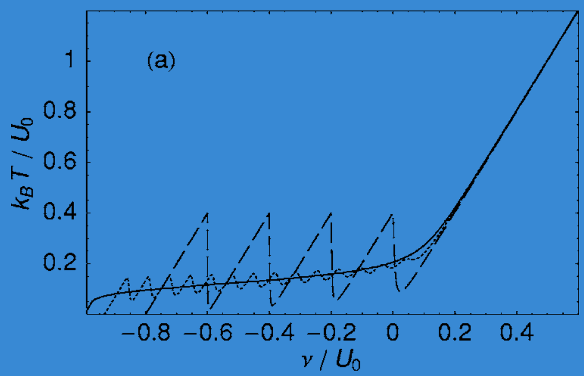
Micro-canonical singularities in finite systems

Jörn Dunkel



DAMTP, Centre for Mathematical Sciences

Many thanks to

Stefan Hilbert
(MPA / Bonn)

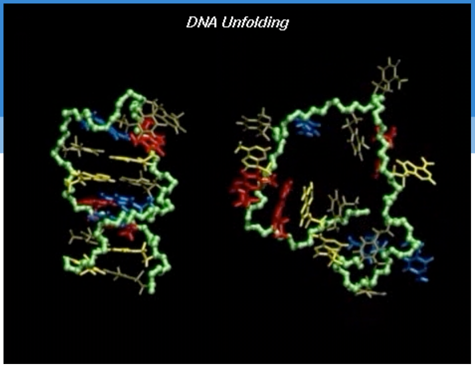
Outline

- introduction
  - motivation & general remarks
  - competing entropy definitions for the micro-canonical ensemble
  - historical remarks
- an exactly solvable 1D model (finite system singularities)
- concluding “conjecture”

Hilbert & Dunkel, PRE 74: 011120 (2006)
Dunkel & Hilbert, Physica A 370: 390-406 (2006)

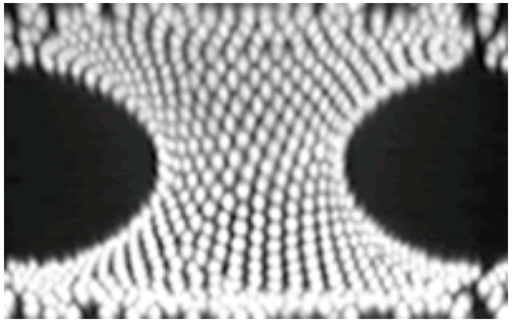
Why TD of finite systems?

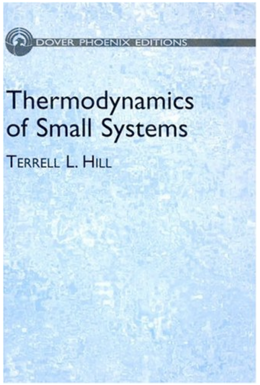
Lin et al, Phys Chem Chem Phys 10: 4227 (2008)

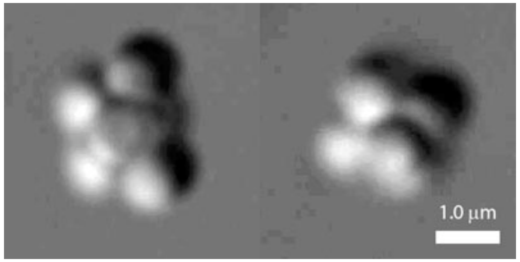


- experimental motivation
  - aggregation, folding transitions in proteins
  - melting transitions in small crystals (dusty plasmas, colloids)
  - cold atoms
- theoretical motivation
  - finite-size effects
  - ensemble non-equivalence [Gross, Phys Rep 279: 119 (1997)]
  - non-equilibrium statistical mechanics (microcanonical fluctuation theorems, etc.) [Campisi et al, PRE 80: 031145 (2008)]
  - “origin” of macroscopic phase transitions in TDL [Kastner, Rev Mod Phys 80: 167 (2008)]

Irvine et al, Nature 468: 947 (2010)





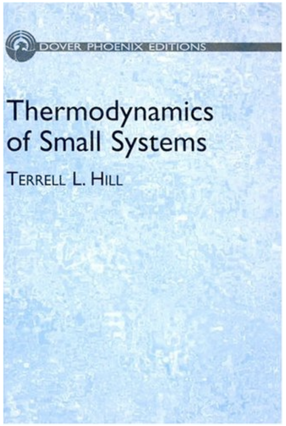


Meng et al, Science 327: 560 (2010)

TD of “small” Hamiltonian systems

$$H_N(\boldsymbol{q},\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + U(\boldsymbol{q}) \qquad\qquad z := (\boldsymbol{q},\boldsymbol{p}) \in \mathbb{R}^{2N}$$

- “top-bottom” approach
  - finite size corrections to infinite system results
  - Lebowitz & Percus, Phys Rev 24: 1672 (1961)



- “bottom-up” approach
  - develop formalism that works for any N ... starting with N=1
  - Paul Hertz, Ann d Phys 33: 225/537 (1910)

Ensembles & entropies

infinite heat bath: canonical ensemble $\forall N$

$$f_C(z) = \frac{\exp[-\beta H(z)]}{Z_C} \quad \leftrightarrow \quad S_C = -\int dz\ f(z) \ln f(z)$$

temperature conserved, energy fluctuates

finite heat bath: Tsallis-Renyi ensembles Campisi & Bagci, Phys Lett A 362: 11(2007) $\forall N$

$$f_{1/q}(z) = \frac{\{1 + (q-1)\beta\,[H(z) - E]\}^{q/(1-q)}}{Z_{1/q}} \quad \leftrightarrow \quad S_{1/q} = \frac{q}{q-1} \ln \int dz\ [f(z)]^{1/q}$$

isolated systems: micro-canonical ensemble $\forall N$

$$f_M(z) = \frac{\delta[E - H(z)]}{Z_M} \quad \leftrightarrow \quad S_M = ???$$

energy conserved, temperature fluctuates

Entropy of the MCE?

$$f_M(z) = \frac{\delta[E - H(z)]}{Z_M} \qquad H(\boldsymbol{q}, \boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + U(\boldsymbol{q}) \qquad z := (\boldsymbol{q}, \boldsymbol{p}) \in \mathbb{R}^{2N}$$

$$\Omega = \int dz\, \Theta[E - H(z)]$$

$$S = \ln \Omega$$

$$Z_M = \int dz\, \delta[E - H(z)] = \frac{\partial \Omega}{\partial E}$$

$$S = \ln Z_M$$

Entropy of the MCE?

$$f_M(z) = \frac{\delta[E - H(z)]}{Z_M} \qquad H(\boldsymbol{q}, \boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + U(\boldsymbol{q}) \qquad z := (\boldsymbol{q}, \boldsymbol{p}) \in \mathbb{R}^{2N}$$

$$\Omega = \int dz\, \Theta[E - H(z)]$$

$$S = \ln \Omega$$

$$\left\langle z_i \frac{\partial H}{\partial z_i} \right\rangle = \frac{\Omega}{Z_M} = \left(\frac{\partial S}{\partial E} \right)^{-1} =: T$$

$$T > 0$$

$$Z_M = \int dz\, \delta[E - H(z)] = \frac{\partial \Omega}{\partial E}$$

$$S = \ln Z_M$$

$$\left\langle z_i \frac{\partial H}{\partial z_i} \right\rangle \neq \left(\frac{\partial S}{\partial E} \right)^{-1} =: T$$

$$T \gtrless 0$$

1910. № 12.

ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 33.

1. *Über die mechanischen Grundlagen der Thermodynamik;*
von Paul Hertz.

(17) $$\int\limits_{\varepsilon<\varepsilon^*}\!\!\int dx_1 \ldots dx_m = V(\varepsilon^*),$$

so ist nach (14)

(18) $$\omega = \frac{dV}{d\varepsilon^*}.$$

(37) $$\overline{\varepsilon_p} = \frac{n}{2}\,\mathfrak{t},$$

wo

(38) $$\mathfrak{t} = \frac{V}{\omega}$$

gesetzt ist. Nach (18) kann man (38) auch schreiben

(39) $$\frac{1}{\mathfrak{t}} = \frac{d \ln V}{d\varepsilon^*}.$$

4. *Über die mechanischen Grundlagen der Thermodynamik;*
von Paul Hertz.

(Fortsetzung von p. 225.)

„ein eindimensionales Gas“ (Fig. 4a)

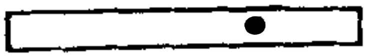


Fig. 4a.

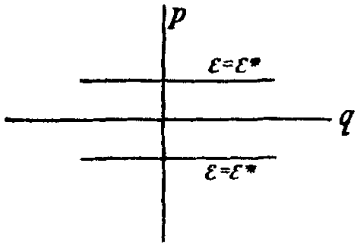


Fig. 4b.

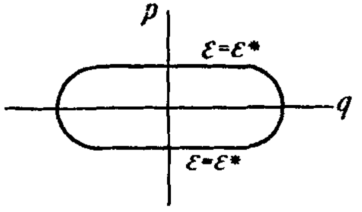


Fig. 4c.

P Hertz, Ann d Phys 33: 225 (1910)
P Hertz, Ann d Phys 33: 537 (1910)

Ann. Phys. (Berlin) **17**, No. 5, 273 – 301 (2008) / **DOI** 10.1002/andp.200810294

Historical Review

"… you can't say to anyone to their face: your paper is rubbish."

Max Planck as Editor of the *Annalen der Physik*

Dieter Hoffmann*

Max Planck Institute for the History of Science, Boltzmannstr. 22, 14195 Berlin, Germany

he was concerned to define an editorial policy that would exclude all too mathematical papers. However he was willing to make exceptions, for instance regarding a very mathematical paper on the mechanical foundations of thermodynamics by the Heidelberg physicist (and also later philosopher) Paul Hertz. But this investigation was dealing with such an important and difficult aspect for understanding statistical mechanics, that in this case "the comprehensiveness is a necessity for clarity" [119] and the author was even allowed to publish his work in two parts [120]; of course the problem discussed was also very close to Planck's own thermodynamical work.

10. *Bemerkungen*
zu den P. Hertzschen Arbeiten:
„Über die mechanischen Grundlagen der Thermodynamik“[1]*;*
von A. Einstein.

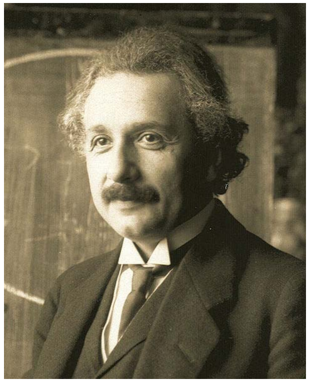
Hr. P. Hertz hat in seinen soeben genannten vortrefflichen Arbeiten zwei Stellen, die sich in Arbeiten von mir über den gleichen Gegenstand vorfinden, angegriffen. Zu

…

ist. Wenn mir das Gibbssche Buch damals bekannt gewesen wäre, hätte ich jene Arbeiten überhaupt nicht publiziert, sondern mich auf die Behandlung einiger weniger Punkte beschränkt.

Zürich, Oktober 1910.

(Eingegangen 30. November 1910.)



Hertz (volume) entropy *vs* surface entropy

$f_M(z) = \frac{\delta[E - H(z)]}{Z_M}$	$S = \ln \Omega$	$S = \ln Z_M$
equipartition	✔	x
$T > 0$	✔	x
$N \to \infty$	✔	✔ (?)

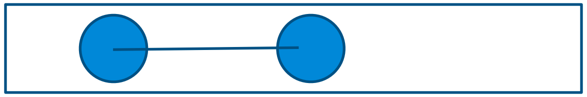
Microscopic singularities & temperature oscillations

in the MCE

... using Hertz (volume) entropy

$$S = k_B \ln \Omega$$

1D classical diatomic L-J molecule ("dissociation")



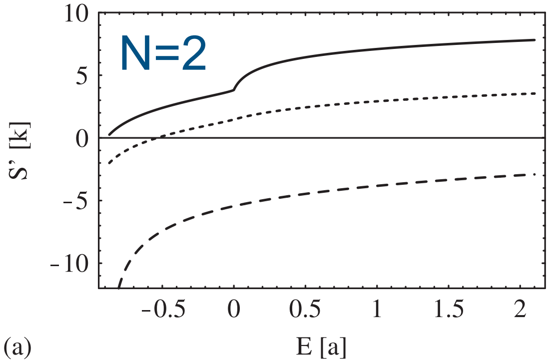
$$U_{\mathrm{LJ}}(r) = \frac{1}{r^{12}} - \frac{2}{r^6}\,.$$

$$\Omega = \frac{2\pi m}{h^2}\left(\frac{L}{11r^{11}} - \frac{1}{10r^{10}} - \frac{2L}{5r^5} + \frac{1}{2r^4} + LrE - \frac{r^2E}{2}\right)\Bigg|_{r_{\min}}^{r_{\max}},$$

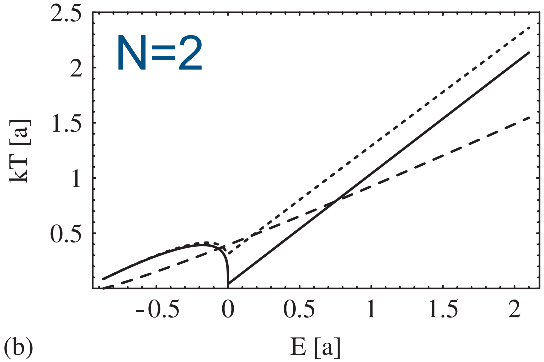
where the boundary values are given by

$$r_{\min} = X^{-1/6}, \quad r_{\max} = \begin{cases} L, & E \geqslant E_c(L) \equiv U_{\mathrm{LJ}}(L), \\ Y^{-1/6}, & E < E_c(L), \end{cases}$$

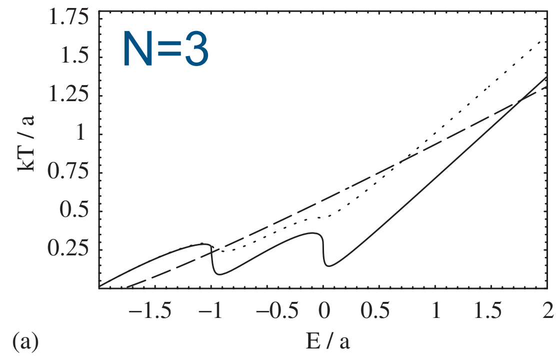
using the convenient abbreviations $X \equiv 1 + \sqrt{1+E}$ and $Y \equiv 1 - \sqrt{1+E}$.



(a)



(b)



(a)

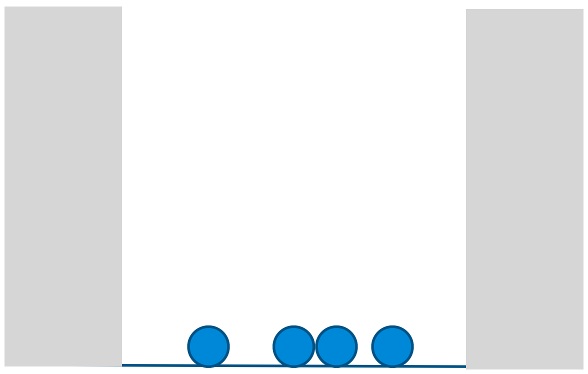
origin of singularity: change in "dimensionality" of phase (configuration space)

Dunkel & Hilbert, Physica A 370: 390-406 (2006)

Exactly solvable model: 1D Takahashi gas

$$H(\mathbf{p},\mathbf{q};L,N)=\frac{\mathbf{p}^2}{2m}+U(\mathbf{q};L,N)=E$$

$$U=U_{\mathrm{int}}+U_{\mathrm{box}}$$



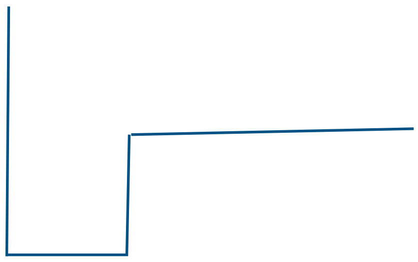
Container

$$U_{\mathrm{box}}(\mathbf{q};L,N)=\begin{cases}0, & \mathbf{q}\in[0,L]^N,\\ +\infty, & \text{otherwise}.\end{cases}$$

NN-interactions

$$U_{\mathrm{int}}(\mathbf{q};N)=\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}U_{\mathrm{pair}}(|q_i-q_j|)$$

$$U_{\mathrm{pair}}(r)=\begin{cases}\infty, & r\leq d_{\mathrm{hc}},\\ -U_0, & d_{\mathrm{hc}}<r<d_{\mathrm{hc}}+r_0,\\ 0, & r\geq d_{\mathrm{hc}}+r_0,\end{cases}$$



$$0<r_0\leq d_{\mathrm{hc}} \qquad L>(N-1)(r_0+d_{\mathrm{hc}}),$$

Hilbert & Dunkel, PRE 74: 011120 (2006)

Exactly solvable model: 1D Takahashi gas

MC phase volume

for $L > (N-1)(r_0 + d_{\mathrm{hc}})$

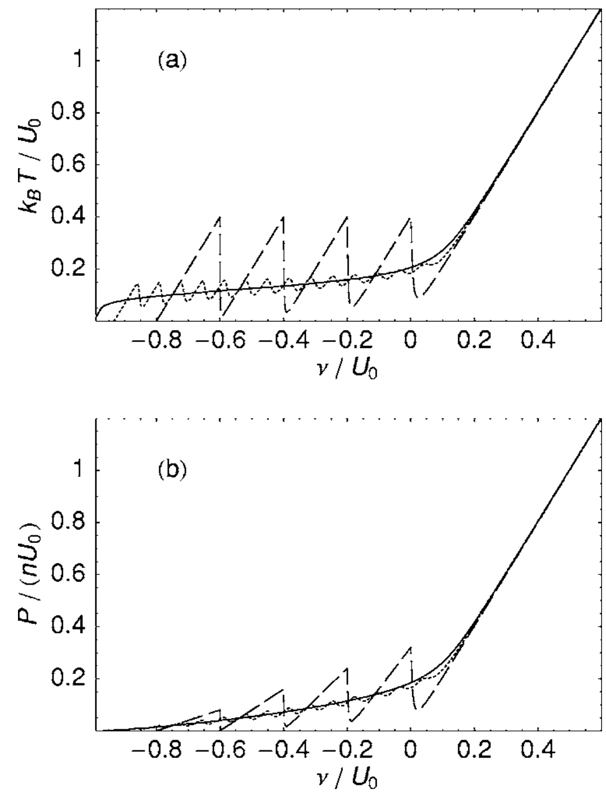
$$\Omega = C \sum_{k=0}^{N-1} \omega_k (E + kU_0)^{N/2} \Theta(E + kU_0),$$

$$C(N) \equiv \frac{2(2\pi m)^{N/2}}{\Gamma(N/2) N! \, N h^N}$$

$$\omega_k(N,L) = \binom{N-1}{k} \sum_{i=0}^{k} \binom{k}{i} (-1)^i \times [L - (N-1)d_{\mathrm{hc}} - r_0(N-1-k+i)]^N$$

MC caloric curve

$$k_B T = \frac{2}{N} \frac{\sum_{k=0}^{N-1} \omega_k (E + kU_0)^{N/2} \Theta(E + kU_0)}{\sum_{k=0}^{N-1} \omega_k (E + kU_0)^{N/2-1} \Theta(E + kU_0)}$$



$\nu := E/N$

Temperature oscillations!

Hilbert & Dunkel, PRE 74: 011120 (2006)

Exactly solvable model: 1D Takahashi gas

Canonical ensemble

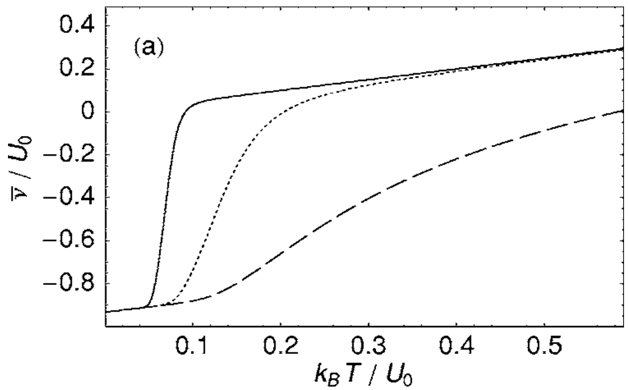
for $L > (N-1)(r_0 + d_{\rm hc})$

$$\mathcal{Z}_{\rm C} = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{N/2} \sum_{k=0}^{N-1} \omega_k e^{\beta k U_0}$$

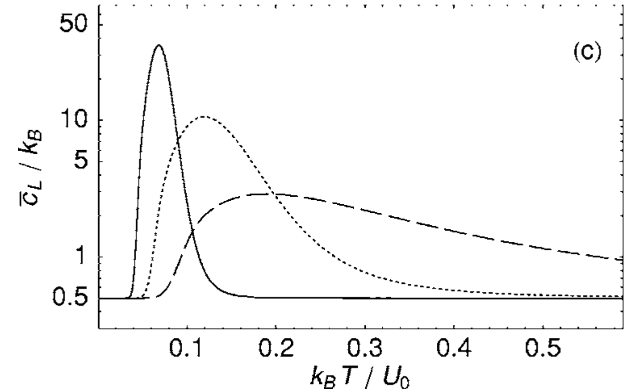
$$\omega_k(N,L) = \binom{N-1}{k} \sum_{i=0}^{k} \binom{k}{i} (-1)^i \times [L-(N-1)d_{\rm hc} - r_0(N-1-k+i)]^N$$

Canonical caloric curve

$$\bar{E} = \frac{N}{2\beta} - \frac{\sum_{k=0}^{N-1} \omega_k e^{\beta k U_0} k U_0}{\sum_{k=0}^{N-1} \omega_k e^{\beta k U_0}}$$



$\overline{\nu} := \overline{E}/N$



non-singular 1D "PT"

Hilbert & Dunkel, PRE 74: 011120 (2006)

"Conjecture"

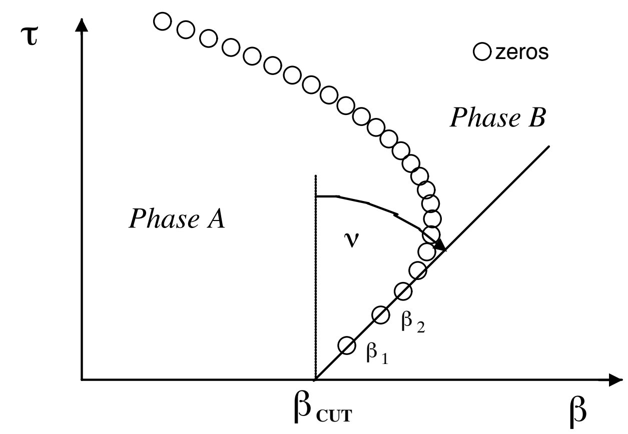
- Relation between micro-canonical temperature oscillations and macroscopic canonical PTs ?

Fisher zeros of $Z_C(\beta + i\tau)$

$$Z_C(\beta) = \beta\mathcal{L}[\Omega(E)]$$

$$\mathcal{L}[\Omega(E)] := \int_0^\infty dE\, e^{-\beta E}\Omega(E)$$

$$\min_z H(z) = 0$$



Yang & Lee, Phys Rev 87: 404/410 (1952)
Grossmann & Rosenhauer, Z Physik 218: 437 (1967)
Janke & Kenna, J Stat Phys 102: 1211 (2001)
Borrmann et al, PRL 84: 3511 (2000)
Muehlken et al, PRE 64: 047105 (2001)

Summary

- Hertz (volume) entropy = micro-canonical thermodynamic entropy
- microscopic dissociation transitions indicated by temperature oscillations in the MCE
- "conjecture":
  - *Fisher zeros* of canonical distribution function reflect/arise from oscillations in the corresponding micro-canonical caloric curve (via Laplace transformation)
  - (order of the) macroscopic PT encoded in the micro-canonical temperature oscillations

Hilbert & Dunkel, PRE 74: 011120 (2006)
Dunkel & Hilbert, Physica A 370: 390-406 (2006)