UNIVERSITY OF GOTHENBURG

Thermodynamics of finite quantum systems

Shell structure in finite quantum systems
Erice summer school, July 25-30, 2010

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Faculty of Science

Topics

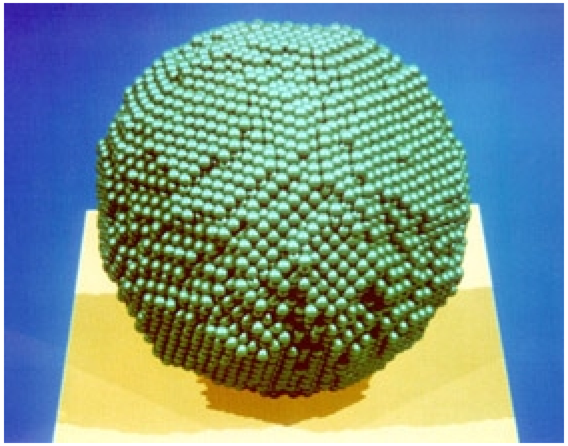
Metal clusters

valence electrons, quantum order, fermion systems

Rare gas clusters

classical equations of motion

What is a metal cluster : M_N, N countable



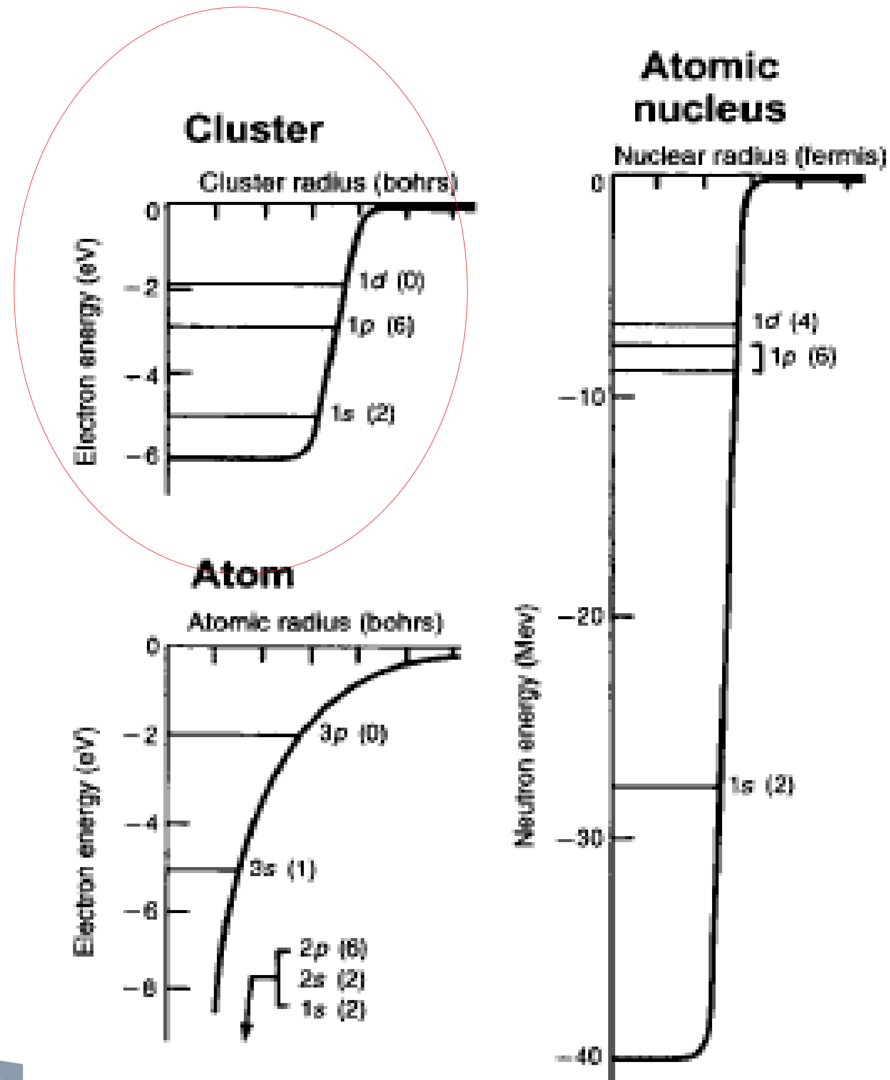
17000 copper atoms
Source: DESY

Spherical, good conductor

=

free electrons in spherical mean field potential

Mean field spherical potential



Clusters have

1) Nuclear degrees of freedom (vibrations, phonons)
2) Electronic degrees of freedom

Vibrations:

N atoms, 3N-6 vibrational degrees of freedom,

Quantum energies:

He droplets	**0.0001 eV**
Na	**0.01 eV**
C	**0.1 eV**

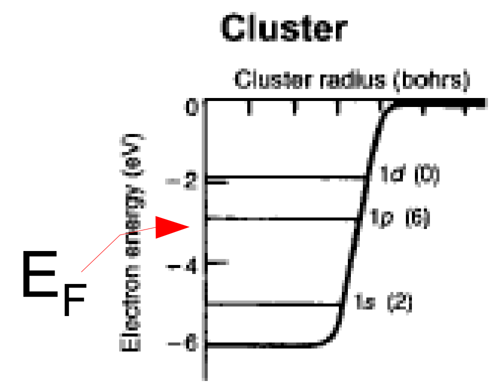
Several vibrational quanta in each mode,
$E \approx (3N-6)\ k_BT$, heat capacities $C \approx (3N-6)k_B$

Electrons:

N atoms, zN valence electrons (z small integer)

Fermions, only top $k_B T$ energy layer thermally excited

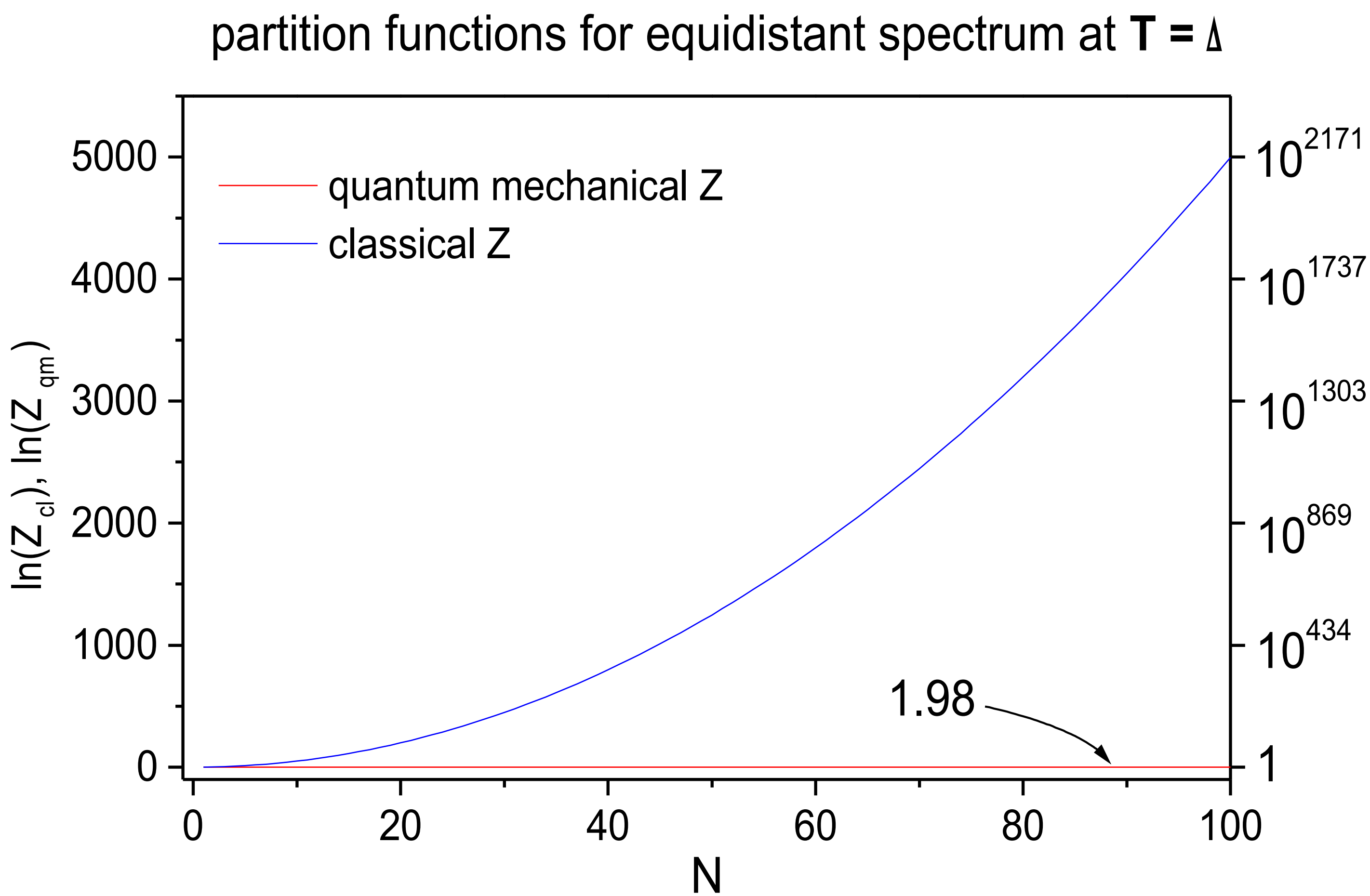
	E_F	T_F
Li	4.7 eV	55 000 K
Na	3.2 eV	38 000 K
K	2.1 eV	25 000 K



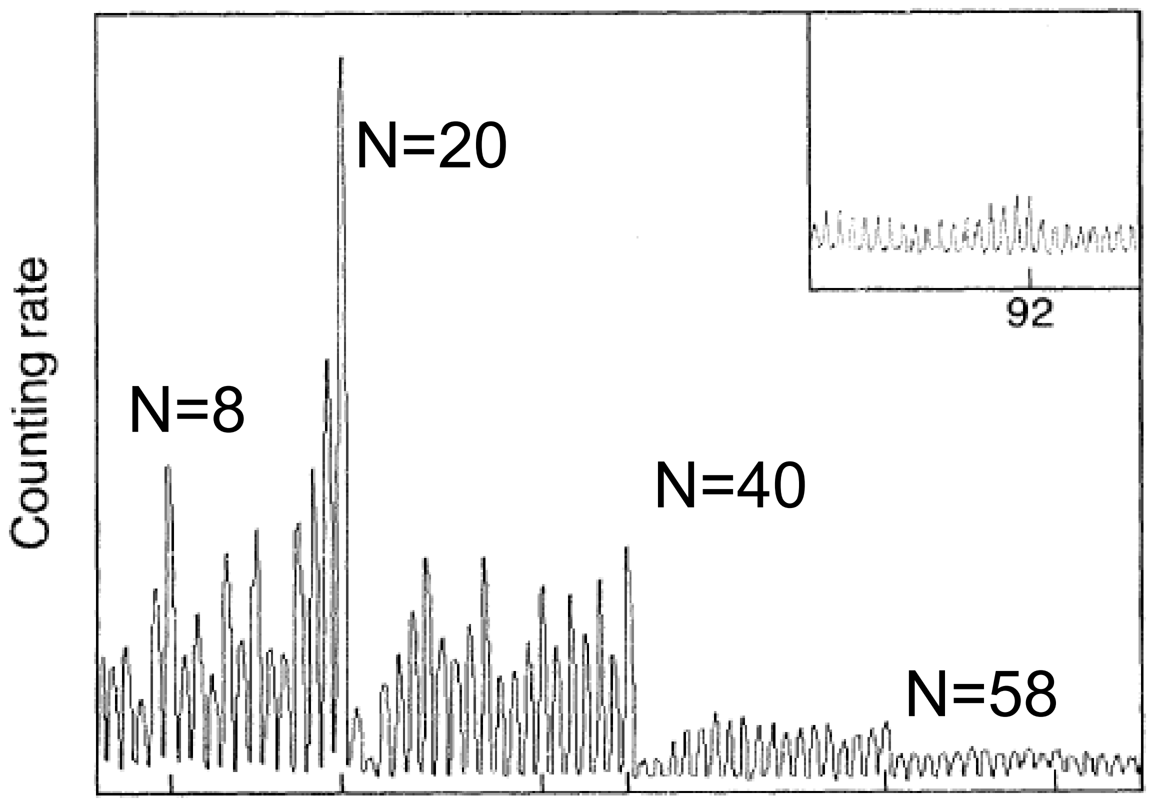
Thermal excitation energy $zN\,(k_B T)^2/E_F$

Heat capacity $zNk_B\,(k_B T)/E_F$

Classical vs. quantum statistics of N electrons

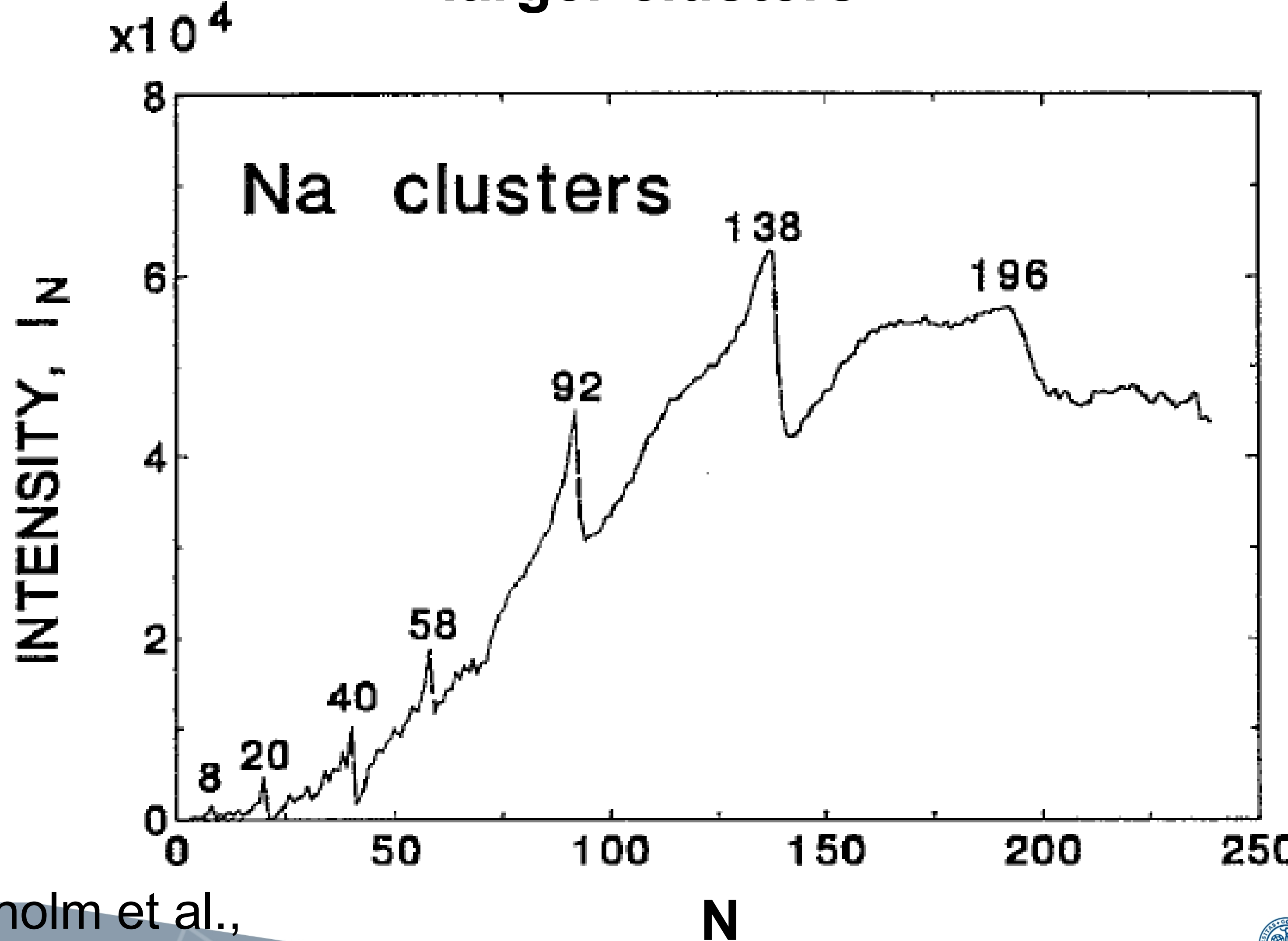


Sodium clusters, abundance spectrum



W.D.Knight et al., Phys. Rev. Lett. **52** (1984) 2141

Sodium clusters, abundance spectrum, larger clusters



S.Bjørnholm et al., Phys.Rev.Lett. **65** (1990) 1627

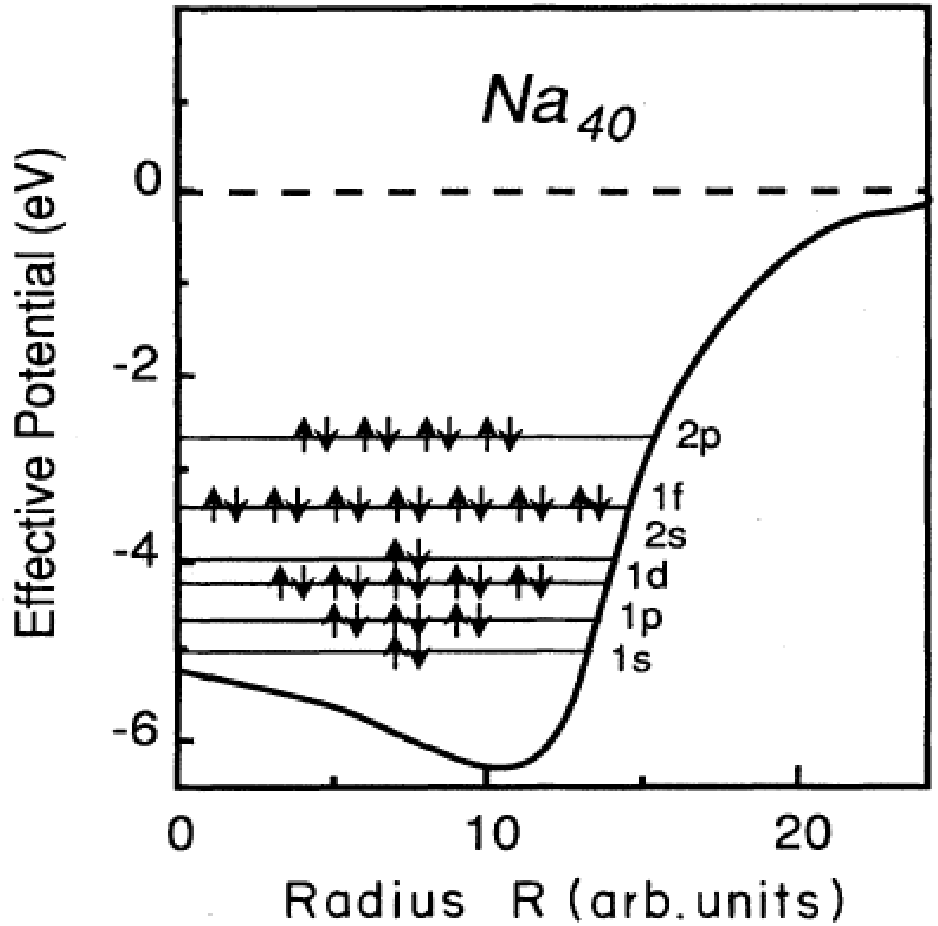


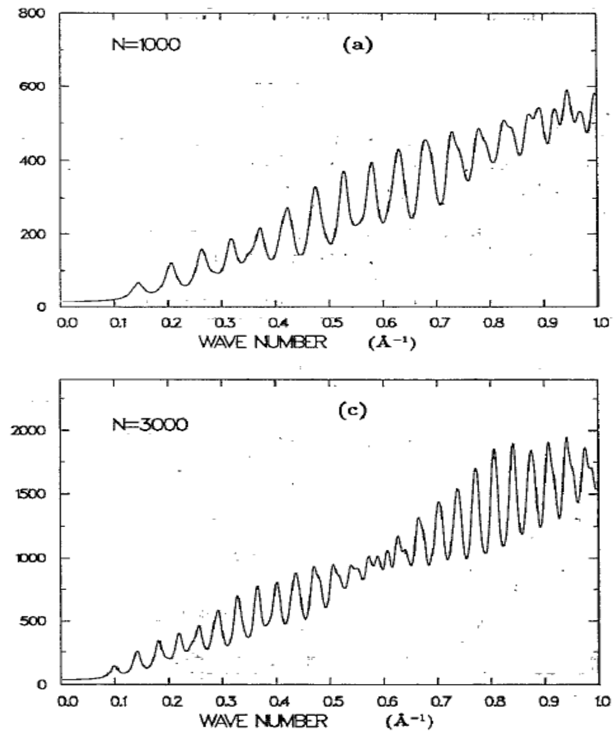
FIG. 3. Self-consistent effective potential of jellium sphere corresponding to Na_{40} with the electron occupation of the energy levels.

M.Y.Chou et al.,
Solid state Comm. **52** (1984) 645

Level diagram for Saxon-Woods potential:

Single particle density of states

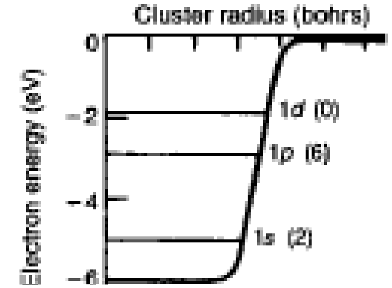
Nishioka et al.
PRB **42**, 9377
(1990)



N=1000

N=3000

Cluster



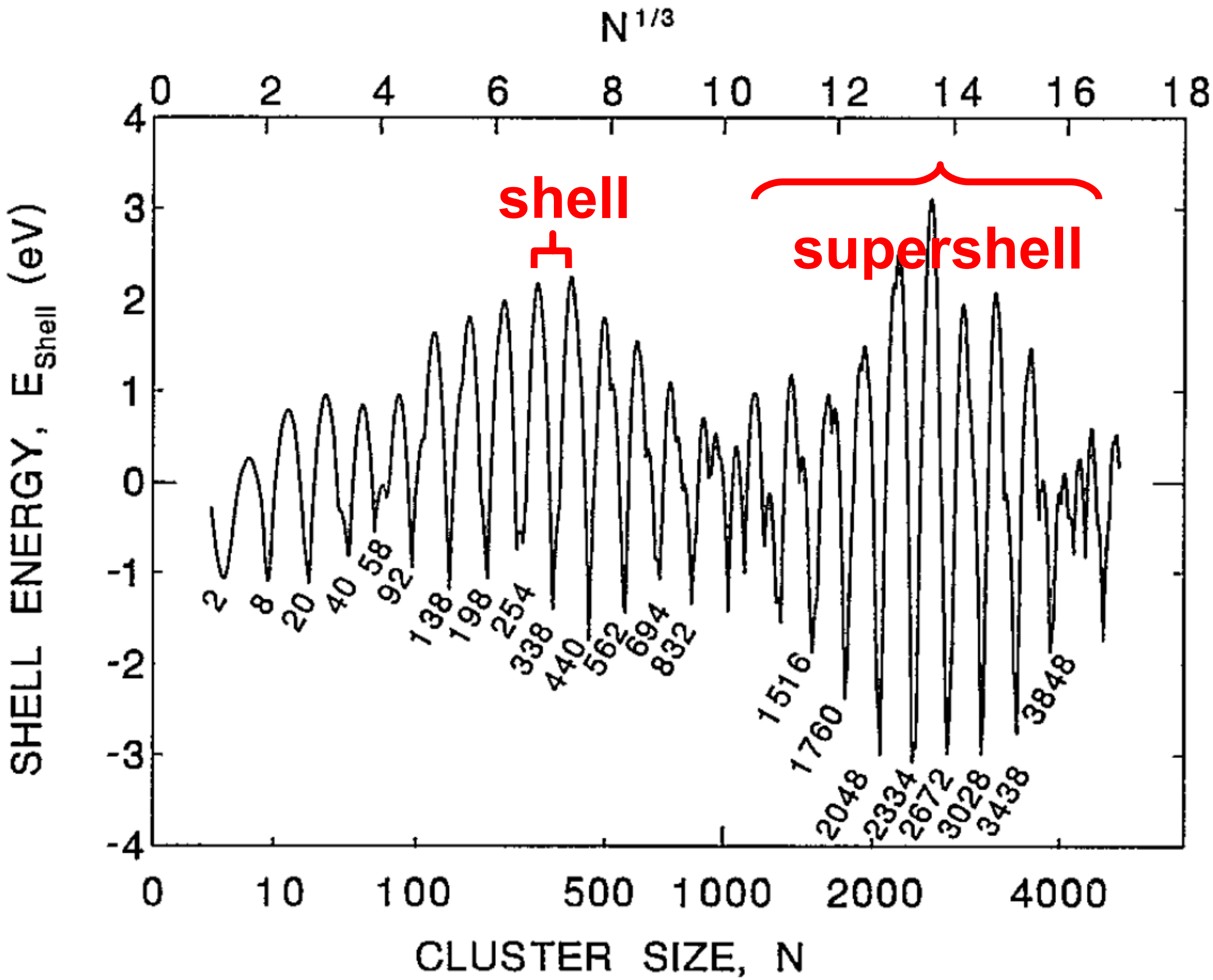
$$U(R) = \frac{V_0}{1+\exp[(R-R_0)/a_0]}$$

Lesson

For large enough N, level spacing < k_BT, thermal excitations of electrons unavoidable!

Shell energy of sodium clusters

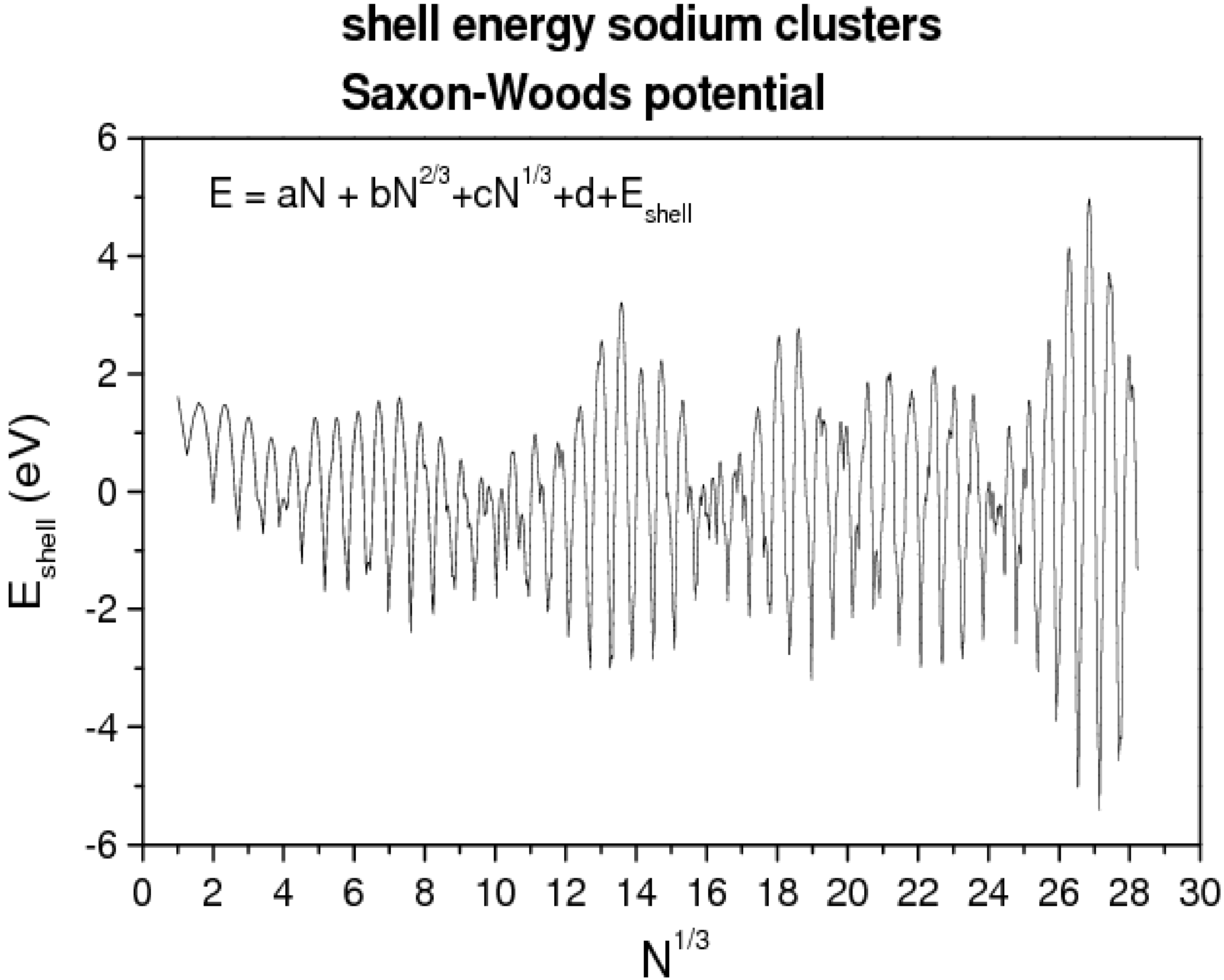
Calculated in mean-field single particle potential



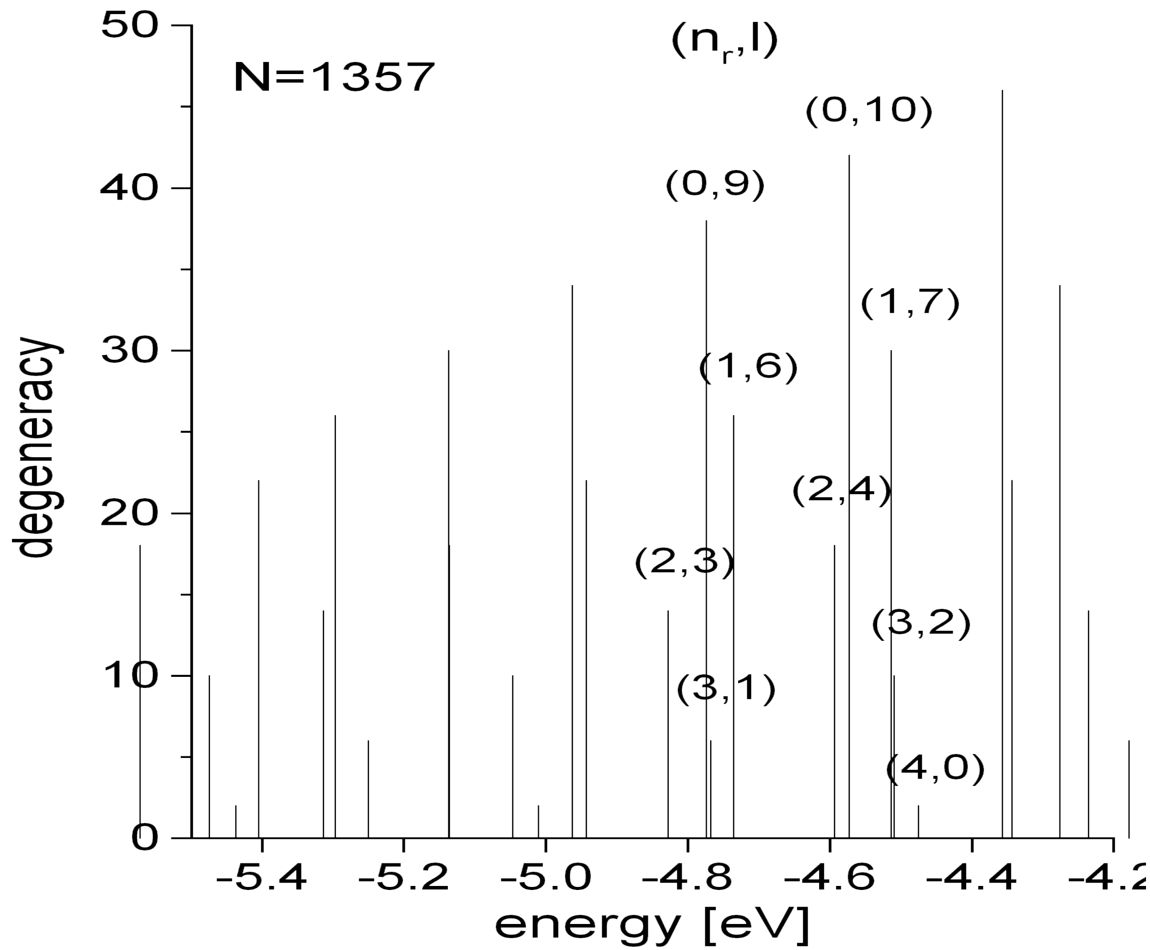
$$E(N) = E_{av}(N) + E_{shell}(N)$$

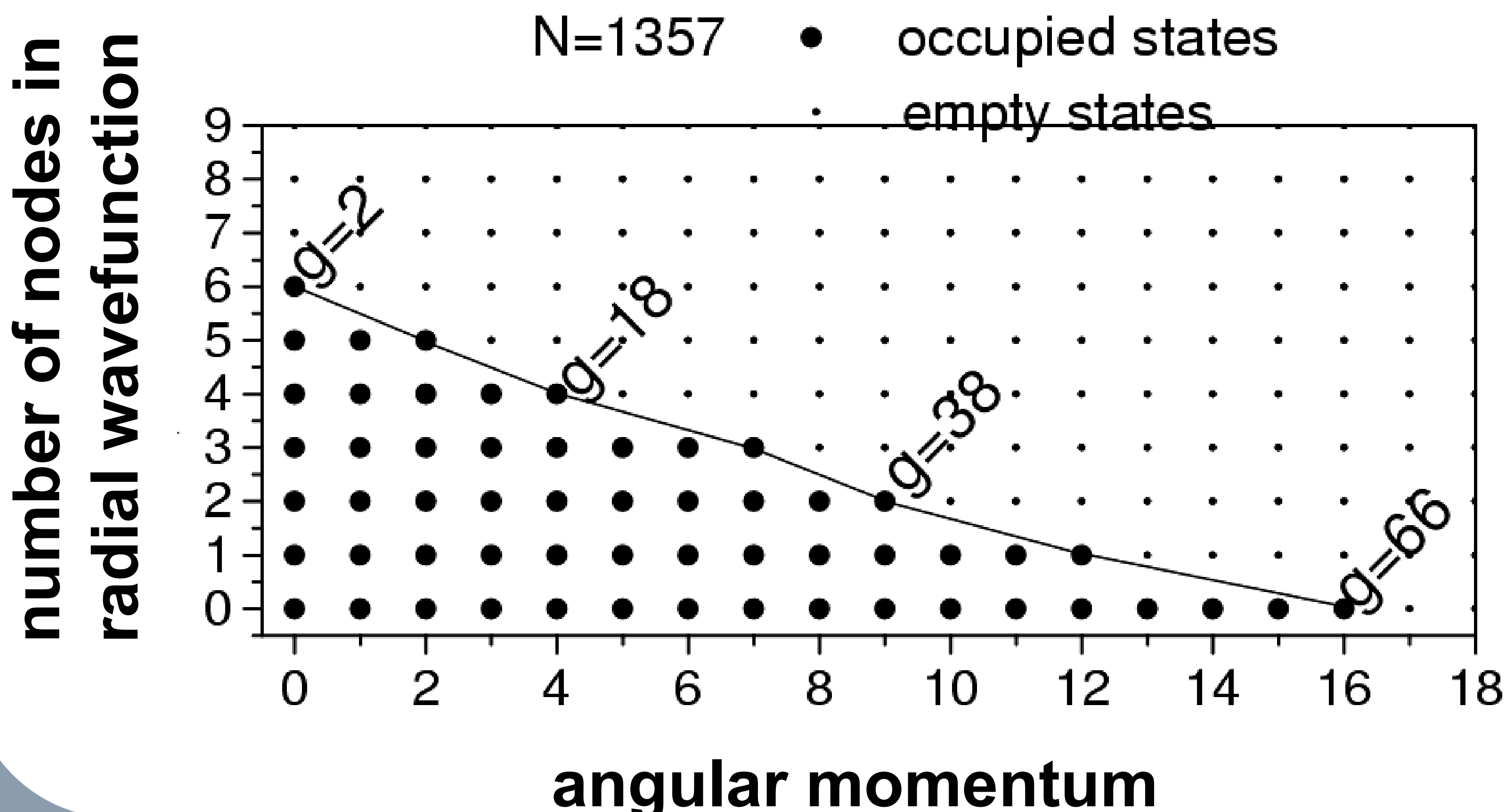
Nishioka et al., PRB **42** (1990) 9377

This is what we were after @ finite T



Single particle states in the Woods-Saxon potential




N=1357
occupied states
empty states
number of nodes in radial wavefunction
angular momentum
g=2
g=18
g=38
g=66
0
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
16
18

Condition for degeneracy (shell structure)

$$\frac{\partial E}{\partial n_r}\Delta n_r + \frac{\partial E}{\partial l}\Delta l = 0$$

n_r and l quantum numbers, i.e. integers.

If

$$\frac{\partial E}{\partial n_r} : \frac{\partial E}{\partial l}$$ = ratio of small integers

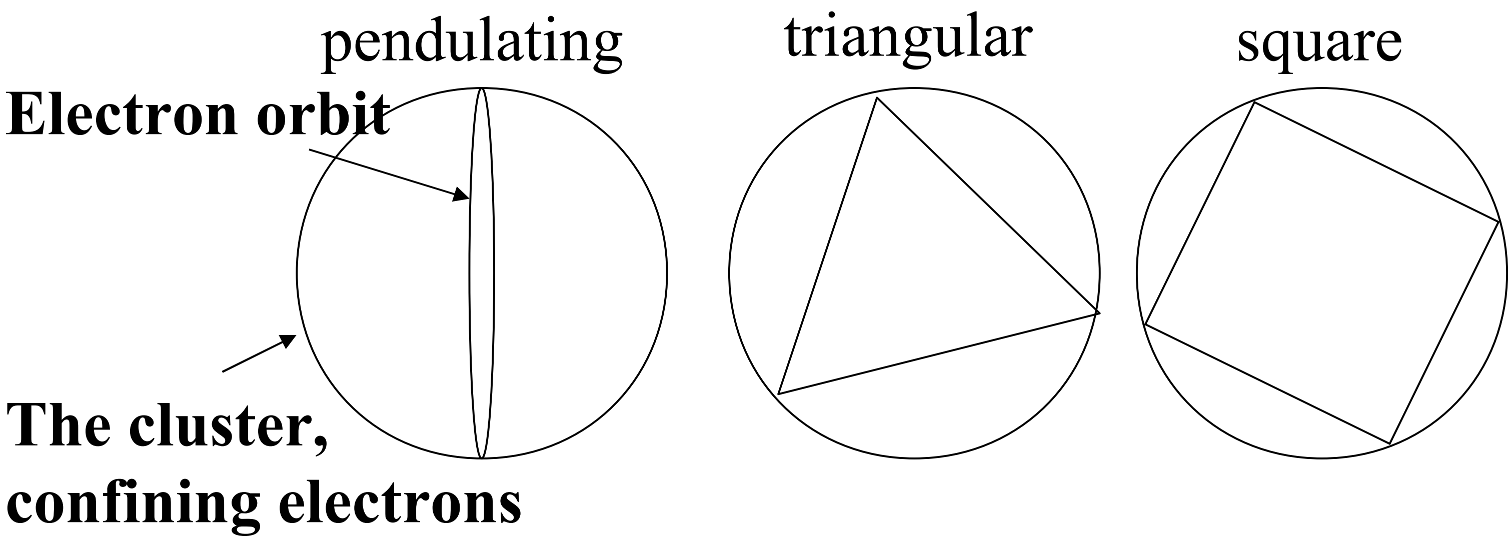
then

bunching of levels,
shell structure

Interpretation of degeneracy/shell structure

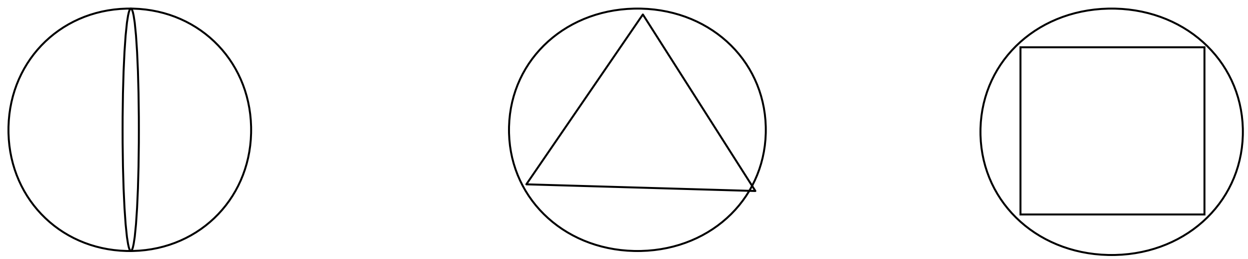
Semiclassically: $\frac{\partial E}{\partial n_r} = \hbar \omega_r$ $\frac{\partial E}{\partial l} = \hbar \omega_l$

$\omega_r/\omega_a =$ 2/1 3/1 4/1



Lengths of orbits

pendulating triangular square



$L_{0} = 4\, r_N$

$L_{\triangle} = 3 \cdot 3^{1/2}\, r_N = 5.196\, r_N$

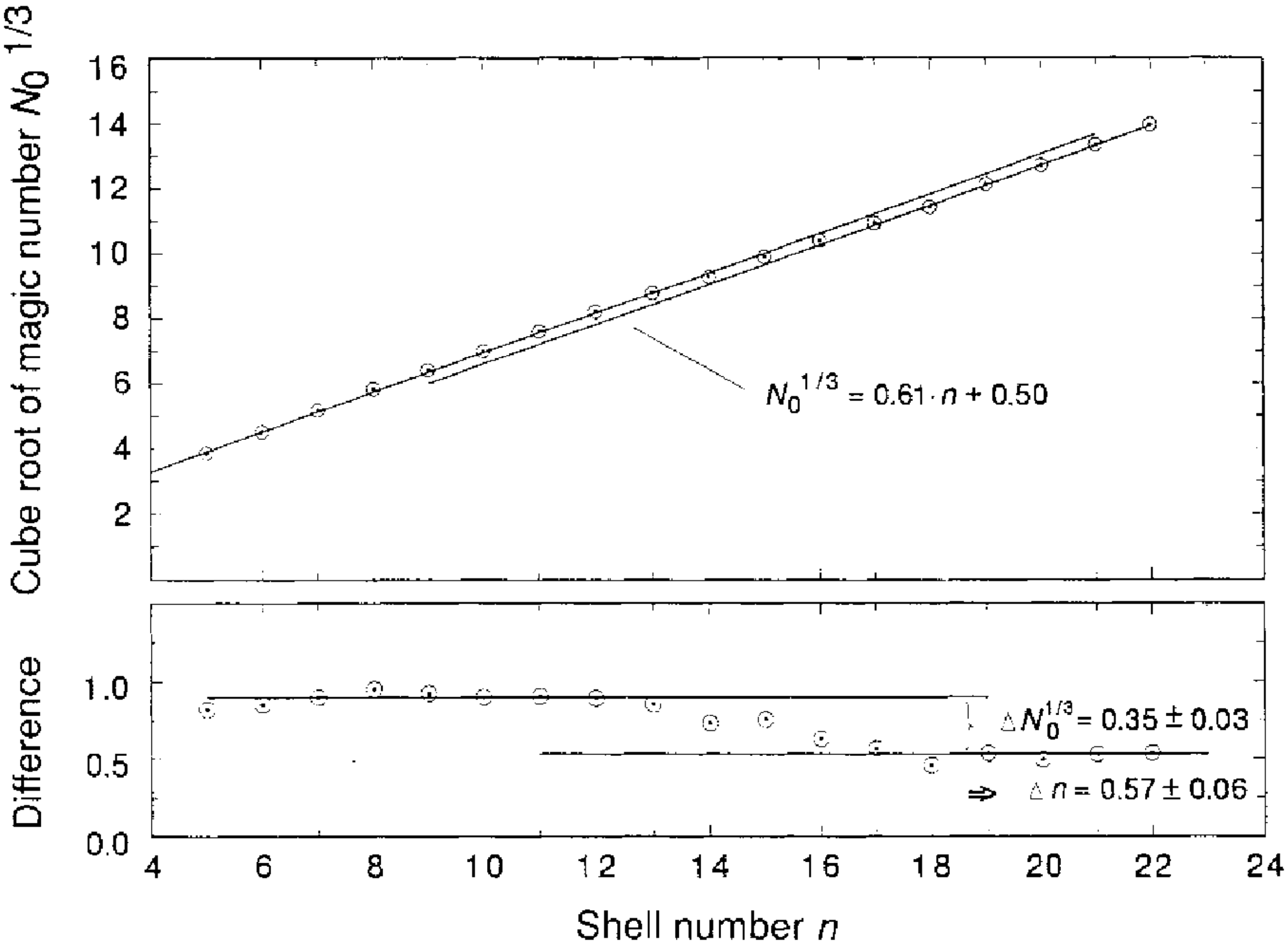
$L_{\square} = 4 \cdot 2^{1/2}\, r_N = 5.657\, r_N$

$$(L_{\triangle} + L_{\square})/2 \cdot \lambda_F^{-1} = 5.427\, r_1\, N^{1/3} / 3.274\, r_1$$

$$= 1.657\, N^{1/3} = N^{1/3} / 0.603$$

Every time $N^{1/3}$ is increased by 0.603 a new shell appears

Experimental result



How do we do thermodynamics with these systems?

Fermi-Dirac distributions (grand canonical ensemble)
(independent particles, standard treatment)

sounds promising

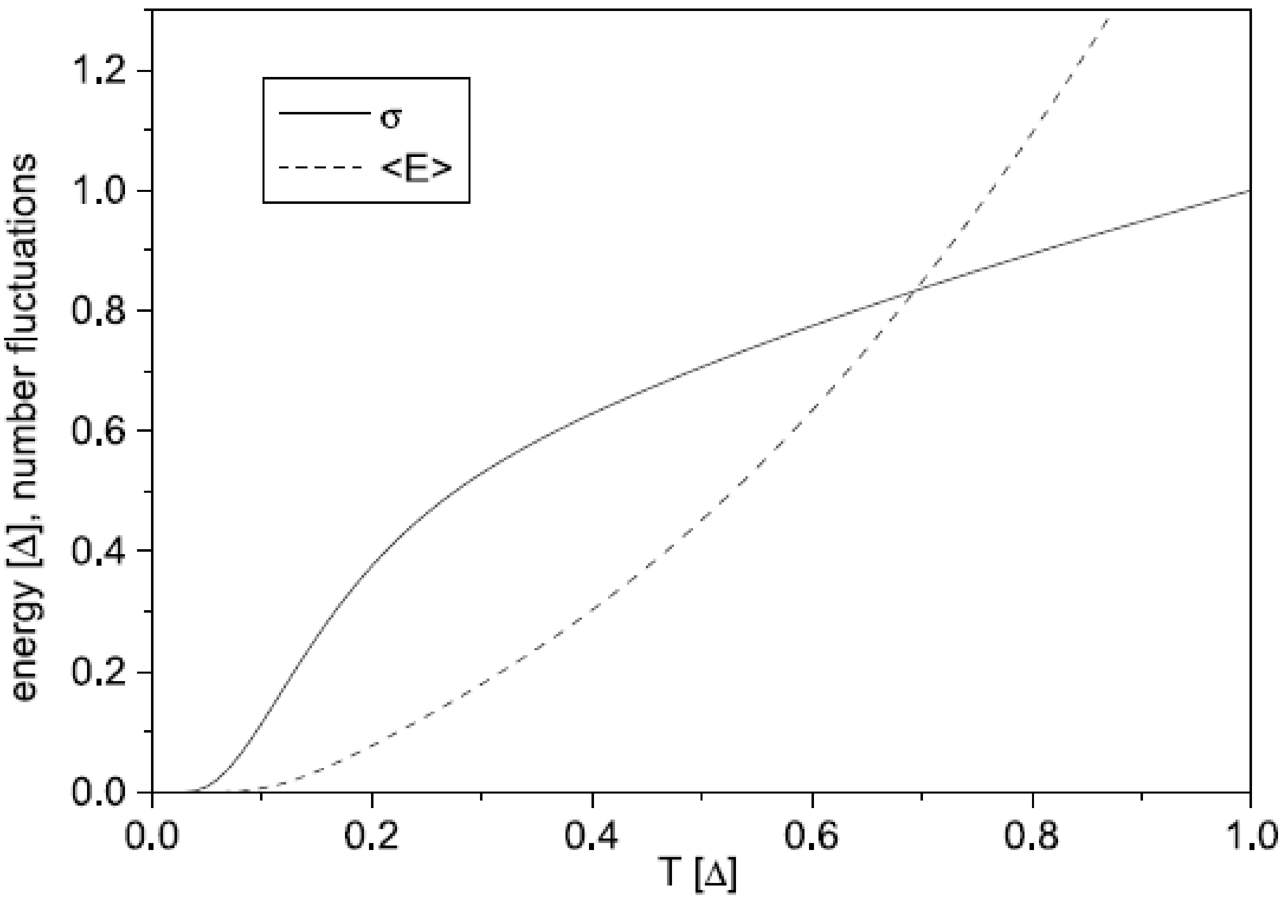
But: **particles not conserved,**

(even for free clusters)

$$n_i = \frac{e^{-\beta(E_i-\mu)}}{1+e^{-\beta(E_i-\mu)}} = \frac{1}{1+e^{\beta(E_i-\mu)}} \qquad (\beta \equiv (k_B T)^{-1})$$

$$\sigma_i^2 = 0 \times (1-n_i) + 1 \times n_i - n_i^2 = n_i(1-n_i)$$

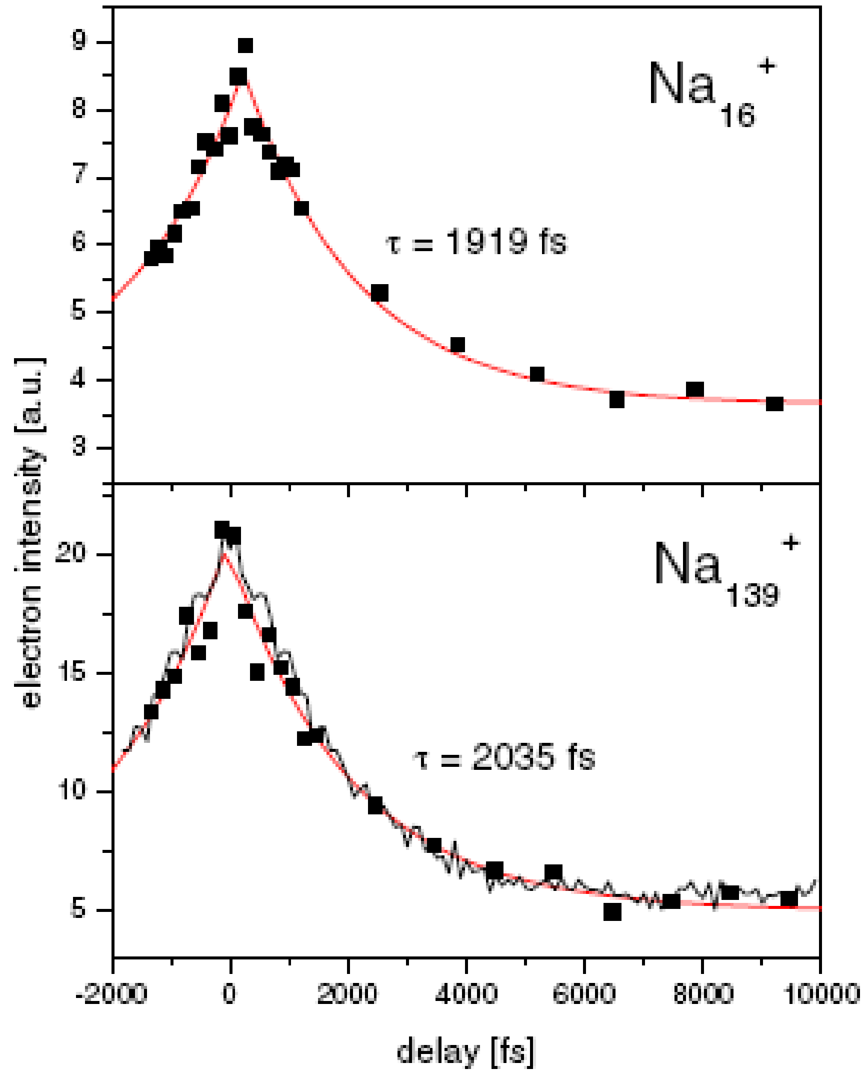
Calculation for equidistant spectrum w. spacing Δ



The microcanonical ensemble then?
(free, isolated particles, sounds promising)

But:
Electrons equilibrate with the vibrations which have a much higher heat capacity.
Electrons in metals are NOT isolated systems
(for very long)

Electron-vibration coupling time
by femtosecond pump-probe experiments



M.Maier et al.
PRL **96** 117405 (2006)

Canonical, then?

The level density, $\rho\left(E\right)$

= derivative wrt. energy of the total number of quantum states below E for the system

= the 'number of states' at energy E

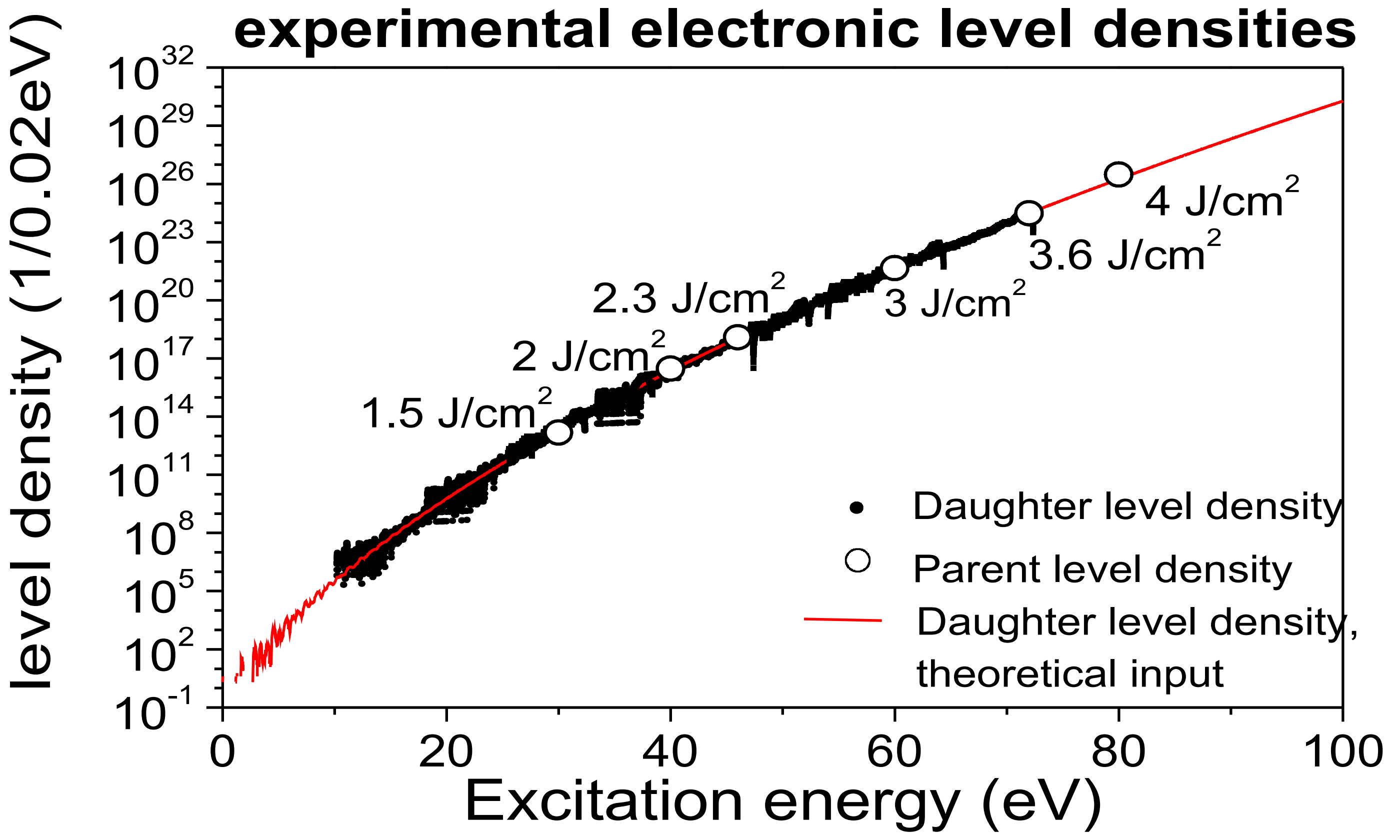
= the microcanonical partition function

= the exponential of the entropy

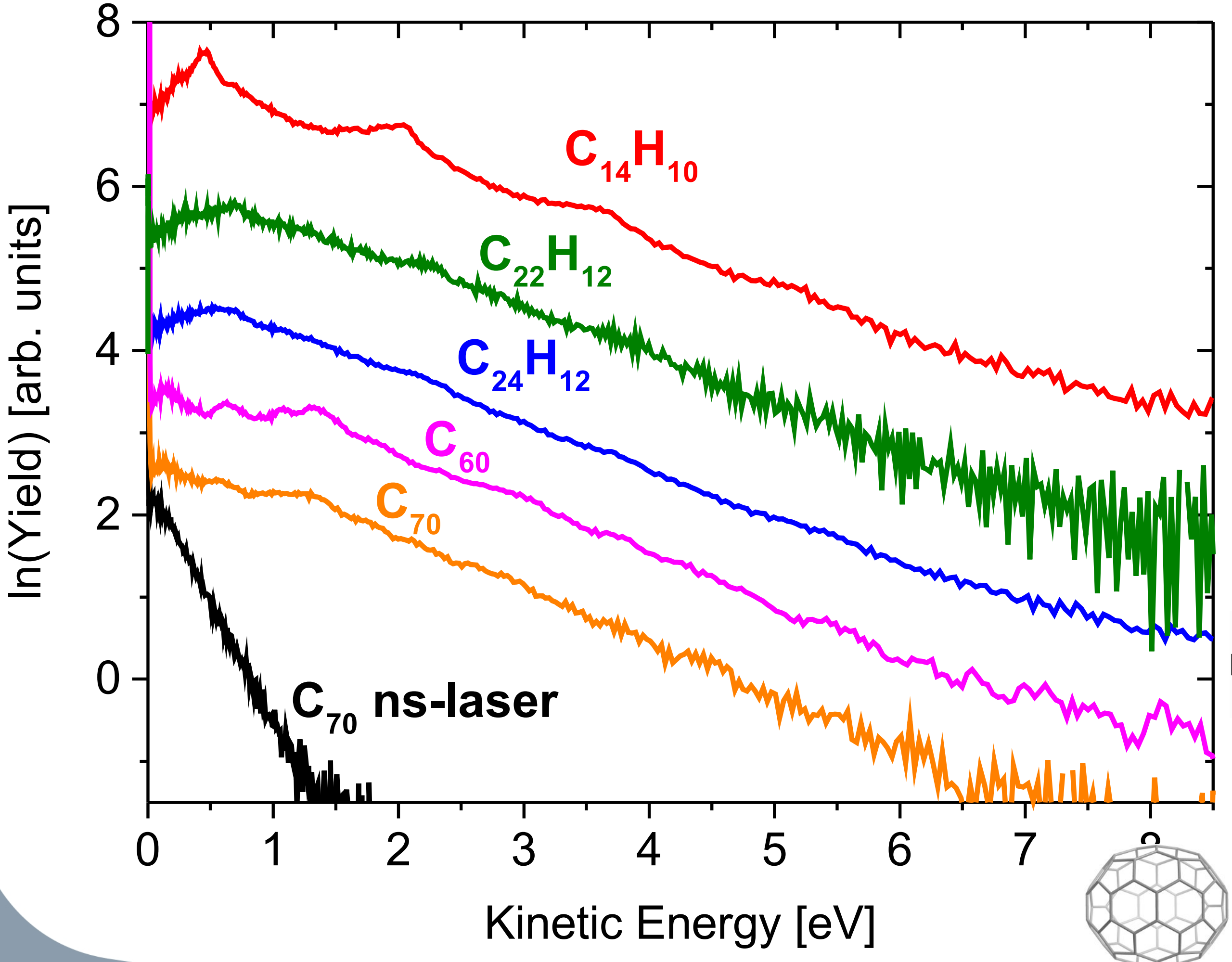
Level density of valence electrons of C_{60}

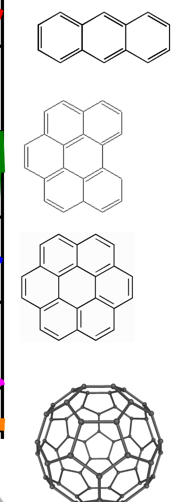
NB: femtosecond experiments

$$k_e(E,\varepsilon)\,d\varepsilon = \frac{2m_e\sigma(\varepsilon)}{\pi^2\hbar^3}\varepsilon\,\frac{\rho_d(E-\Phi-\varepsilon)}{\rho_p(E)}\,d\varepsilon$$



Electron emission from hot molecules





$Y \propto \exp(-\varepsilon/k_B T)$.

T (Electron temperatures) up to 20 000 K.

Laser parameters:
λ=780 nm, τ=150 fs,
I=1.2×10^{13} W/cm^2.

Partitioning of energy between the vibrations and the electrons

$$\rho(E)=\int \rho_{vib}(E-E_{el})\,\rho_{el}(E_{el})\,dE_{el}$$

Motion on a Born-Oppenheimer surface

Excitation onto a Born-Oppenheimer surface

Energy partitioning, continued

1) The energy stored in the vibrations is much bigger than that stored in the electronic excitations

$\Rightarrow$ **expand in E_{el}**

2) The level density is a rapidly growing function of energy

$\Rightarrow$ **expand ln($\rho(E)$)**

$$\ln\left(\rho_{vib}(E-E_{el})\right)\approx\ln\left(\rho_{vib}(E)\right)-E_{el}\frac{d\ln\rho_{vib}(E)}{dE}$$

$$\boxed{\rho_{vib}(E-E_{el})\approx\rho_{vib}(E)e^{-\beta E_{el}}}$$

Finally

$$\rho(E) \approx \rho_{vib}(E) \int \rho_{el}(E_{el}) e^{-\beta E_{el}} dE_{el}$$

$$= \rho_{vib}(E) Z_{el}(\beta)$$

Z_{el} is the canonical partition function of the electron system

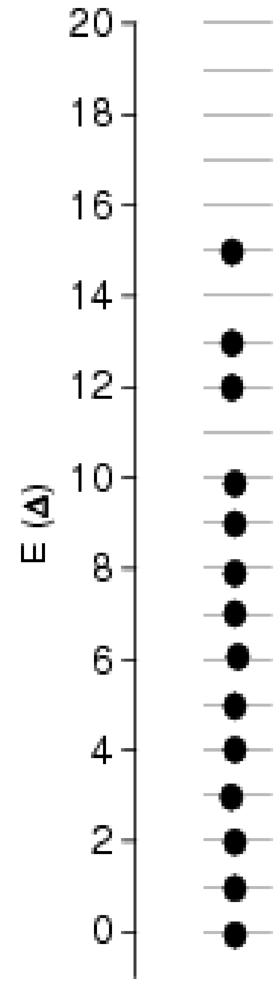
An excursion into the zoo of computational methods and results

Start with the simplest model
(ladder levels, harmonic oscillator)

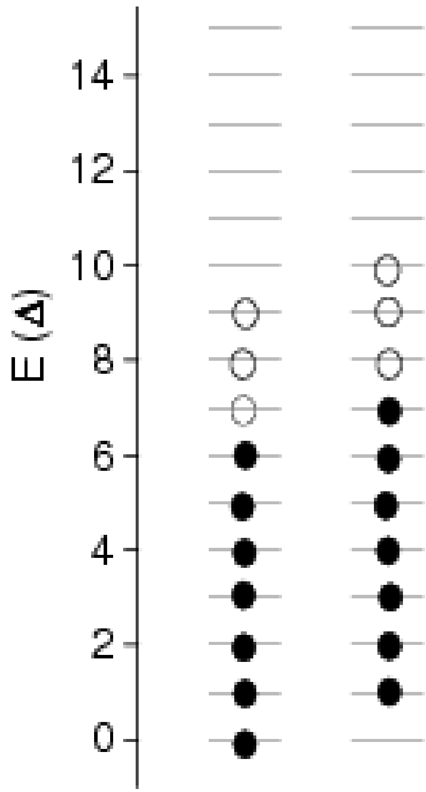
$$E_n = n\Delta \, ; n = 0, \ldots, \infty ; \quad g_n = 1$$

$$\Delta \sim \frac{E_F}{N}$$

Simplest model of Fermi gas



Calculation of the canonical partition function



$$Z(\beta, N) = Z(\beta, N-1)e^{-\beta(N-1)\Delta} + Z(\beta, N)e^{-\beta N \Delta}$$

Solution to recurrence relation:

$$Z(\beta, N) = \prod_{j=1}^{N} \frac{1}{1-e^{-j\beta\Delta}}$$

Curious facts:

i) partition function of ***N*** harmonic oscillators with spectrum $\hbar\omega_j = j\,\Delta$

ii) partition function of bosonic system with same spectrum

Thermal energy of the equidistant spectrum

$$\bar{E} = \frac{\int E\,\rho(E)\,e^{-\beta E}\,dE}{\int \rho(E)\,e^{-\beta E}\,dE} = -\frac{\partial \ln(Z)}{\partial \beta}$$

$$= \sum_{j=1}^{\infty} \frac{j\Delta}{e^{j\beta\Delta}-1} \approx \sum_{n=1}^{\infty} \frac{1}{n^2}\frac{T^2}{\Delta} = \frac{\pi^2}{6}\frac{T^2}{\Delta}$$

Technical note:

$\sum \to \int$ first term in Euler-Maclaurin series

Calculation of level densities

(Reminder: $\rho \sim e^{S}$)

$$Z = \int \rho(E) e^{-\beta E} dE$$

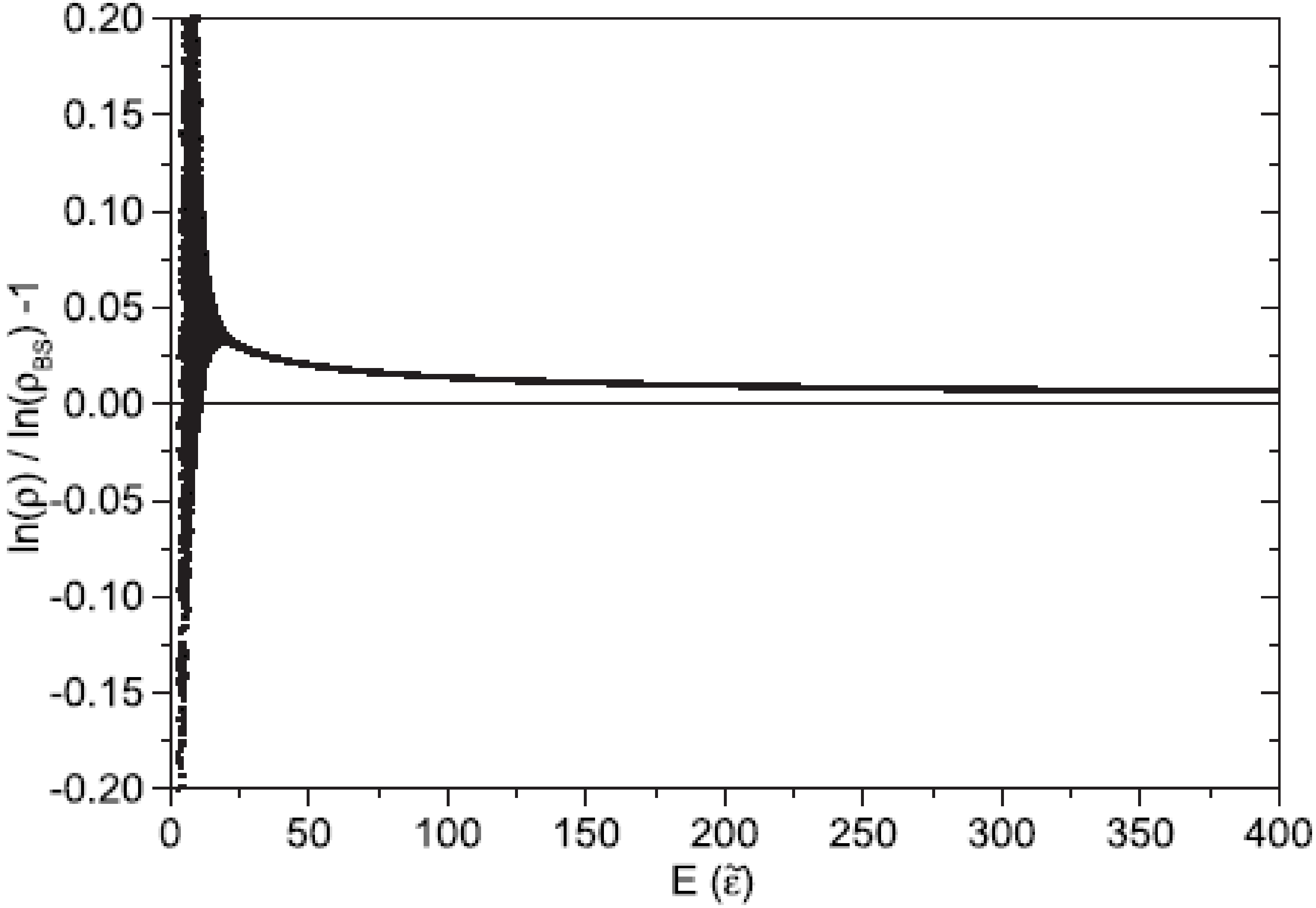
$$\approx [incoherent \quad mumbling]$$

$$= \rho(E_0) \sqrt{2\pi C T^2} e^{-\beta E_0}$$

$$\rho(E_0) \approx Z(T) e^{\beta E_0} \frac{1}{\sqrt{2\pi C T^2}}$$

Find T as solution to $\overline{E}(T) = E_0 + k_B T$

Quality control:
Helium droplets (ripplon) level density, comparison with exact count



Phys. Rev. B **76** (2007) 235424

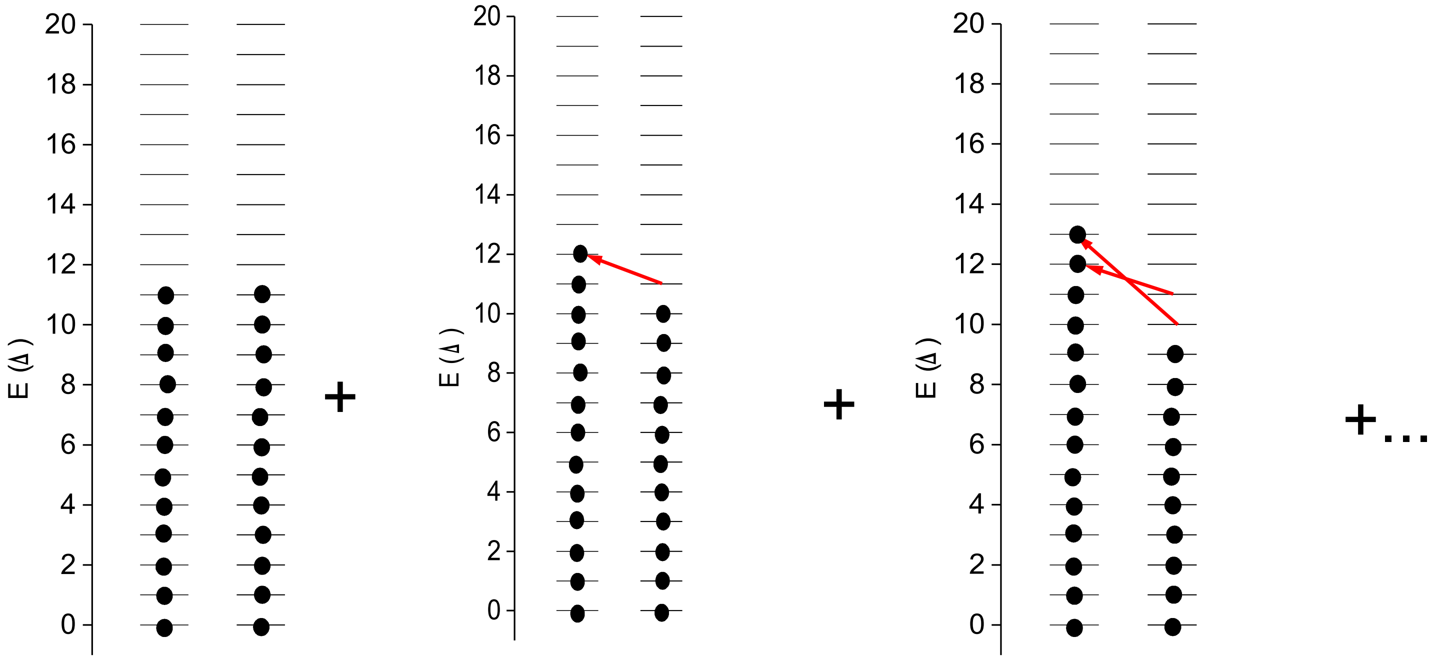
Level densities of equidistant spectrum

integrate $\overline{E} = -\frac{\partial \ln(Z)}{\partial \beta}$ to get $Z \approx \frac{\pi^2}{6\Delta}\beta^{-1}$

$$\rho(E_0) \approx \frac{1}{\sqrt{2\pi C T^2}} e^{\sqrt{\frac{2\pi^2 E_0}{3\Delta}}}$$

Let's try a quasirealistic spectrum

add spin degeneracy



$$\prod_{j=1}^{N}\frac{1}{(1-e^{-j\beta\Delta})^{2}} + e^{-\beta\Delta}\prod_{j=1}^{N}\frac{1}{(1-e^{-j\beta\Delta})^{2}} \times 2 + e^{-4\beta\Delta}\prod_{j=1}^{N}\frac{1}{(1-e^{-j\beta\Delta})^{2}} \times 2 + \ldots$$

Total partition functions

convolution of all electron partitionings

$$Z(N=even)=\prod_{j=1}^{\infty}\left(1-e^{-j\beta\Delta}\right)^{-2}\sum_{m=-\infty}^{\infty}e^{-m^2\beta\Delta}$$

$$Z(N=odd)=\prod_{j=1}^{\infty}\left(1-e^{-j\beta\Delta}\right)^{-2}\sum_{m=-\infty}^{\infty}e^{-m(m+1)\beta\Delta}$$

low temperature limt easy

High temperature limit

$$S(x) = \sum_{m=-\infty}^{\infty} e^{-\beta\Delta m(m+x)} = e^{\beta x^2 \Delta/4} \sum_{m=-\infty}^{\infty} e^{-\beta\Delta(m+x/2)^2}$$

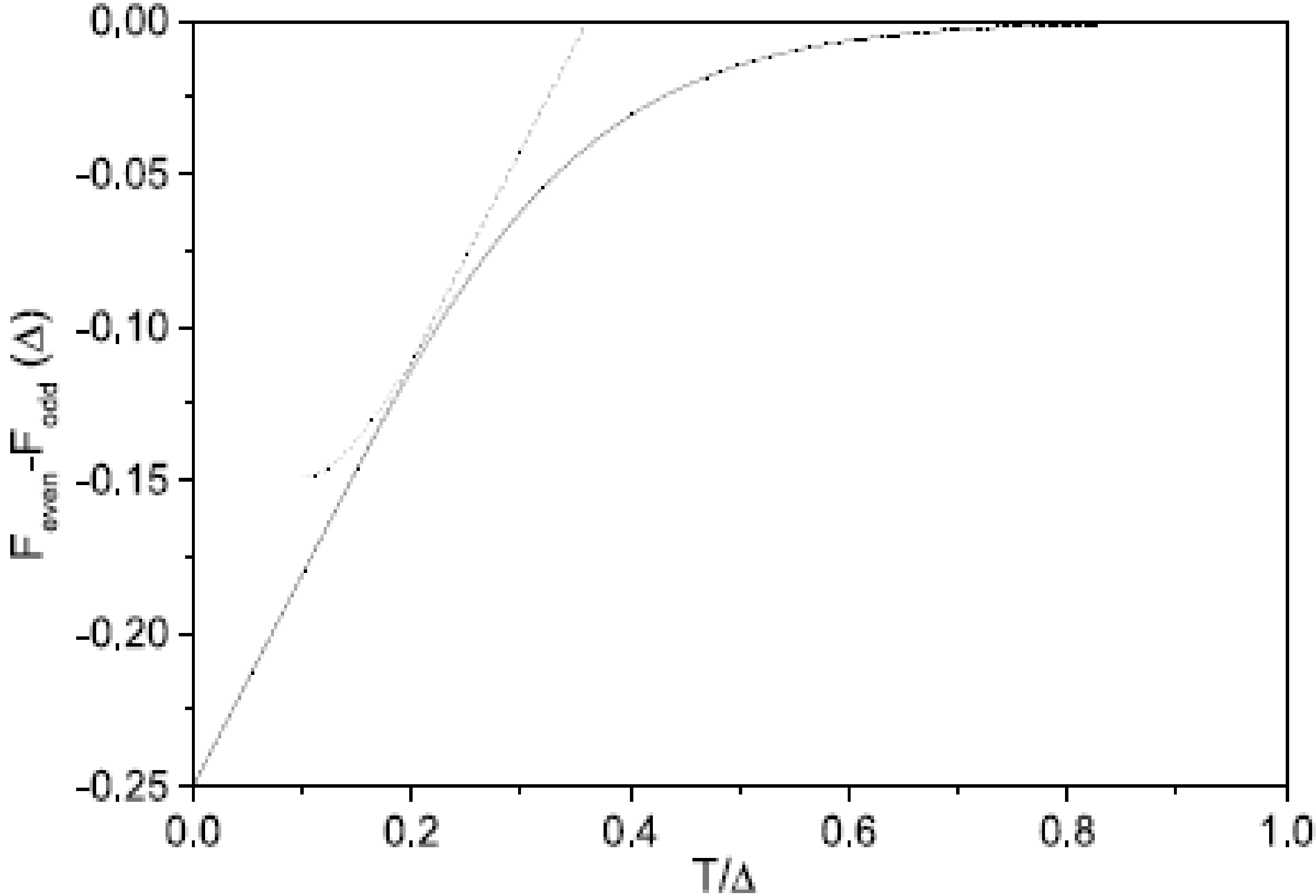
(we want *S(0)*, *S(1)*)

Periodic in x: Fourier expansion

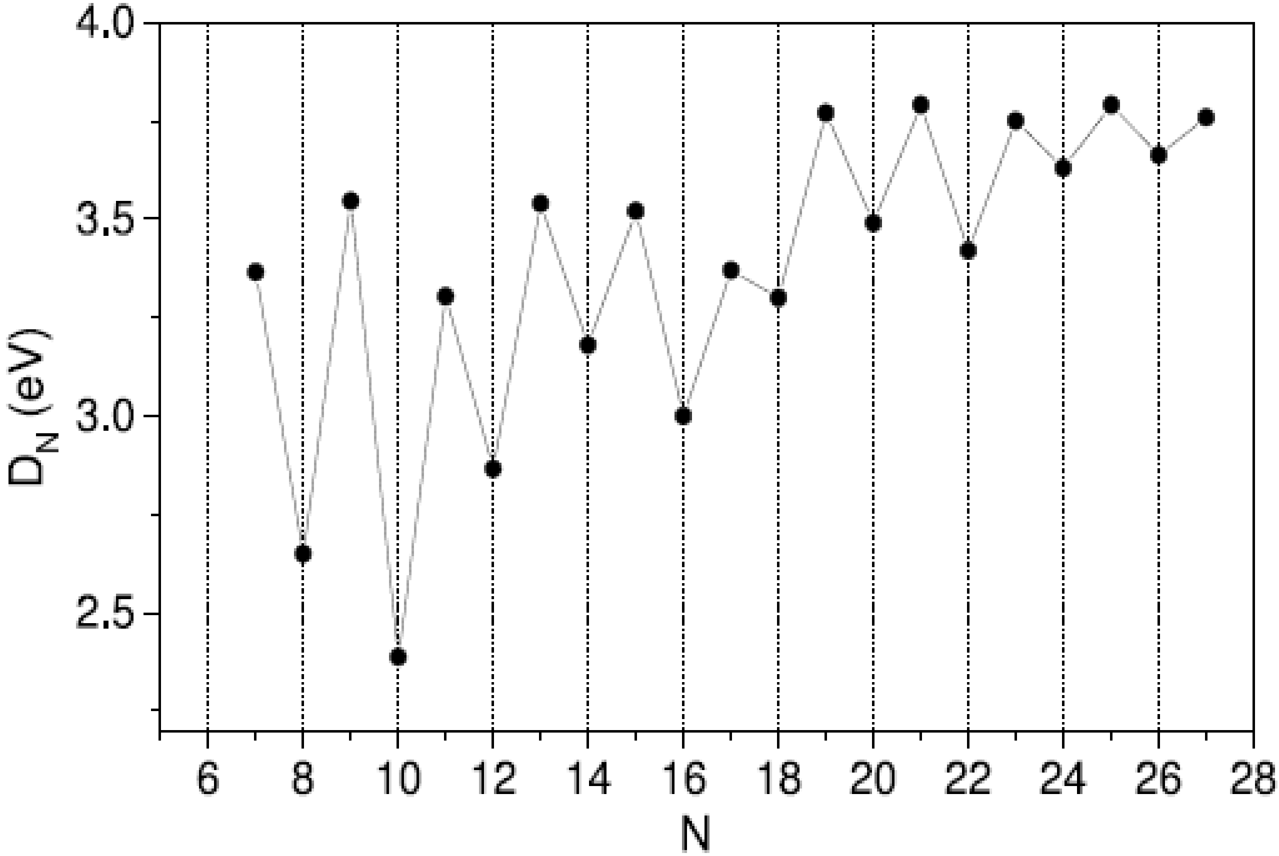
$$s(0) = \left(\frac{\pi^2 T}{\Delta}\right)^{1/2} \left(1 + 2e^{-\pi^2 T/\Delta} + \ldots\right)$$

$$s(1) = e^{\beta\Delta/4} \left(\frac{\pi^2 T}{\Delta}\right)^{1/2} \left(1 - 2e^{-\pi^2 T/\Delta} + \ldots\right)$$

Comparison to exact calculation:

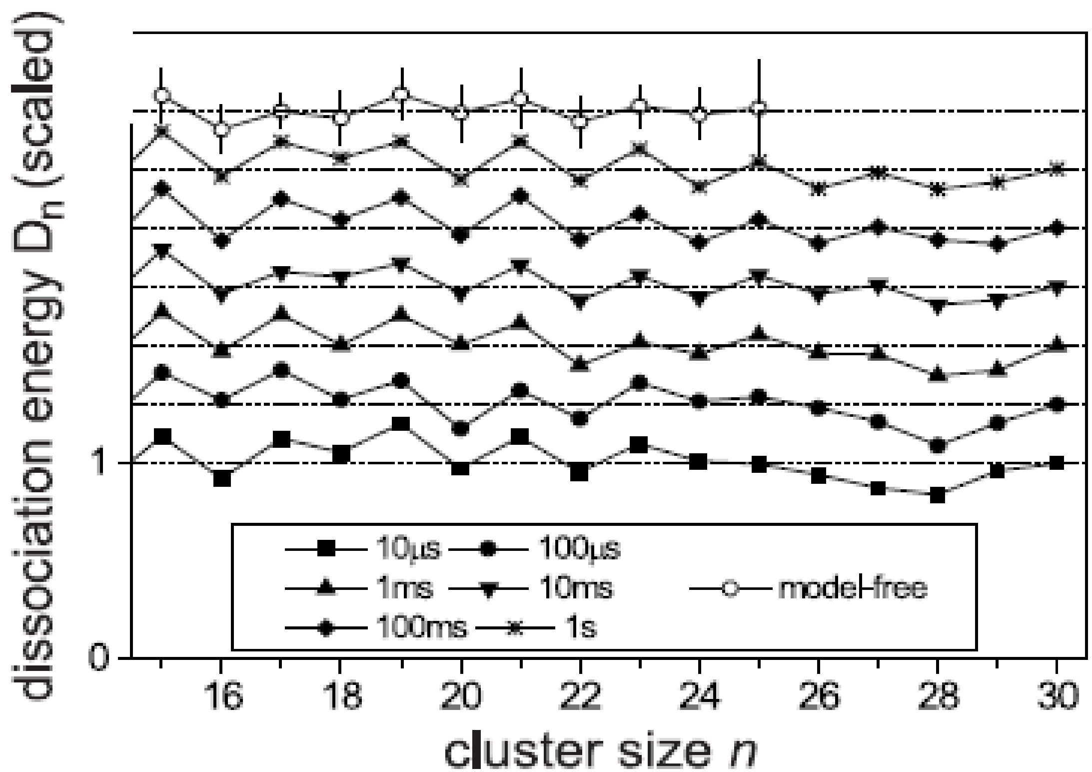


Au_N^+ dissociation energies



w. L. Schweikhard

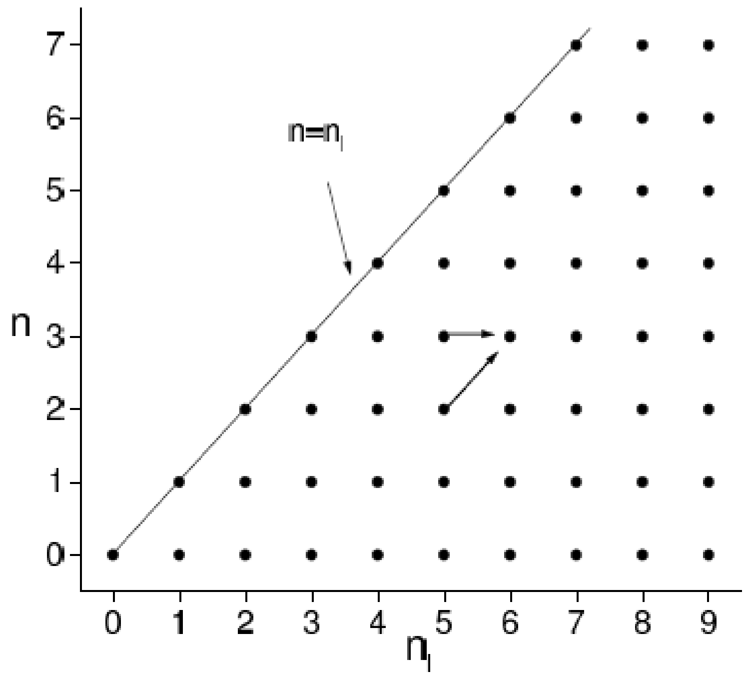
Laser excitation and evaporation of Au_N^+ in the Greifswald Penning trap



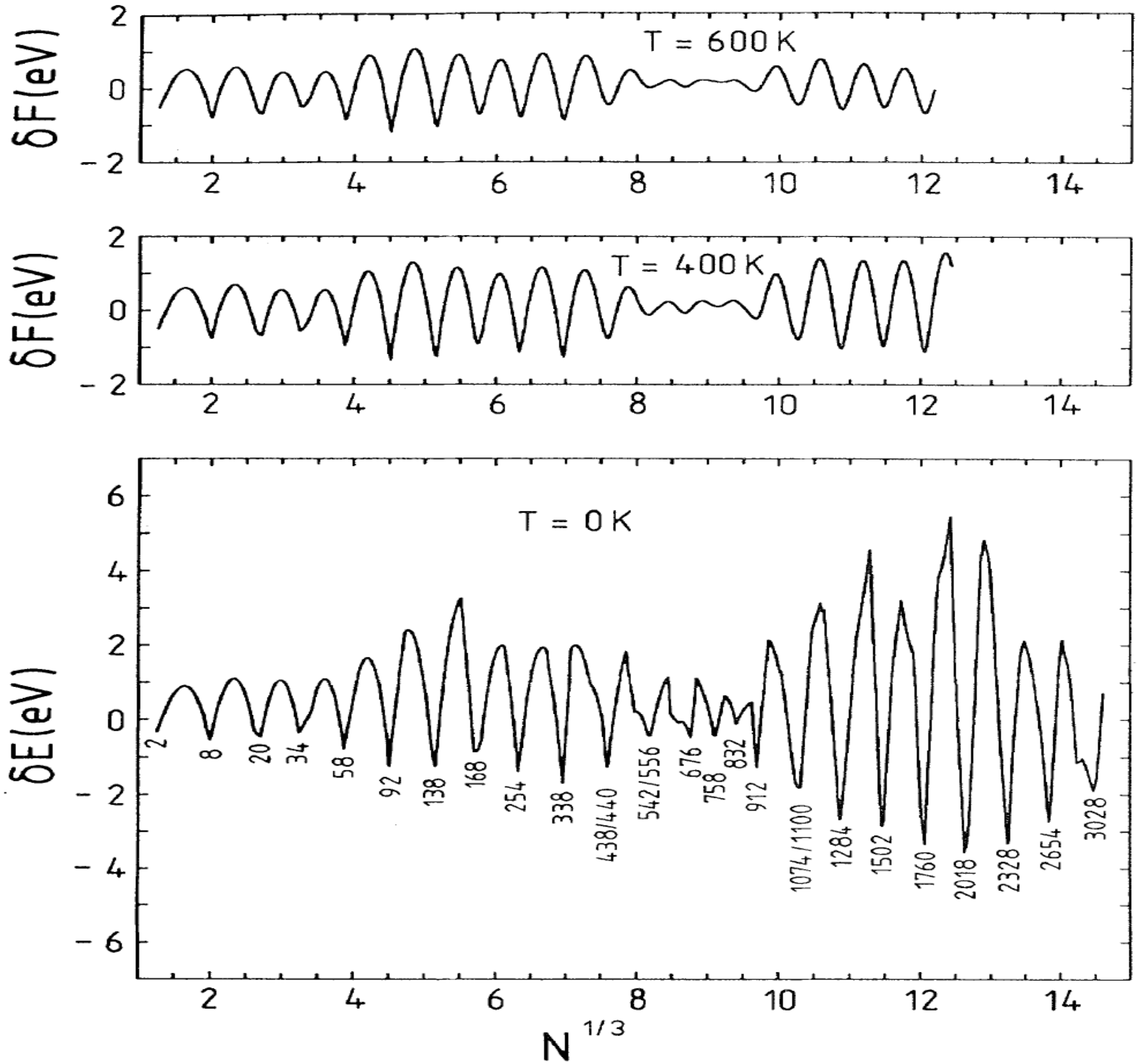
Numerical calculation of the thermal properties of mean field electrons

define partition function of n electrons and n_l levels

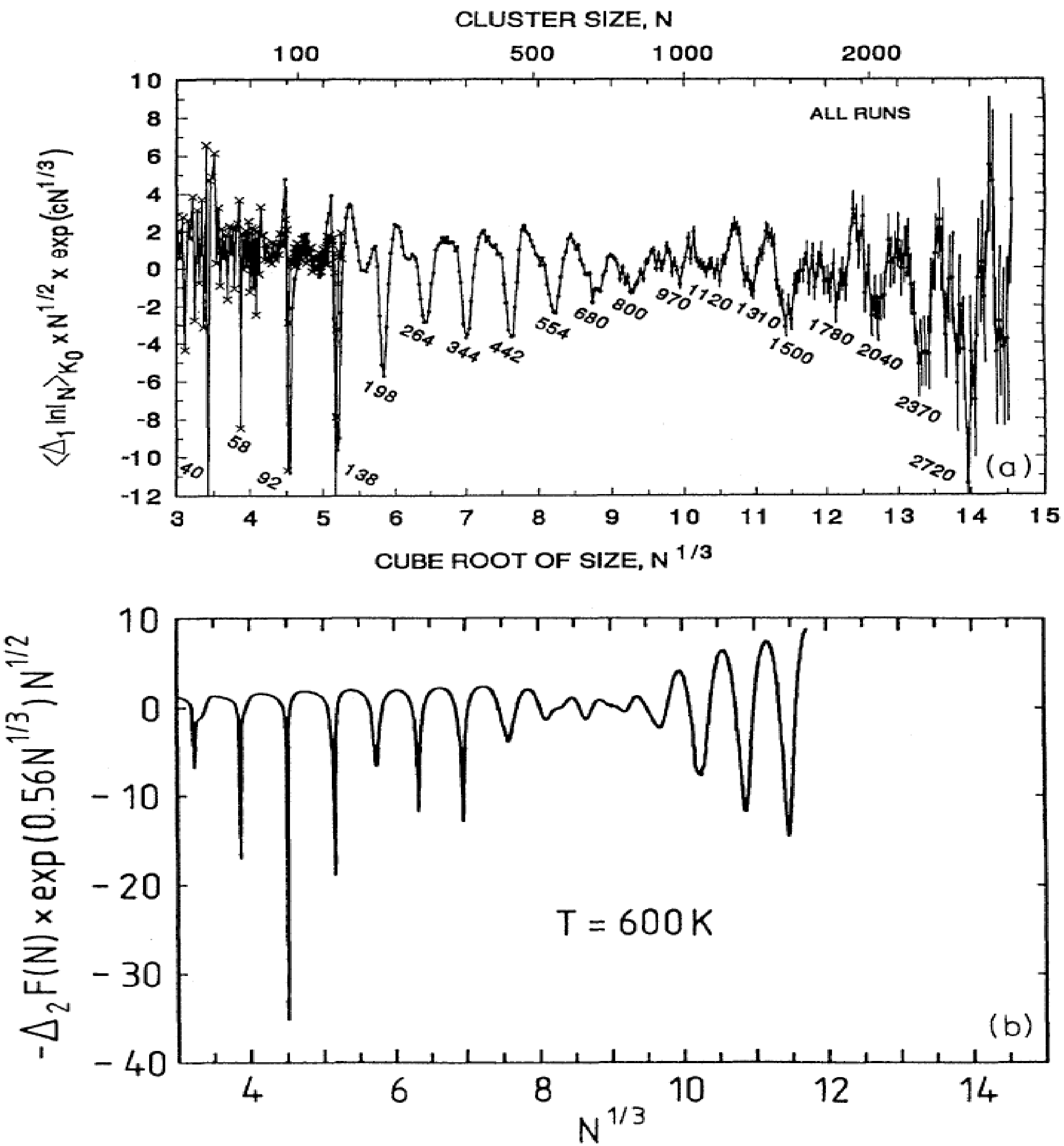
$$z(n_l, n) = z(n_l - 1, n) + z(n_l - 1, n - 1)\exp\left(-\beta(\varepsilon_{n_l} - \varepsilon_n)\right)$$



Finite temperature shell energies



O.Genzken,
M.Brack
Phys.Rev.Lett.
67 (1991) 3286



Experiments,
Niels Bohr Institute
Copenhagen

Theory,
Regensburg

M.Brack
Rev. Mod. Phys.
65 (1993) 677

Calculation of level densities

$$\rho(E, n_l, n) = \rho(E - \varepsilon_{n_l}, n_l - 1, n - 1) + \rho(E, n_l - 1, n)$$

Another recurrence relations

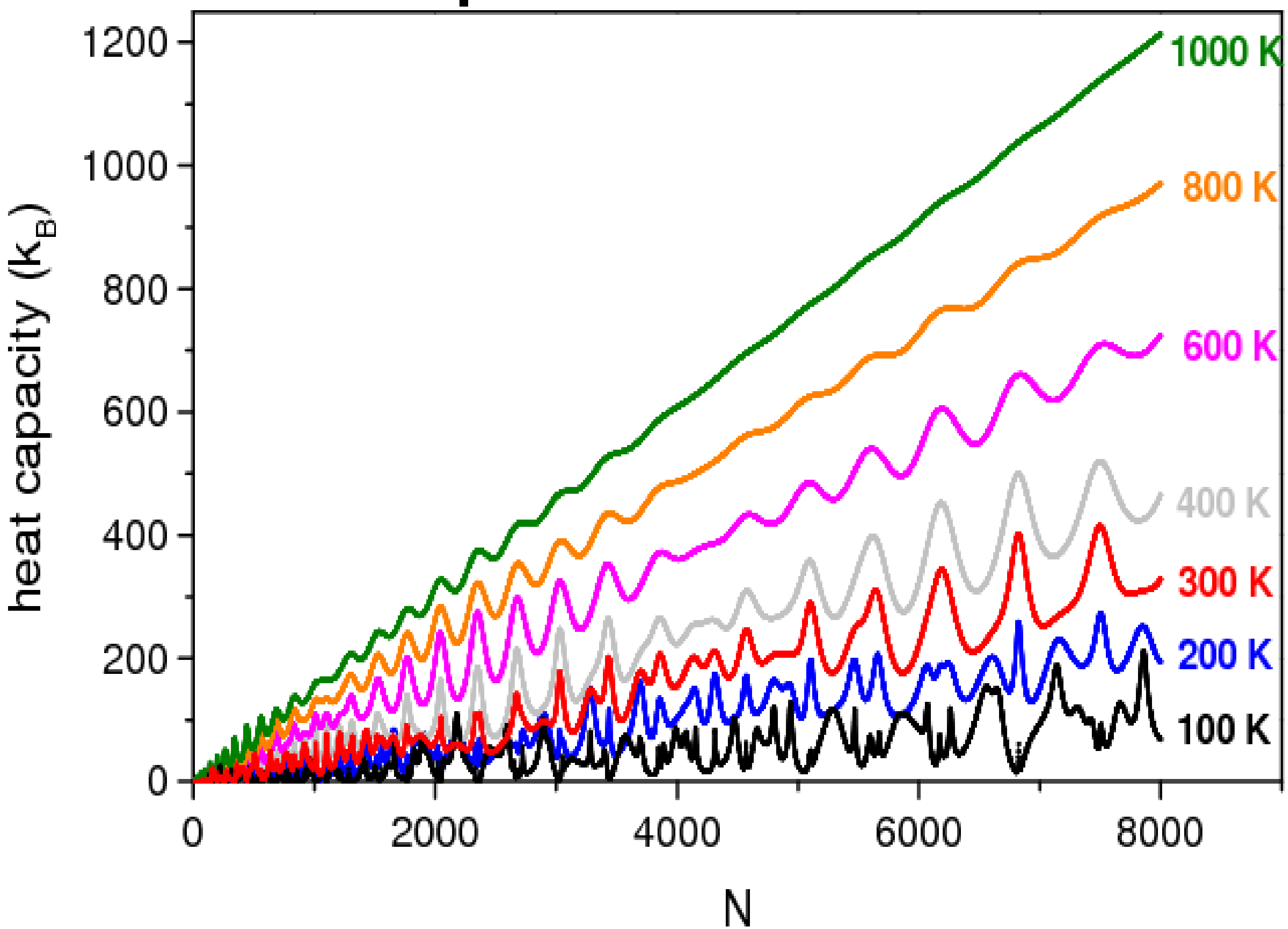
$$\overline{E}z = \int E\,\rho(E)\,e^{-\beta E}\,dE$$

$$\overline{E}z(n_l,n) = \overline{E}z(n_l-1,n) + [\overline{E}z(n_l-1,n-1)$$
$$+(\varepsilon_{n_l}-\varepsilon_n)z(n_l-1,n-1)]e^{-\beta(\varepsilon_{n_l}-\varepsilon_n)}.$$

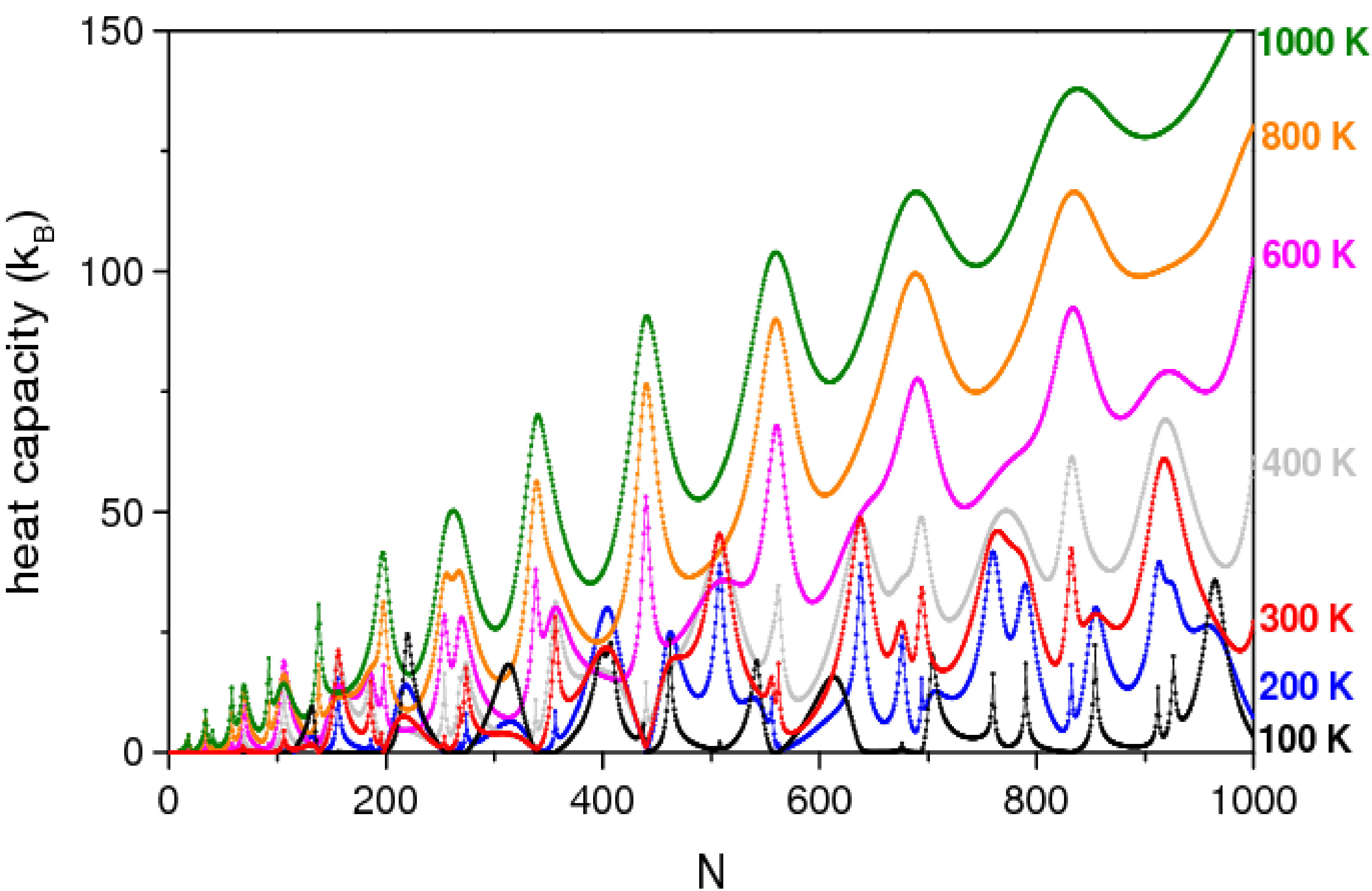
One more for the heat capacity

$$\overline{E^2}z(n_l, n) = \overline{E^2}z(n_l - 1, n) + (\overline{E^2}z(n_l - 1, n - 1) \quad (9.84)$$
$$+ 2(\varepsilon_(n_l) - \varepsilon_n)\overline{E}z(n_l - 1, n - 1)$$
$$+ (\varepsilon_(n_l) - \varepsilon_n)^2 z(n_l - 1, n - 1)))e^{-\beta(\varepsilon_{n_l} - \varepsilon_n)}.$$

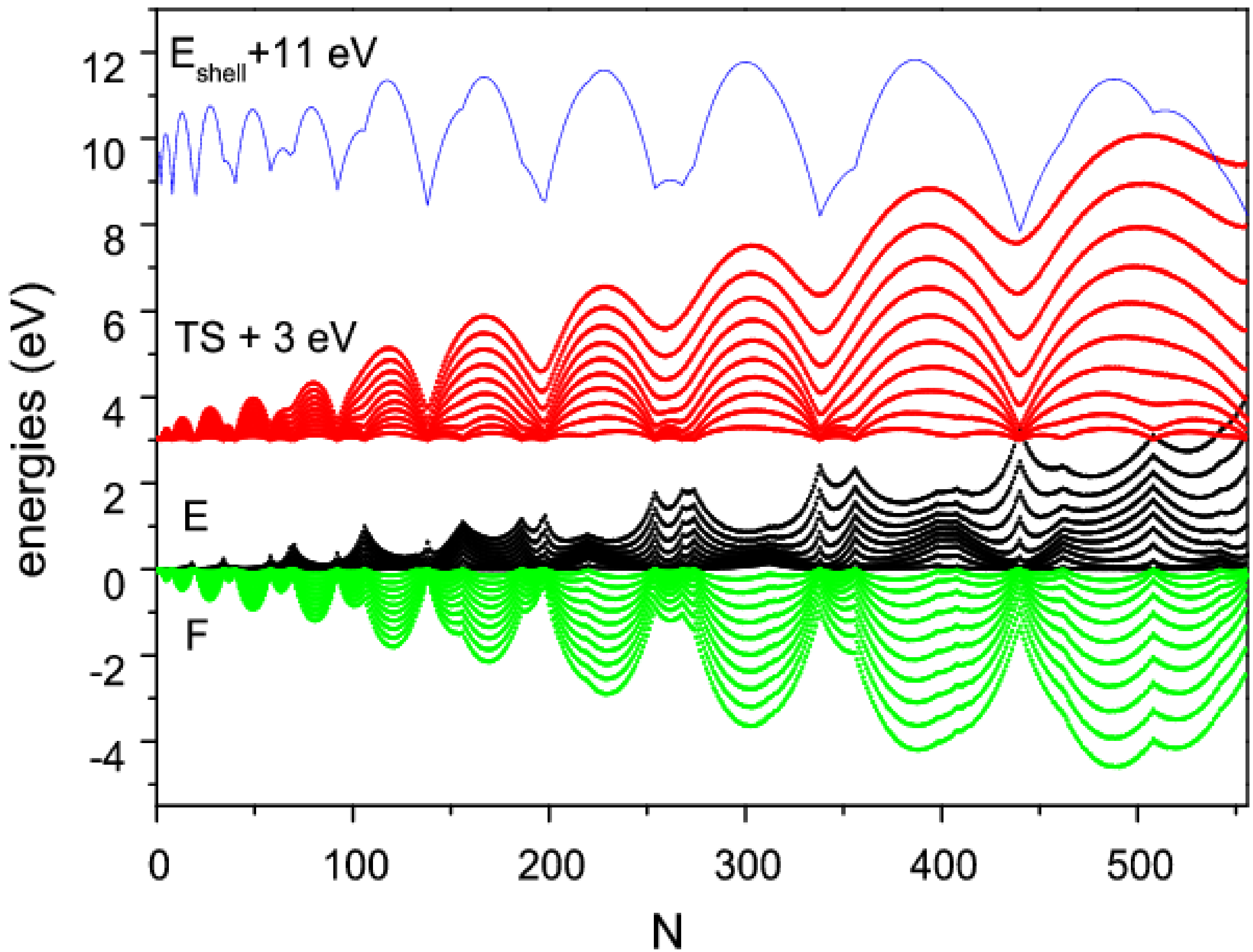
Heat capacities



Heat capacities, small clusters



URG



100K
to
1000K
in
100K
steps

That was it