NEGATIVE SPECIFIC HEAT IN A THERMODYNAMIC MODEL OF MULTIFRAGMENTATION

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Plateau in caloric curve

$\Downarrow$

Singularity in specific heat

$\Downarrow$

First order phase transition

The claims are :

- under suitable conditions, nuclear systems exhibit negative heat capacities:
- negative heat capacities are obtainable only in the microcanonical ensemble:
- negative heat capacities also appear in canonical models but disappear once the drop size crosses the value ≈ 60.

Thermodynamic Model

- Finite systems: Canonical Model
- Thermodynamic limit: Grandcanonical Model

THE CANONICAL THERMODYNAMIC MODEL

For a system of A identical particles of one kind in an enclosure at temperature T, the canonical partition function is given by:

$$Q_A = \sum \prod_i \frac{\omega_i^{n_i}}{n_i!} \tag{1}$$

n_i : number of composites with i nucleons

ω_i : partition function of the composite with i nucleons.

The above sum is restrictive as the constraint $\sum_i in_i = A$ has to be satisfied.

To compute Q_A we use the recursion relation (derived by Chase and Mekjian):

$$Q_A = \frac{1}{A} \sum_{k=1}^{k=A} k\omega_k Q_{A-k} \tag{2}$$

with $Q_0 = 1$.

The average number of composites of i nucleons is :

$$\langle n_i \rangle = \omega_i \frac{Q_{A-i}}{Q_A} \tag{3}$$

The single pariticle partition function:

$$\omega_k = \frac{V_{fr}}{h^3}(2\pi mT)^{3/2}(k)^{3/2} \times q_k \tag{4}$$

V_{fr} (free volume) = V_{fo} - V_{ex} $\quad (V_{ex} = \frac{A}{\rho_0})$.

The internal partition function q_k:

$$\begin{aligned} q_k &= 1, \quad \text{for} \quad k = 1 \\ &= \exp[(W_0 k - \sigma(T)k^{2/3} + T^2 k/\epsilon_0)/T] \quad \text{for} \quad k \geq 1 \end{aligned} \tag{5}$$

The explicit expression for $\sigma(T)$ used here is:

$$\sigma(T) = \sigma_0[(T_c^2 - T^2)/(T_c^2 + T^2)]^{5/4} \tag{6}$$

with $\sigma_0 = 18$ MeV and $T_c = 18$ MeV.

Using

$$E = T^2 \frac{\partial lnQ_A}{\partial T} \quad \text{and} \quad p = T\frac{\partial lnQ_A}{\partial V}$$

We get

$$\begin{aligned} E &= \sum \langle n_k \rangle \Big[\frac{3}{2}T + k(-W_0 + T^2/\epsilon_0) \\ &\quad + \sigma(T)k^{2/3} - T[\partial\sigma(T)/\partial T]k^{2/3}\Big] \end{aligned} \tag{7}$$

$$p = \frac{T}{V}\sum < n_i > \tag{8}$$

THE SPECIFIC HEAT

$$C = \left(\frac{\partial E}{\partial T}\right)$$

$\longrightarrow$ C_V is ALWAYS positve

but;

$\longrightarrow$ C_p **CAN BE** negative

$$p = m\frac{T}{V} \quad (m = \Sigma\langle n_k\rangle)$$

If one has only monomers:

$$m = A$$

$$\longrightarrow p \text{ decreases , as } V \text{ increases: } (\frac{\partial p}{\partial V} < 0)$$

For an interacting system:

$m << A$ and m increases when V increases (at const. T).

$$\text{If } (\frac{\partial m}{\partial V})_T > \frac{m}{V},$$

then one can have

$\longrightarrow$ p increasing, as V increases: $(\frac{\partial p}{\partial V} > 0)$

Using;

$$\begin{aligned} p &= T\frac{m}{V} = (T+\delta T)\frac{m+\delta m}{V+\delta V} \\ \rightarrow \frac{\delta m}{m} &= \frac{\delta V}{V} - \frac{\delta T}{T} \end{aligned}$$

In the instability region,

$\delta V \rightarrow$ -ve; $\delta T \rightarrow$ +ve: $\Rightarrow \delta m \rightarrow$ -ve

IF, m decreases; E_{kin} and E_{pot} also decrease

$\Rightarrow E_{total}$ decreases, while T increases , at const. p

	T	ρ/ρ_0	e_k/A	e_{pot}/A	e_{tot}/A
$\frac{\partial p}{\partial \rho} < 0$	6.0	0.146	0.978	-5.235	-4.257
	6.1	0.212	0.638	-6.970	-6.332
	6.2	0.392	0.294	-8.708	-8.414
$\frac{\partial p}{\partial \rho} > 0$	6.0	0.104	1.422	-3.271	-1.849
	6.1	0.090	1.653	-2.513	-0.859
	6.2	0.082	1.824	-2.027	-0.202

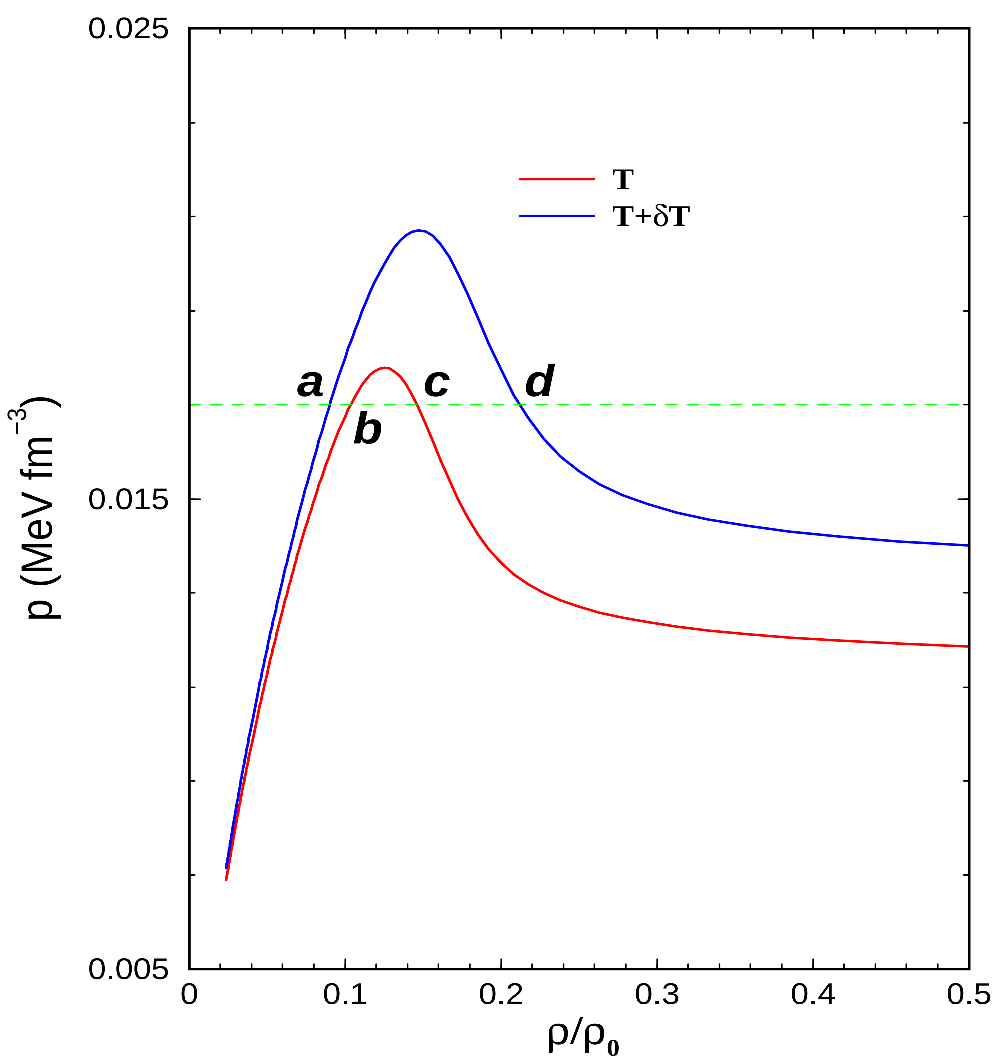

Figure 1: EOS in the canonical model for a system of A=200. The largest cluster also has N=200.

The occurrence of a negative C_p in spite of a positive C_V is allowed in the following well-known relation:

$$C_p - C_V = VT\tfrac{\alpha^2}{\kappa}$$

where α is the volume coefficient expansion and κ is the isothermal compressibility given by:

$$\begin{aligned}\alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\ \kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.\end{aligned}$$

For negative κ, C_p is less than C_V and can become negative.

Using the equality,

$$\left(\tfrac{\partial V}{\partial T}\right)_p = -\left(\tfrac{\partial V}{\partial p}\right)_T\left(\tfrac{\partial p}{\partial T}\right)_p$$

$$C_p - C_V = VT\left(\tfrac{\partial p}{\partial T}\right)_V\tfrac{1}{V}\left(\tfrac{\partial V}{\partial T}\right)_p.$$

This shows that, C_p can drop below C_V if isobaric volume coefficient of expansion becomes negative which is the case in the mechanical instability region.

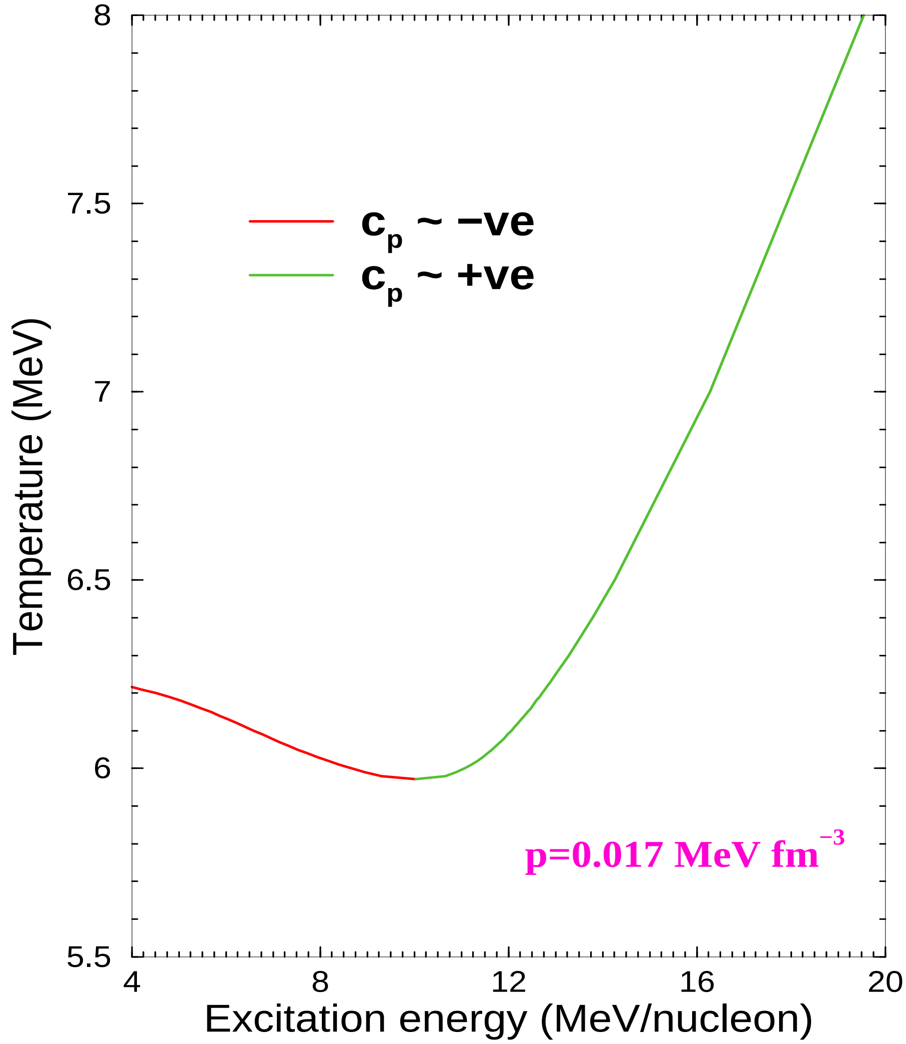

Figure 2: Caloric curve at a constant pressure ($p = 0.017\ MeV\ fm^{-3}$) in the canonical model with A=200 and N=200. The red and green portions of the curve give -ve and +ve c_p respectively.

THE GRAND CANONICAL MODEL

In a grand conical formalism, for a system which is very large but, for which, the heaviest cluster has N nucleons and no more; we need to solve:

$$\rho = \sum_1^N k \exp(k\mu/T)\tilde{\omega}_k \quad (9)$$

where $\tilde{\omega}_i = \omega_i/V$.

Given ρ and T, $\Rightarrow$ μ is found.

Then, $A = \rho V$ where V and A are very large (thermodynamic limit).

The phase space consideration implies that chemical equilibrium exists:

$\Rightarrow \mu_k = k\mu$.

The average number of composites of k nucleons is :

$$\langle n_k \rangle = \frac{V_{fr}}{h^3}(2\pi mT)^{3/2}k^{3/2} \\ exp[\beta(\mu k + W_0 k + T^2 k/\epsilon_0 - \sigma(T)k^{2/3})] \quad (10)$$

Pressure is given by:

$$
\begin{aligned}
p &= (T/V) ln Z_{grand} \\
&= (T/V) \sum \langle n_k \rangle
\end{aligned}
\quad (11)
$$

Use of the grand canonical ensemble always implies that A is very large but N may be large or small.

The mechanical instability which led to negative values of c_p is not only a finite number effect but it is also dependent on details of parameters:

CASE I Consider a system for which $A = 200$, but $N = 100$. That means:

$$\omega_k = \frac{V}{h^3}(2\pi mT)^{3/2}k^{3/2}q_k, \quad \text{for} \quad k \leq 100$$
$$= 0, \quad \text{for} \quad k > 100$$

CASE II Even the mechanical instability region dissapears with the following minimal change:

$$q_k = \exp[(W_0k - \sigma(T)k^{2/3} + T^2k/\epsilon_0)/T], \quad \text{for} \quad k \leq 100$$
$$= \exp[0.97 \times (W_0k - \sigma(T)k^{2/3} + T^2k/\epsilon_0)/T], \quad \text{for} \quad k > 100$$

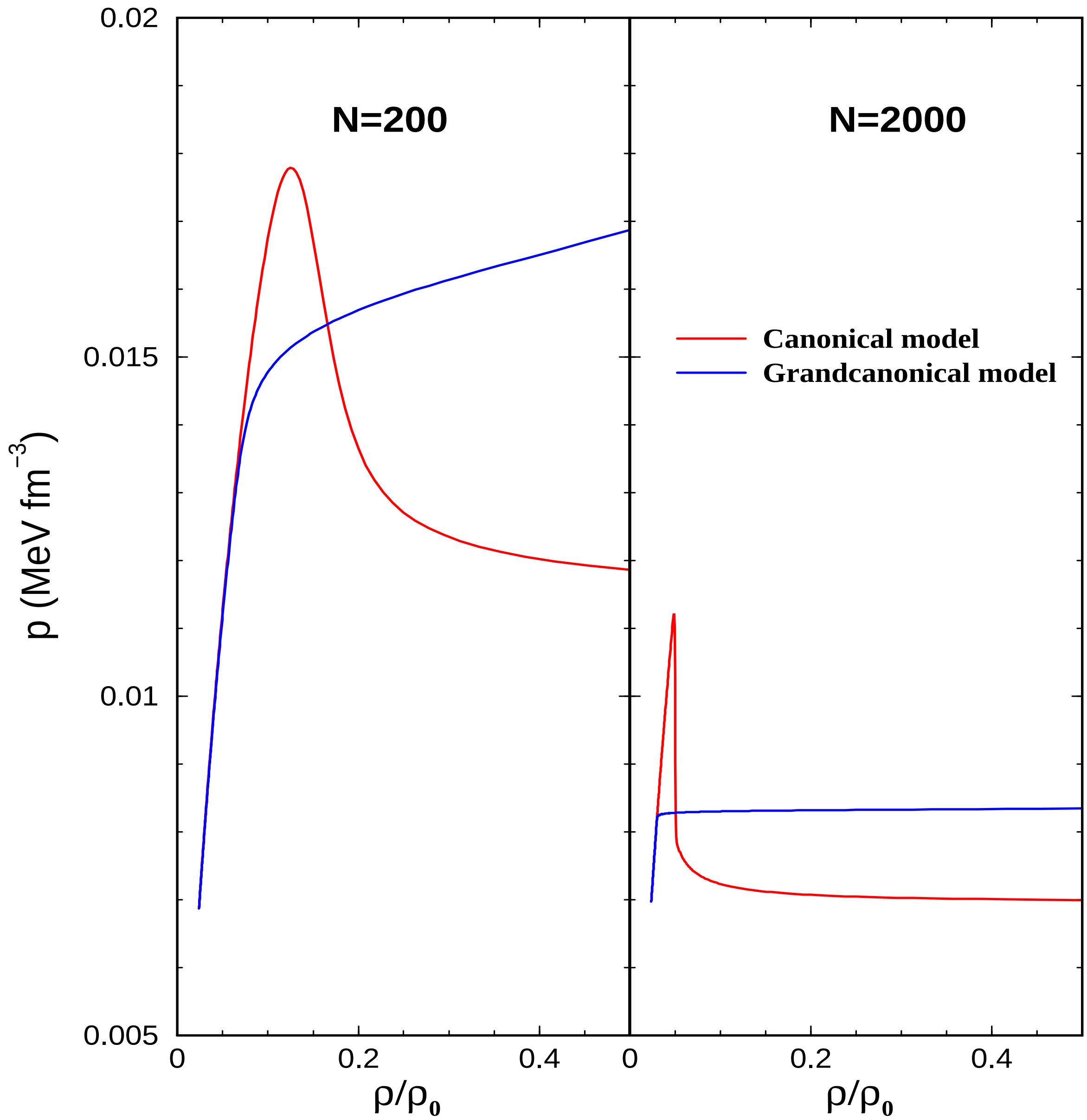

Figure 3: EOS at $T = 6\ MeV$ in the two models. For the left panel the largest cluster has N=200 and for the right panel N=2000. For the canonical calculation, the left and right panel has A=200 and 2000 respectively, but for the grandcaonocal calculations, $A = \infty$.

SUMMARY

- We have shown that with usual concepts one can obtain a negative value of C_p in part of the $T - E$ plane within the framework of a thermodynamic model.

- The C_V is positive and its origin is the cost in surface energy to break large clusters into smaller clusters and nucleons.

- A negative C_p is seen in our exactly soluble canonical ensemble model for small systems. This negative value arises in regions of mechanical instability where the isothermal compressiblity is negative or equivalently, the isobaric volume expansion coefficient is negative.

- For larger systems these regions disappear and in the grand canonical limit, C_p is always positive.

- The mechanical instability which led to negative values of C_p is not only a finite number effect but also dependent on details of parameters of the model.

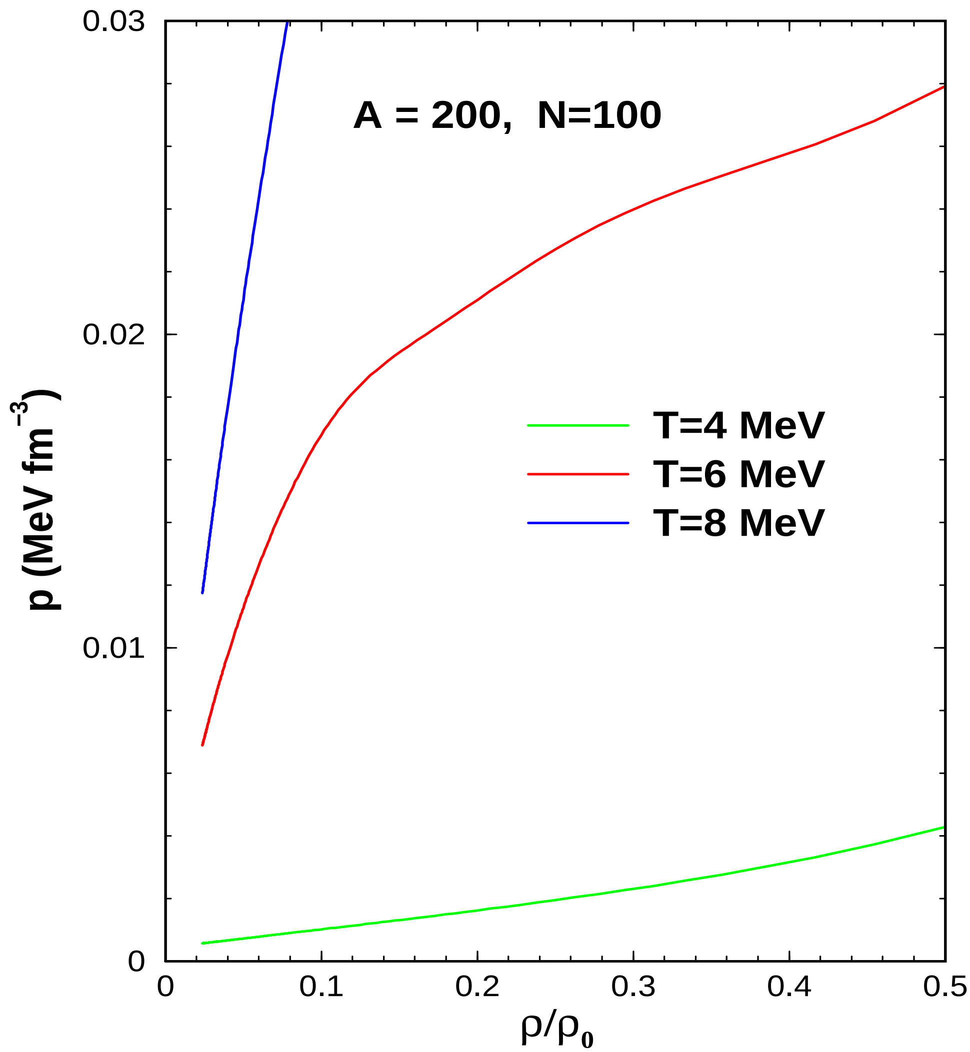

Figure 4: EOS in the canonical model for a system of 200 particles, but the number of nucleons of the largest cluster is restricted to 100.