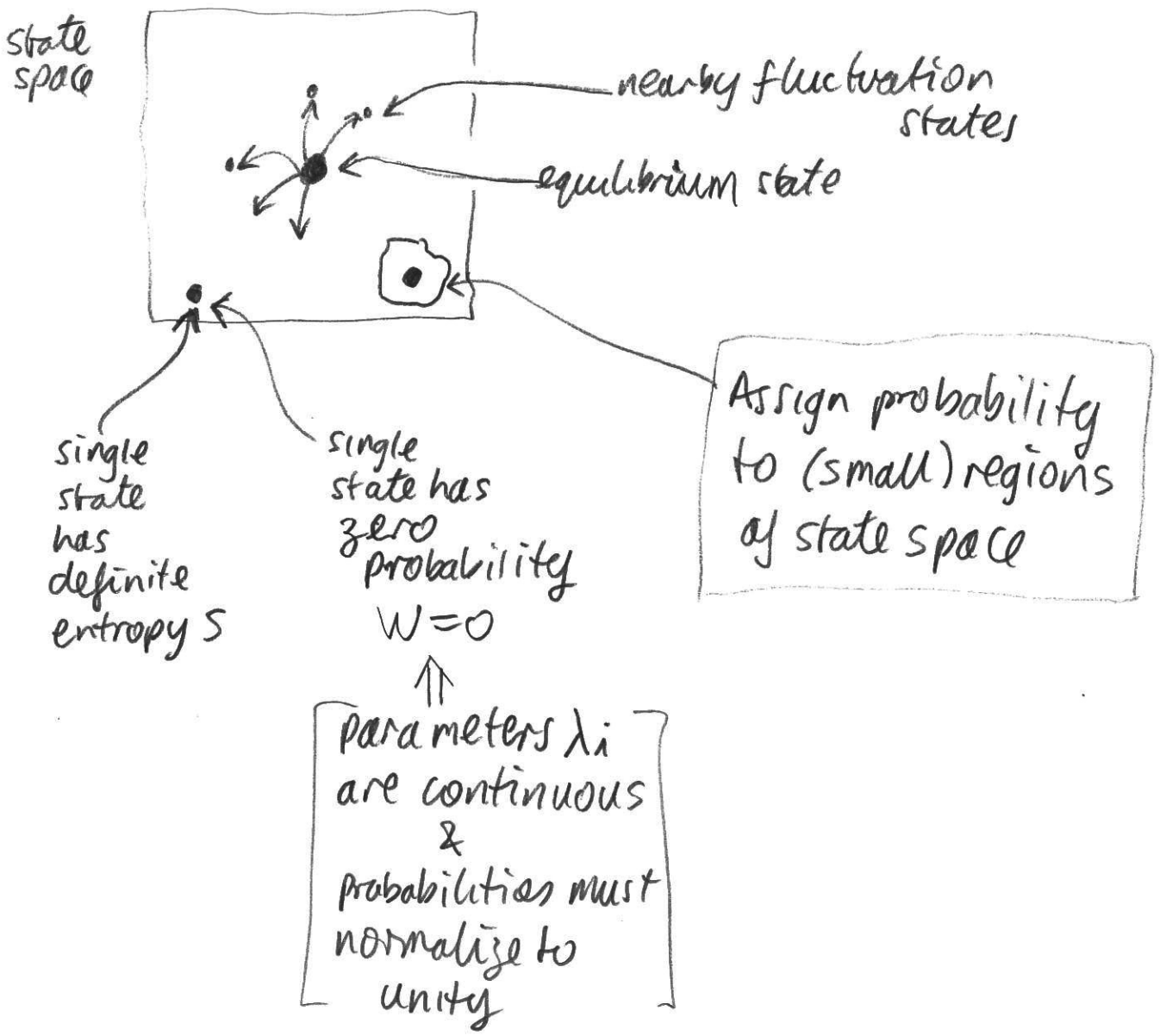
Therefore

$$\begin{aligned} S_1 &= k \log W_1 \\ S_2 &= k \log W_2 \\ &\vdots \end{aligned}$$

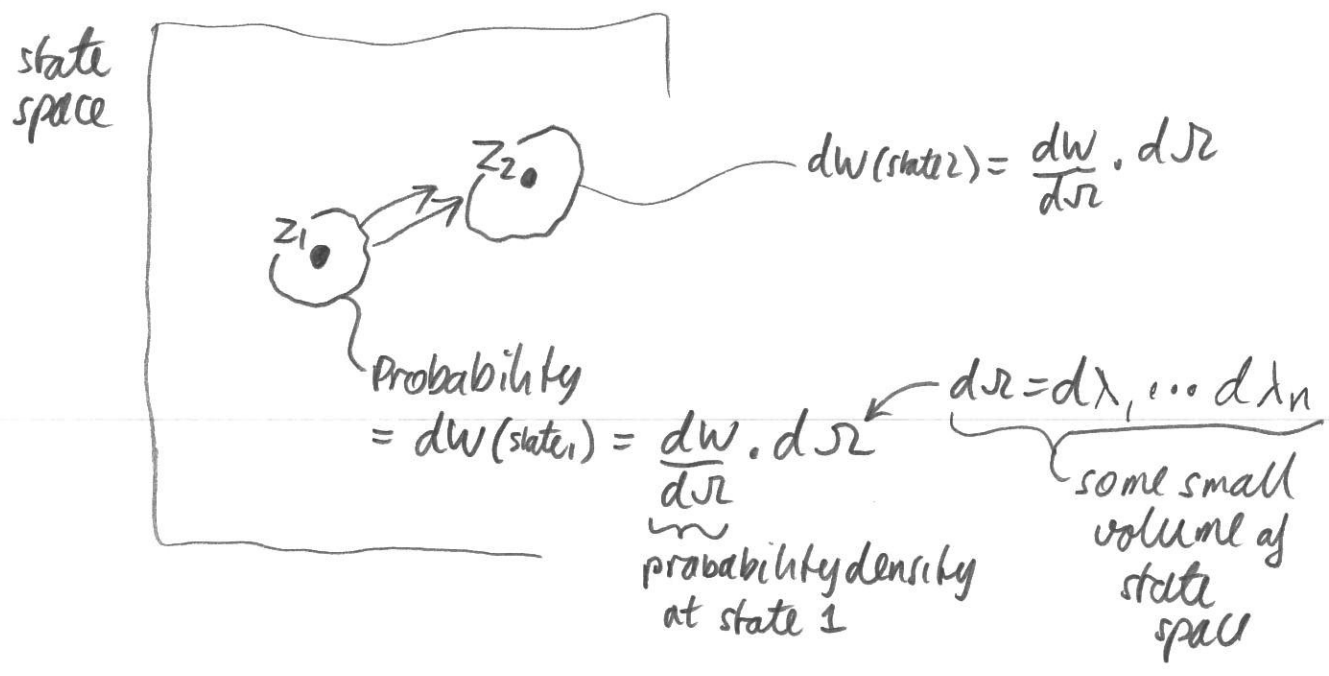
$$(S = S_1 + S_2 + \dots) = k \log(W_1 W_2 \dots)$$

Problem: mismatch of quantities

The following objection can be raised against this interpretation of Boltzmann's principle: one cannot speak of the statistical probability of a *state*, but only of that of a *state region*. The latter is defined by a portion g of the "energy surface" $E(\lambda_1, \dots, \lambda_n) = 0$. Obviously, W tends toward zero along with the size of the chosen portion of the energy surface. For this reason, equation (1) would be totally meaningless if the relation between S and W were not of a quite special kind. That is to say, $\lg W$ appears in the equation (1) multiplied by the very small factor R/N . If one imagines that W has been obtained for a region G_w just large enough that its dimensions lie on the border of the perceptible, then $\lg W$ will have a certain value. If the region is reduced perhaps e^{10} times, then the right-hand side will only be diminished by the vanishingly small quantity $10(R/N)$ on account of the reduction in the size of the region. Thus, if the dimensions of the region are indeed chosen small compared with perceptible dimensions, but nevertheless large enough for $R/N \lg G_w/G$ to be a numerically negligible quantity, then equation (1) will have a sufficiently exact meaning.



Repair



Boltzmann's principle is really

$$S = k \log(\underbrace{dW}_{\text{probability}}) = k \log\left(\underbrace{\frac{dW}{d\Omega}}_{\text{probability density}}\right) + k \log(d\Omega)$$

not invariant under change of λ variables

FIXED correction for volume size.

prefer this form

OR

$$S = k \log(dW) = k \log\left(\frac{dW}{d\Omega} \cdot d\Omega\right) = k \log\left(\frac{dW}{d\Omega} \cdot d\Omega'\right) + k \log\left(\frac{d\Omega}{d\Omega'}\right)$$

different small volumes of just perceptible size

very small

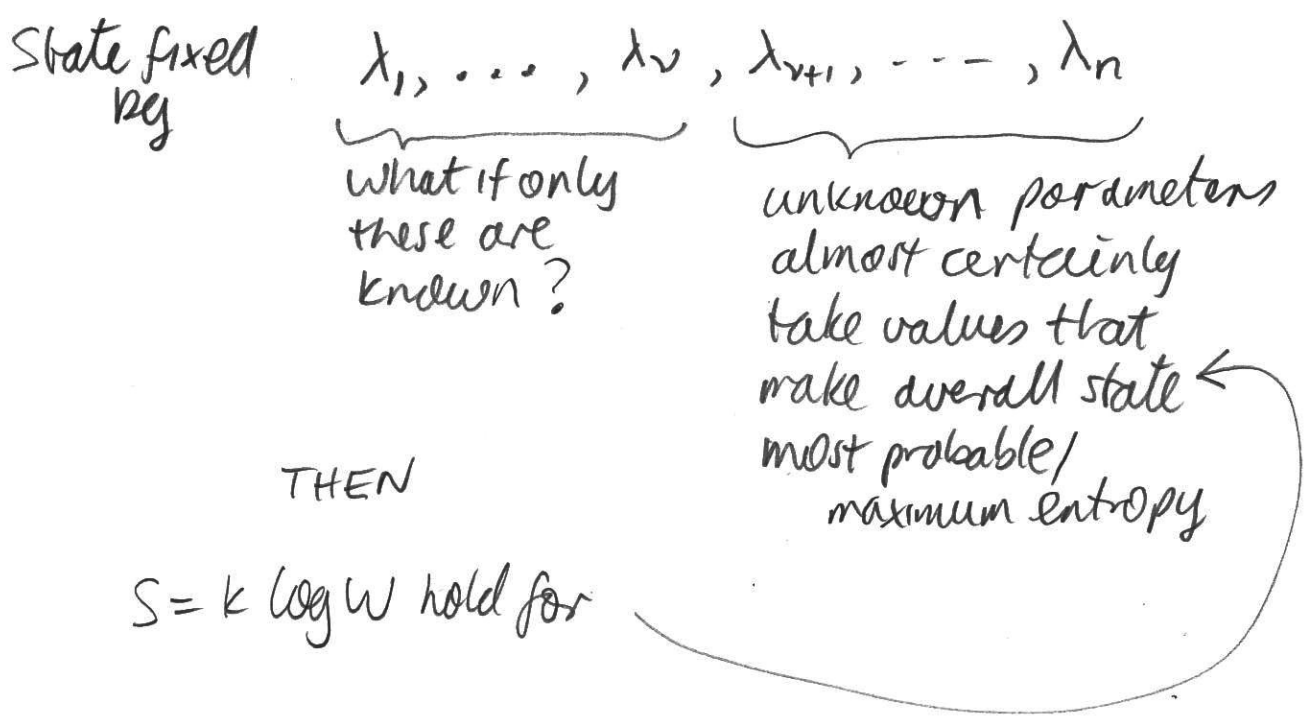
Fixed by volume chosen \therefore invariant under parameter change

$\therefore S$ has "sufficiently exact meaning"

Einstein's version

Some minor housekeeping:

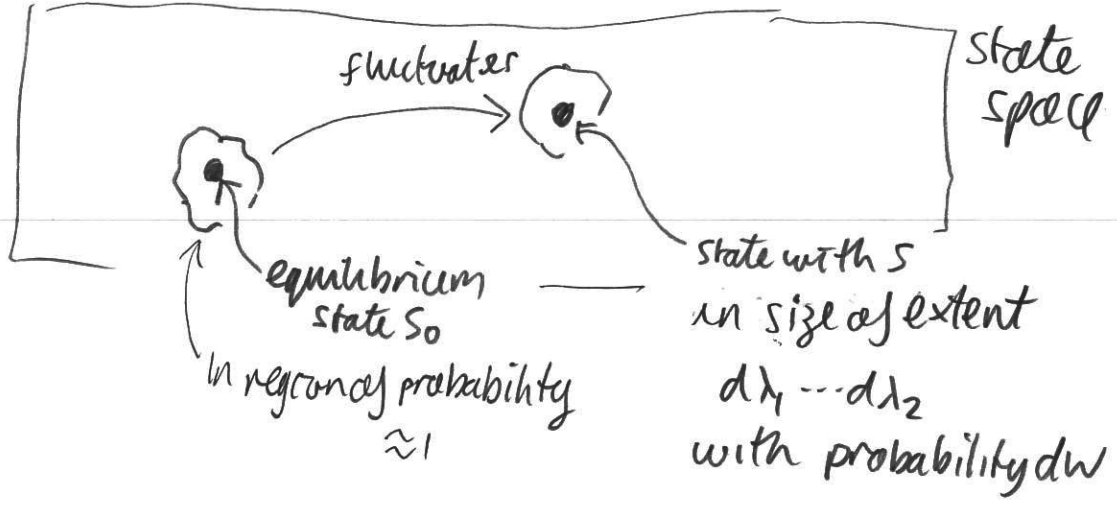
We have assumed so far that $\lambda_1 \dots \lambda_n$ determines *completely*, in the phenomenological sense, the state of the system in question. However, equation (1) also retains its meaning undiminished if we seek the probability of a state that is incompletely determined in the phenomenological sense. For let us seek the probability of a state that is defined by specific values of $\lambda_1 \dots \lambda_v$ (where $v < n$), while the values of $\lambda_{v+1} \dots \lambda_n$ are left indeterminate. Among all the states with the values $\lambda_1 \dots \lambda_v$, those values of $\lambda_{v+1} \dots \lambda_n$ will be far and away the most frequent which make the entropy of the system at constant $\lambda_1 \dots \lambda_v$ a maximum. In that case, equation (1) will hold between this maximum value of the energy and the probability of *this* state.



Computing Fluctuations

Step 1 Generate

$$dW = \text{const.} \cdot e^{-\frac{1}{k}(s-s_0)} d\lambda_1 \dots d\lambda_n$$



- Result seems to follow from a very simple inversion of $S = k \log W$ (OVER)
- Einstein gives a longer power series argument (not shown here)

EASY
VERSION

For fluctuation state $S = k \log(dw/d\Omega)$

For equilibrium state $S_0 = k \log(dw_0/d\Omega)$

$$S - S_0 = k \log \left(\frac{dw/d\Omega}{dw_0/d\Omega} \right)$$

Inverting:

$$\frac{dw}{d\Omega} = \underbrace{\frac{dw_0}{d\Omega}}_{\text{"const"}} \cdot e^{\frac{S-S_0}{k}} \quad \text{or} \quad dw = \text{const.} \cdot e^{\frac{S-S_0}{k}} \underbrace{dx_1 \dots dx_n}_{\text{"d}\Omega"}$$

Einstein proceeds as:

$$e^{\frac{S-S_0}{k}} = \frac{w}{w_0} = w \quad \text{since } w_0 \approx 1 \text{ for the equilibrium state}$$

Then

$$dw = \underbrace{e^{\frac{S-S_0}{k}}}_{\text{NO CONSTANT}} dx_1 \dots dx_n \quad dw = \text{prob of fluctuation to state in } x_i \text{ to } x_i + dx_i$$

Then long argument recovers constant

Step 2. Replace $S-S_0$ by "elementary work" A

(2) becomes

$$dW = \text{const.} \cdot e^{\frac{1}{k} \frac{A}{T_0}} d\lambda_1 \dots d\lambda_n$$

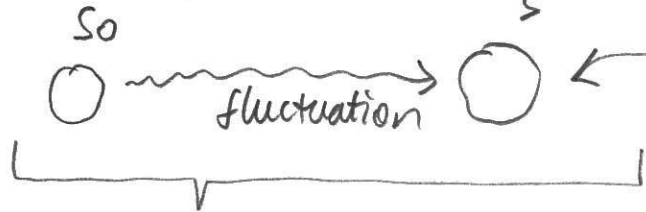
$$S-S_0 = \frac{1}{T_0} A$$

should have minus
↑
equilibrium temperature

↓ DV: should $(-\frac{A}{kT_0})$ since the greater the work the less probable the state?

Equilibrium state

Nearly non-equilibrium state



Imagine this momentarily appearing state somehow "locked in" as an equilibrium state

Imagine this process implemented as a thermodynamically reversible process with external intervention

$$dU = dA + T_0 dS = 0$$

$\underbrace{dU}_{\text{change internal energy}} = \underbrace{dA}_{\text{work done ON system}} + \underbrace{T_0 dS}_{\text{heat gained by system}} = 0$

since by supposition original system is isolated

$$dS = -\frac{dA}{T_0} \Rightarrow S-S_0 = -\frac{A}{T_0}$$

WHERE DOES THE MINUS SIGN GO?

I think it should stay!

Hence above formula follows.

Assume negligible temperature changes, so all T_i are T_0

My Illustration



corresponding change between equilibrium states with external intervention

compute work A done on system

$$dA = -PdV = -nKT \frac{dV}{V}$$

$$A = -nKT \int_{V_0}^{V_1} \frac{dV}{V} = -nKT \ln \frac{V_1}{V_0} = nKT \ln \left(\frac{V_0}{V_1} \right)$$

$$\frac{A}{KT} = \ln \left(\frac{V_0}{V_1} \right)^n$$

$$dW = \text{const.} e^{-\frac{A}{KT_0}} dV = \text{const.} \exp \left(-\ln \left(\frac{V_0}{V_1} \right)^n \right) dV = \text{const.} \left(\frac{V_1}{V_0} \right)^n dV$$

Rewrite as

$$\frac{dW}{dV} = \text{const.} \left(\frac{V_1}{V_0} \right)^n$$

probability density over volume

Result matches 1905 light quantum fluctuation argument

set as normalization constant

Step 3. Fluctuations around equilibrium yield Gaussian error law

$$dW = \text{const.} e^{-\frac{1}{2k} \sum a_\nu \lambda_\nu^2} d\lambda_1 \dots d\lambda_n$$

all $a_\nu > 0$

Since $A = A_0 + \sum A_\nu \lambda_\nu + \frac{1}{2} \sum_{\mu\nu} a_{\mu\nu} \lambda_\mu \lambda_\nu + \dots$ small-discard.

0
by definition

0
since origin state is equilibrium state (check?!)

A has local minimum at equilibrium.

Hence all $a_{\mu\nu} > 0$

Diagonalize and introduce new λ 's. This term becomes

$$\frac{1}{2} \sum_\nu a_\nu (\lambda_\nu)^2$$

All λ 's vanish at equilibrium state

Hence work done to attain $\lambda_\nu = \frac{1}{2} a_\nu (\lambda_\nu)^2$

Mean work to attain λ_ν

$$\overline{A_\nu} = \overline{\frac{1}{2} a_\nu (\lambda_\nu)^2} = \frac{kT_0}{2}$$

(How computed?)