Thermodynamic Properties of Small Quantum Systems

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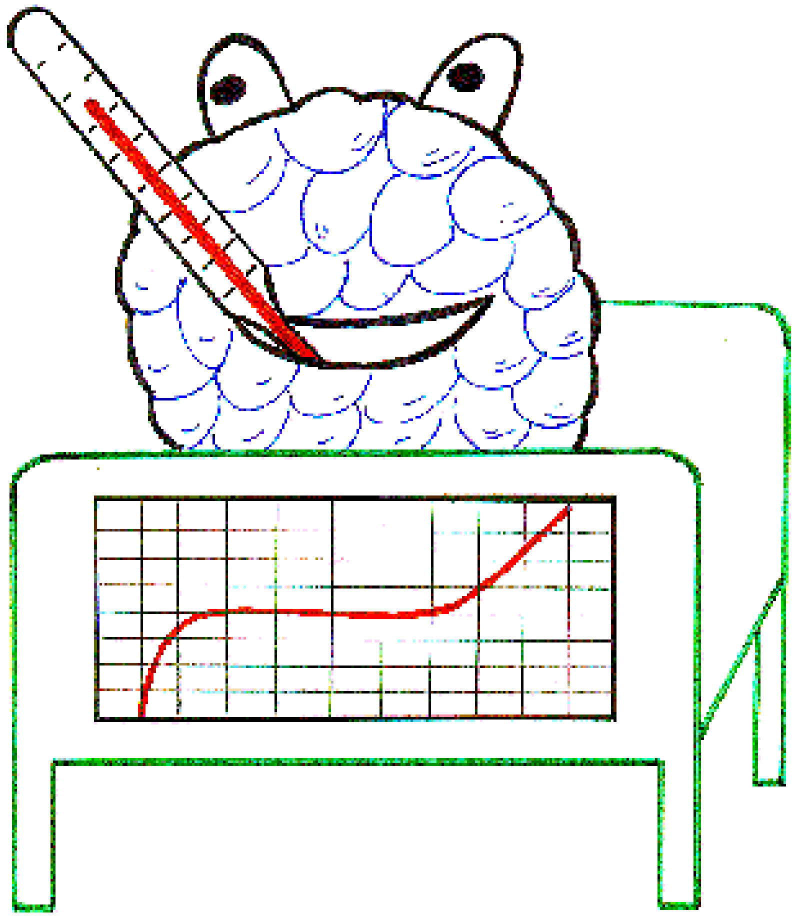

H. Feldmeier, K. Bieler, J. Schnack, Nucl. Phys. **A586** (1995) 403

J. Schnack, H. Feldmeier, Nucl. Phys. **A601** (1996) 181

J. Schnack, H. Feldmeier, Phys. Lett. B409 (1997) 6

J. Schnack, PHYSICA A (1998)

http://obelix.physik.uni-osnabrueck.de/∼schnack/

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Problem

Statistical operator and partition function:

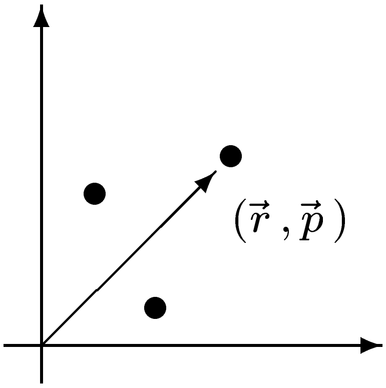
$$
\begin{aligned}
\underset{\sim}{R} &= \exp\left\{-\frac{1}{T}\underset{\sim}{H}\right\} \\
Z &= \mathrm{tr}\left(\exp\left\{-\frac{1}{T}\underset{\sim}{H}\right\}\right)
\end{aligned}
$$

- For realistic systems, i.e. $\underset{\sim}{H}$ contains at least a two-body interaction and the systems consists of many particles, Z cannot be evaluated (easily).
- Equations of motion can be derived on the level of approximation one can effort, e.g. TDHF.
- If the system is ergodic ensemble averaging can be replaced by time averaging.

Time averaging of an operator $\underset{\sim}{B}$:

$$
\overline{\langle\, \underset{\sim}{B}\, \rangle} = \lim_{t_2\to\infty} \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} \mathrm{d}t \, \langle\, Q(t) \,|\, \underset{\sim}{B} \,|\, Q(t) \,\rangle
$$

Classical Molecular Dynamics



- N–particle–state:
  $\{\vec{r}_1, \vec{p}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{p}_N\}$

Hamilton function:

$$\begin{aligned} H &= H(\vec{r}_1, \vec{p}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{p}_N) \\ &= \sum_i \frac{\vec{p}_i^{\,2}}{2m_i} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \end{aligned}$$

Dynamics:

$$\frac{d}{dt}\,\vec{r}_i = \frac{\partial H}{\partial \vec{p}_i} \quad \& \quad \frac{d}{dt}\,\vec{p}_i = -\frac{\partial H}{\partial \vec{r}_i}$$

Hoover–Nosé–Thermostat

Introduction[a][b] of a pseudo friction coefficient ξ:

$$\begin{aligned}
\frac{d}{dt}\,\vec{r}_i &= \frac{\vec{p}_i}{m_i} \\
\frac{d}{dt}\,\vec{p}_i &= -\frac{\partial V}{\partial \vec{r}_i} - \xi\,\vec{p}_i \\
\frac{d}{dt}\,\xi &= \frac{1}{M_s}\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m_i} - \frac{3N}{2}k_B T\right)
\end{aligned}$$

- this special thermostat uses the equipartition theorem
- $\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m_i} - \frac{3N}{2}k_B T\right) > 0 \quad \Rightarrow \quad$ cooling
- $\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m_i} - \frac{3N}{2}k_B T\right) < 0 \quad \Rightarrow \quad$ heating
- can be generalized[c]

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[a] W.G. Hoover, Phys. Rev. **A31** (1985) 1685

[b] S. Nosé, Prog. of Theor. Phys. Suppl. **103**(1991) 1

[c] D. Kusnezov, A. Bulgac, W. Bauer, Ann. of Phys. **204** (1990) 155

Quantum Mechanics

No equipartition theorem:

$$
\begin{aligned}
\underset{\sim}{R} &= \exp\left\{-\frac{1}{T}\underset{\sim}{H}\right\} \\
\langle\langle\, \underset{\sim}{T} \,\rangle\rangle &= \langle\langle \sum_i \frac{\underset{\sim}{\vec{k}}_i^{\,2}}{2m_i} \rangle\rangle \\
&\neq \frac{3N}{2} k_B T
\end{aligned}
$$

Idea - Coupling to a system with known $E(T)$, e.g. a harmonic oscillator:

$$
\begin{aligned}
\langle\langle\, \underset{\sim}{H} \,\rangle\rangle &= \langle\langle \sum_i \left(\frac{\underset{\sim}{\vec{k}}_i^{\,2}}{2m_i} + \frac{1}{2}\, m_i \omega^2 \underset{\sim}{\vec{x}}_i^{\,2} \right) \rangle\rangle \\
&= \frac{3}{2} N\omega \coth\left(\frac{\omega}{2\,T}\right)
\end{aligned}
$$

- read off the temperature
- run a thermostat

Time-dependent variational principle

TDVP[a]**:**

$$0 \quad = \quad \delta \int_{t_1}^{t_2} \mathrm{d}t \, \langle\, Q(t) \,|\, i \frac{d}{dt} - \underset{\sim}{H} \,|\, Q(t) \,\rangle$$

A variation of $\langle\, Q(t) \,|$ in the complete Hilbert space yields the Schrödinger equation.

Euler–Lagrange equations in their most general form:

$$\sum_\nu \mathcal{A}_{\mu\nu}(Q(t)) \; \dot{q}_\nu = -\frac{\partial}{\partial q_\mu} \; \langle\, Q(t) \,|\, \underset{\sim}{H} \,|\, Q(t) \,\rangle$$

$$\mathcal{A}_{\mu\nu}(Q(t)) = \frac{\partial^2 \langle\, Q(t) \,|\, i \frac{d}{dt} \;\, |\, Q(t) \,\rangle}{\partial \dot{q}_\mu \partial q_\nu} - \frac{\partial^2 \langle\, Q(t) \,|\, i \frac{d}{dt} \;\, |\, Q(t) \,\rangle}{\partial \dot{q}_\nu \partial q_\mu}$$

- variation in the set of Slater determinants leads to TDHF
- variation with localized single-particle states leads to various kinds of quantum molecular dynamics models

[a] P. Kramer, M. Saraceno, Lecture Notes in Physics **140**, Springer, Berlin (1981)

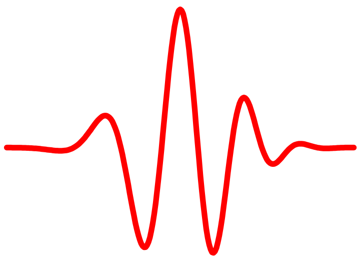
Fermionic Molecular Dynamics (FMD)

Many-body state (Slater determinant):

$$
\begin{aligned}
|\, Q(t)\,\rangle &= \frac{1}{\langle\, \widehat{Q}(t)\,|\,\widehat{Q}(t)\,\rangle^{\frac{1}{2}}}\;|\,\widehat{Q}(t)\,\rangle \\
|\,\widehat{Q}(t)\,\rangle &= \frac{1}{N!}\sum_{\pi} \mathrm{sgn}(\pi)\;|\,q_{\pi(1)}(t)\,\rangle \otimes \cdots \otimes |\,q_{\pi(A)}(t)\,\rangle
\end{aligned}
$$

Single-particle state (Gaussian wave packet):

$$
\langle\, \vec{x}\,|\,q(t)\,\rangle = \exp\left\{ -\frac{(\,\vec{x}-\vec{b}(t)\,)^2}{2\,a(t)} \right\} \otimes |\,m_s\,\rangle \otimes |\,m_t\,\rangle
$$



$\vec{b}(t) = \vec{r}(t) + ia(t)\vec{p}(t)$

$\vec{r}(t)$: mean position

$\vec{p}(t)$: mean momentum

$a(t)$: complex width

m_s : magnetic quantum number

m_t : Isospin–3–component

Special expectation values:

$$
\langle\, \underset{\sim}{\vec{x}}\,\rangle = \vec{r} \quad , \quad \langle\, \underset{\sim}{\vec{k}}\,\rangle = \vec{p}
$$

$$
(\Delta x)^2 = \frac{3}{2}\,\frac{a_R^2 + a_I^2}{a_R} \quad , \quad (\Delta k)^2 = \frac{3}{2}\,\frac{1}{a_R}
$$

FMD: Special Solutions

Free motion:

$$\underset{\sim}{h}(l) = \frac{\underset{\sim}{\vec{k}}^{\,2}(l)}{2m} \quad \Rightarrow \quad \frac{d}{dt}\,\vec{b}_l = 0\ , \quad \frac{d}{dt}\,a_l = \frac{i}{m}$$

$$\frac{d}{dt}\,\vec{p}_l = 0 \quad , \quad \frac{d}{dt}\,\vec{r}_l = \frac{\vec{p}_l}{m}$$

Common harmonic oscillator:

$$\underset{\sim}{h}(l) = \frac{\underset{\sim}{\vec{k}}^{\,2}(l)}{2m} + \frac{1}{2}\,m\omega^2\,\underset{\sim}{\vec{x}}^{\,2}(l) \quad \Rightarrow \quad \frac{d}{dt}\,\vec{b}_l = -im\omega^2 a_l \vec{b}_l$$

$$\frac{d}{dt}\,a_l = -im\omega^2 a_l^2 + \frac{i}{m}$$

$$\frac{d}{dt}\,\vec{r}_l = \frac{\vec{p}_l}{m} \quad , \quad \frac{d}{dt}\,\vec{p}_l = -m\omega^2 \vec{r}_l$$

Both solutions coincide with those of the Schrödinger equation and remain the same irrespective of whether we describe bosons, fermions or distinguishable particles.

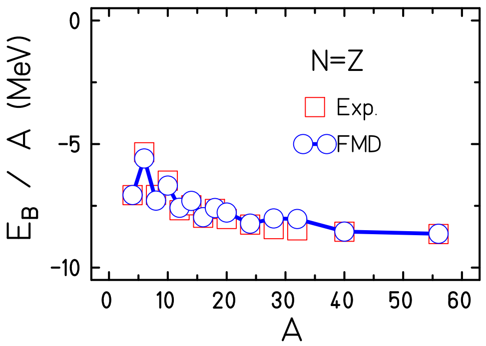
FMD: Ground States

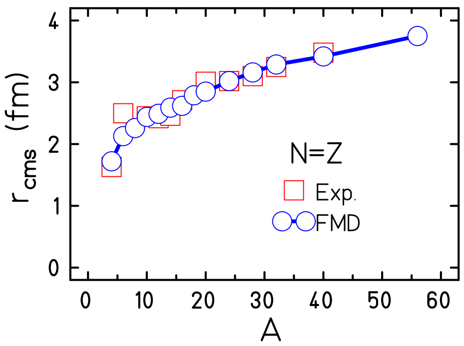
Ground state (Ritz):

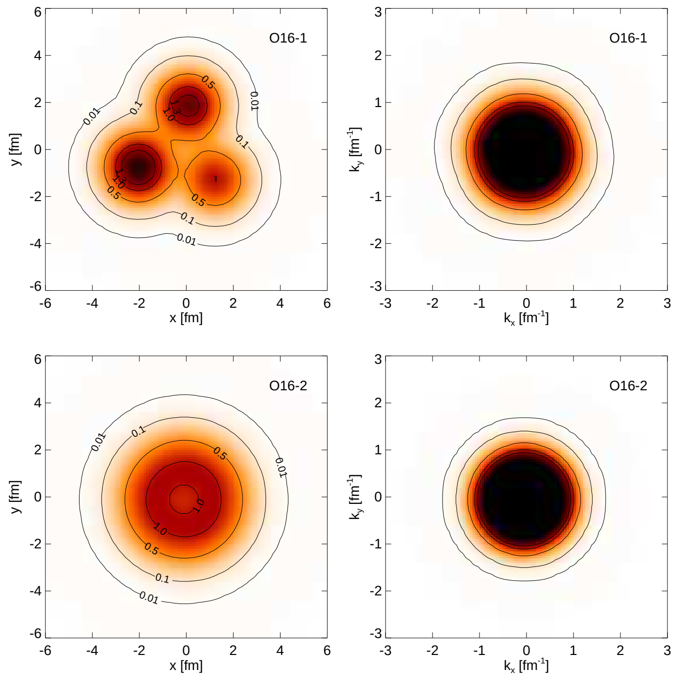
$$\mathcal{H} := \langle\, Q(t) \,|\, \underset{\sim}{H} \,|\, Q(t) \,\rangle \qquad \text{minimal}$$

$$\forall q_\mu : \qquad 0 = \frac{\partial}{\partial q_\mu} \;\langle\, Q(t) \,|\, \underset{\sim}{H} \,|\, Q(t) \,\rangle \qquad \text{necessary}$$

Ground states can be reasonably well described by a phenomenological N-N interaction:







Time-Averaging

Ergodic ensemble and statistical operator $\underset{\sim}{R}_{\text{erg}}$:

$$\underset{\sim}{R}_{\text{erg}} \quad := \quad \lim_{t_2 \to \infty} \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} \mathrm{d}t \; |\, Q(t)\,\rangle\langle\, Q(t)\,|$$

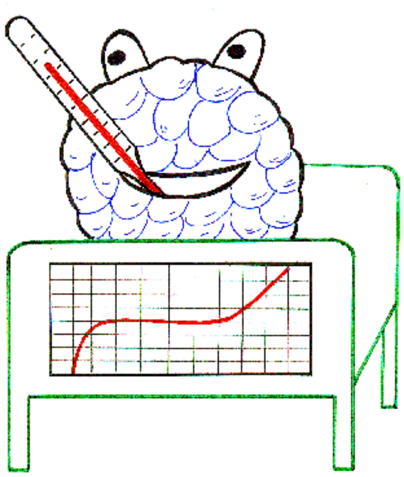
The ergodic mean of an operator $\underset{\sim}{B}$:

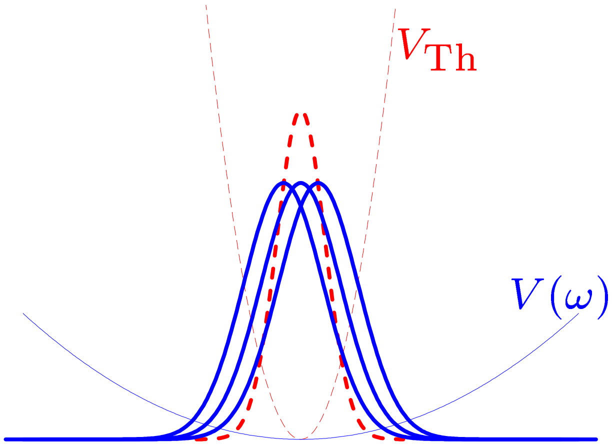
$$\overline{\langle\, \underset{\sim}{B}\,\rangle}\Big|_{\langle\, \underset{\sim}{H}\,\rangle} \quad := \quad \mathrm{Tr}\,(\underset{\sim}{R}_{\text{erg}}\; \underset{\sim}{B})$$

$$= \quad \lim_{t_2 \to \infty} \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} \mathrm{d}t \,\langle\, Q(t)\,|\, \underset{\sim}{B}\,|\, Q(t)\,\rangle$$

- Ergodic assumption: $\underset{\sim}{R}_{\text{erg}}$ depends only on $\langle\, \underset{\sim}{H}\,\rangle$ and $|\, Q(t)\,\rangle$ covers the available Hilbert space.
- $\langle\, \underset{\sim}{H}\,\rangle$ is a constant of motion.
- $\langle\, \underset{\sim}{H}^2\,\rangle - \langle\, \underset{\sim}{H}\,\rangle^2 > 0$, i.e. quantum fluctuations.

Coupling to a thermometer



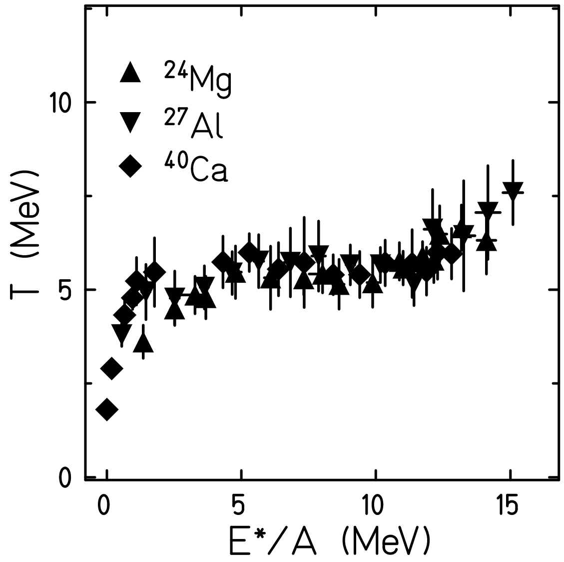


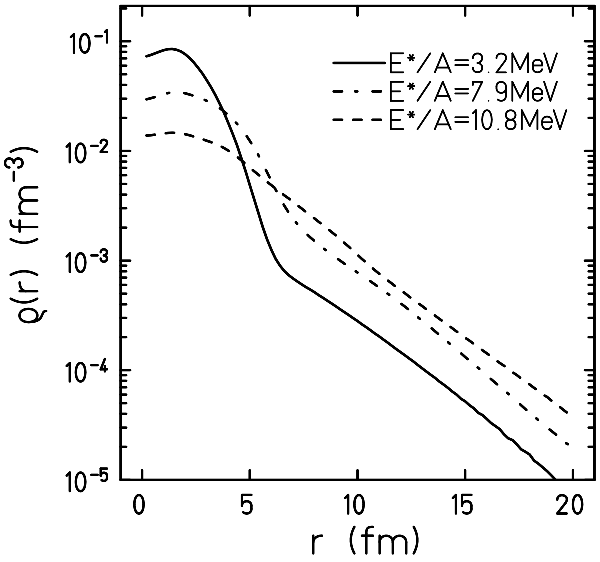
Procedure:

- **excited nucleus:** self-bound liquid drop in a large container (harmonic oscillator)
  $\underset{\sim}{H}_{\mathrm{N}} = \underset{\sim}{T}_{\mathrm{N}} + \underset{\sim}{V}_{\mathrm{NN}} + \underset{\sim}{V}(\omega)$,
- **thermometer:** single wave packet in a second oscillator with ω_{Th}, ideal gas thermometer
  $\underset{\sim}{H}_{\mathrm{Th}} = \underset{\sim}{T}_{\mathrm{Th}} + \underset{\sim}{V}_{\mathrm{Th}}$,
- **coupling** of all nucleons to the thermometer wave-packet:
  $\underset{\sim}{V}_{\mathrm{N-Th}}$, $\quad \underset{\sim}{H} = \underset{\sim}{H}_{\mathrm{N}} + \underset{\sim}{H}_{\mathrm{Th}} + \underset{\sim}{V}_{\mathrm{N-Th}}$,
  $| \, Q(t) \, \rangle = | \, nucleus \, \rangle \otimes | \, thermometer \, \rangle$,
- **time-averaging:**
  $E_{\mathrm{Th}} = \overline{\langle \, \underset{\sim}{H}_{\mathrm{Th}} \, \rangle} \Big|_{\langle \underset{\sim}{H} \rangle}$, $\quad E^* = \overline{\langle \, \underset{\sim}{H}_{\mathrm{N}} - E_0 \, \rangle} \Big|_{\langle \underset{\sim}{H} \rangle}$,
- **zeroth law:** both subsystems approach the same T

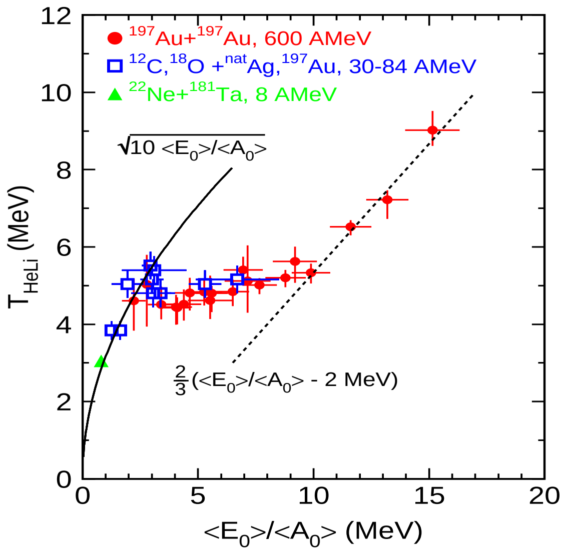
$$T = \omega_{Th} \left[\ln \left(\frac{E_{\mathrm{Th}} + \frac{3}{2}\omega_{Th}}{E_{\mathrm{Th}} - \frac{3}{2}\omega_{Th}} \right) \right]^{-1}$$

Caloric Curve





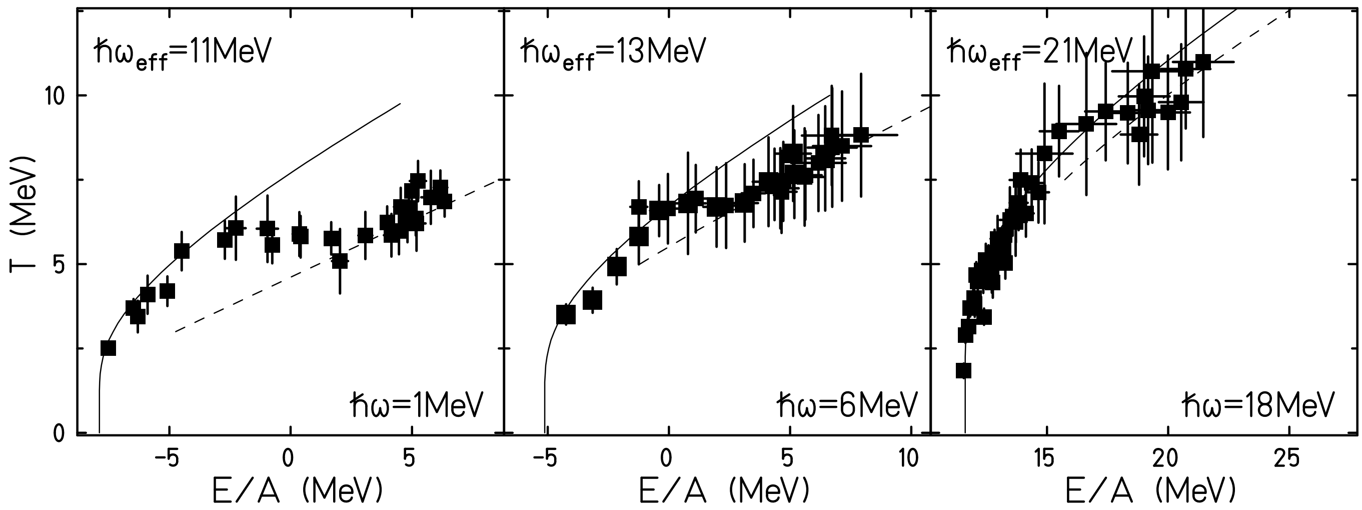
J. Pochodzalla et al., Phys. Rev. Lett. 75 (1995) 1040:



- simulation: equilibrium due to evolution in container over long time, ideal gas thermometer
- experiment: event–ensemble shows equilibrium properties, chemical thermometer

Caloric Curve
Critical Temperature

Critical temperature of ^{16}O:



- ω serves as external parameter like volume or pressure.
- critical point: latent heat vanishes
- system finite and charged: $T_c = T_c(N, Z)$

Thermostat

Total system:

$$|\,Q(t)\,\rangle \quad = \quad |\,system(t)\,\rangle \otimes \,|\,thermometer(t)\,\rangle$$

Complex time steps:

$$d\tau = dt - i d\beta \ , \quad d\beta \propto (T_{th} - T)/T_{th} \ , \quad |\,Q(t)\,\rangle \rightarrow \,|\,Q(t + d\tau)\,\rangle$$

- T desired temperature
- T_{th} temperature measured by the thermometer
- $d\beta > 0 \ \Rightarrow$ cooling; $\quad d\beta < 0 \ \Rightarrow$ heating

Fermions in an Oscillator Potential

Total system:

$$
\begin{aligned}
|\,Q(t)\,\rangle &= |\,Q_f(t)\,\rangle \otimes |\,Q_{th}(t)\,\rangle \\
|\,Q_f(t)\,\rangle &= \underset{\sim}{A}\Big(|\,q_{f1}(t)\,\rangle \otimes |\,q_{f2}(t)\,\rangle \otimes |\,q_{f3}(t)\,\rangle \otimes |\,q_{f4}(t)\,\rangle\Big) \\
|\,Q_{th}(t)\,\rangle &= |\,q_{th1}(t)\,\rangle \otimes |\,q_{th2}(t)\,\rangle
\end{aligned}
$$

$$
\begin{aligned}
\underset{\sim}{H} &= \underset{\sim}{H}_f + \underset{\sim}{H}_{th} + \underset{\sim}{V}_{f,f} + \underset{\sim}{V}_{f,th} \\
\underset{\sim}{H}_f &= \sum_{i=1}^{N_f} \left(\frac{\underset{\sim}{k}_i^{\,2}}{2m_f} + \frac{1}{2}\, m_f \omega_f^2 \underset{\sim}{x}_i^{\,2} \right) \\
\underset{\sim}{H}_{th} &= \sum_{i=1}^{N_{th}} \left(\frac{\underset{\sim}{k}_i^{\,2}}{2m_{th}} + \frac{1}{2}\, m_{th} \omega_{th}^2 \underset{\sim}{x}_i^{\,2} \right)
\end{aligned}
$$

- $\underset{\sim}{V}_{f,f}$ short-range repulsion between fermions
- $\underset{\sim}{V}_{f,th}$ momentum dependent short-range repulsion between fermions and thermometer wave packets

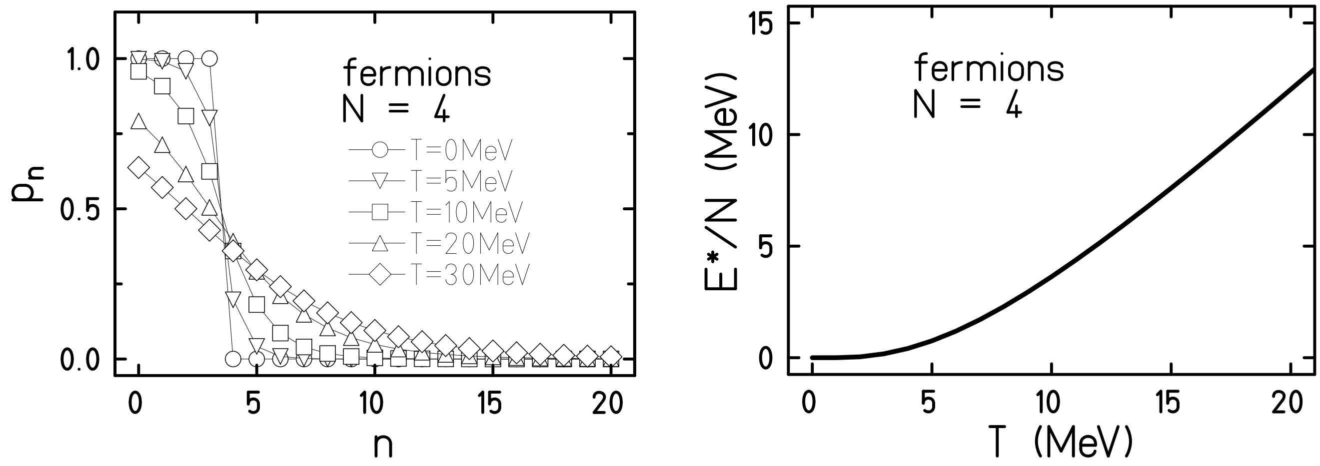
Fermions in an Oscillator Potential
Canonical Ensemble

Mean energy and occupation numbers of N fermions in a common one-dimensional harmonic oscillator potential:

$$\langle\langle\, \underset{\sim}{H}_f \,\rangle\rangle\Big|_T = E_0(N) + \sum_{k=1}^{N} k\,\frac{\omega_f}{2}\left[\coth\left(k\,\frac{\omega_f}{2\,T}\right) - 1\right]$$

$$E_0(N) = N^2\,\frac{\omega_f}{2}$$

$$p_n = \langle\langle\, \underset{\sim}{c}_n^{+}\, \underset{\sim}{c}_n \,\rangle\rangle\Big|_T \;,$$



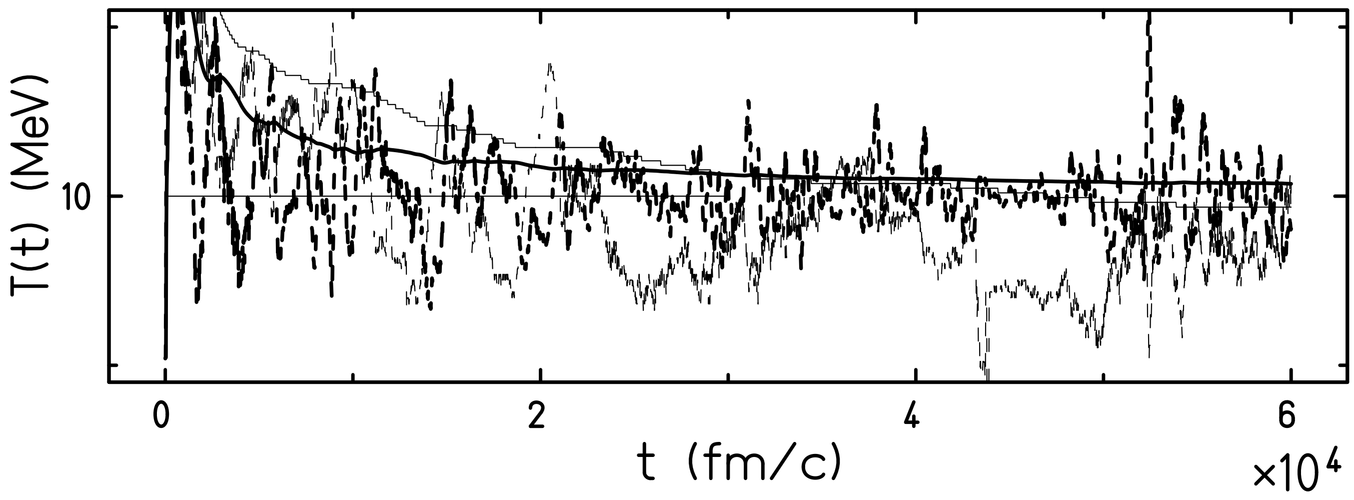
$\omega_f = 8\,\mathrm{MeV}$

Fermions in an Oscillator Potential
Time Averaging

Temperatures:

$$\langle\langle \underset{\sim}{H}_f \rangle\rangle\Big|_T = E_0(N) + \sum_{k=1}^{N} k\frac{\omega_f}{2}\left[\coth\left(k\frac{\omega_f}{2T}\right) - 1\right]$$

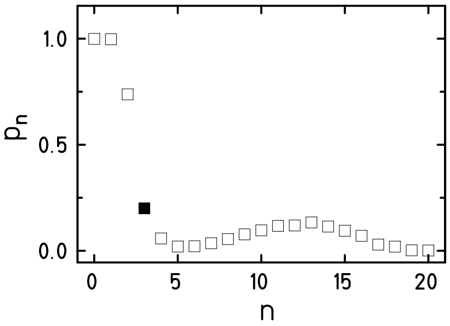
$$\overline{\langle \underset{\sim}{H}_f \rangle} \Rightarrow T_f$$



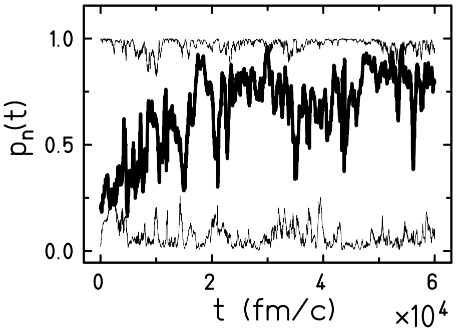
- actual temperatures – dashed lines
- time averaged temperatures – solid lines
- thermometer – thick lines, fermions – thin lines

Fermions in an Oscillator Potential Time Averaging

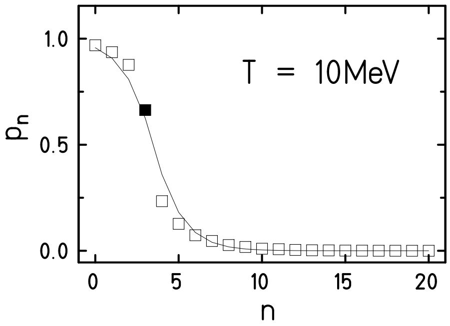
Occupation numbers:



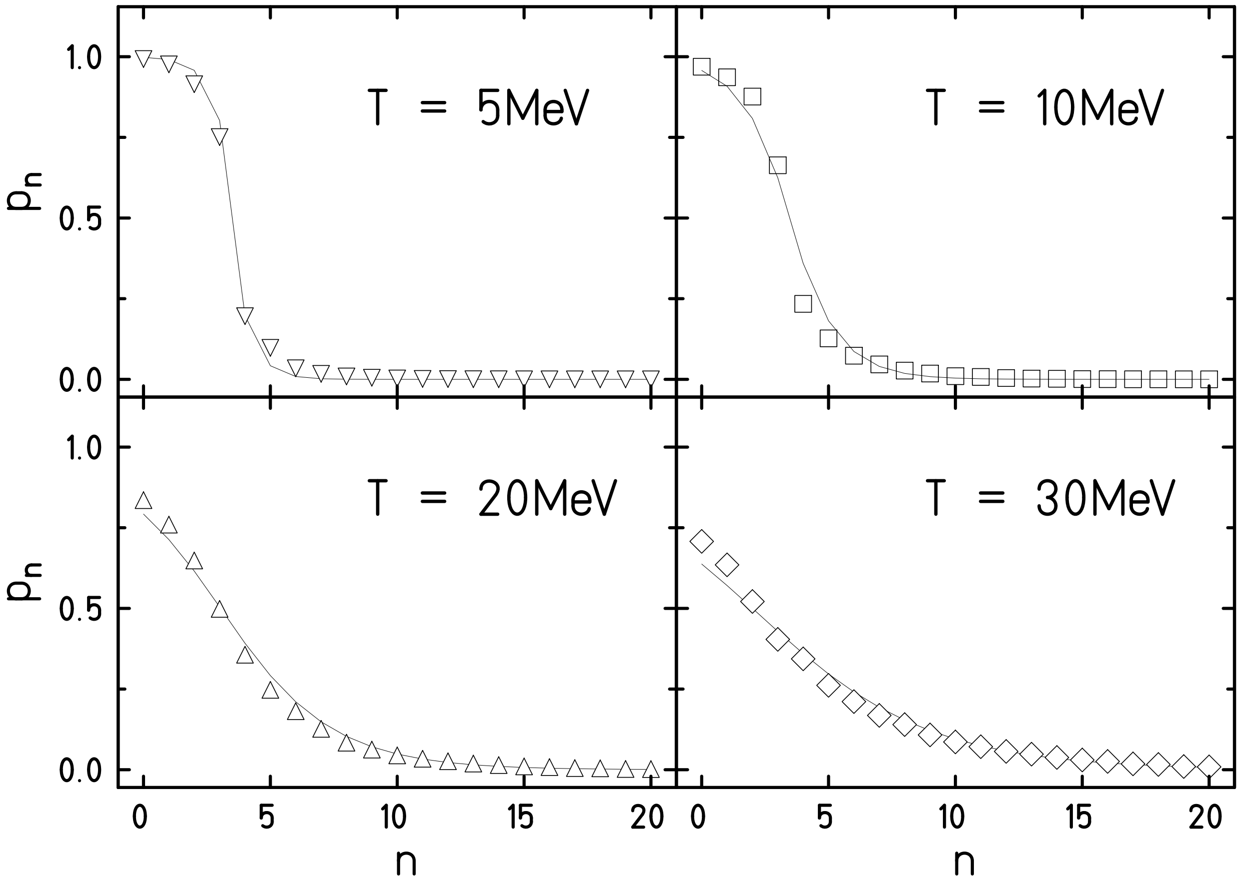
initial state



time evolution ($n = 0, 3, 6$)



time averaged



Mean occupation numbers; time averaged (symbols), canonical ensemble (solid lines)

Summary

Thanks to:

- Hans Feldmeier, GSI, Darmstadt, Germany
- Robert Roth & Thomas Neff, GSI, Darmstadt, Germany

Summary:

- Coupling to a thermometer provides a method to determine thermodynamic properties of (small) quantum systems.
- System and thermometer are described with trial states using the time-dependent variational principle.
- If the system is ergodic, ensemble averages can be replaced by time averages.
- Method works for the toy system of fermions in a common harmonic oscillator potential and for nuclei with reasonable nucleon-nucleon interactions.