# Partition function of the perfect gas of clusters model for interacting fluids

**Grzegorz Siudem**,
Faculty of Physics, Warsaw University of Technology,
Koszykowa 75, PL-00-662 Warsaw, Poland

## Outline

The last papers of A. Fronczak [1, 2] present a new, combinatorial approach to the perfect gas of clusters model of interacting fluids. This poster presents, an exact proof of one of the important assertions from [1]. The assertion states that for the canonical system in which one can distinguish $k$ non-interacting clusters the partition function is given by the adequate Bell polynomial.

## Notation

Let us consider a system of $N$ interacting particles. It can be shown that the grand partition function can be written as

$$\Xi(\beta,\, z) = \sum_{\Omega} e^{-\beta(E(\Omega)-\mu N(\Omega))} = 1 + \sum_{N=1}^{\infty} z^N Z(\beta,\, N), \qquad (1)$$

where $z = e^{\beta\mu}$ is fugacity and $Z(\beta,\, N)$ is the partition function

$$Z(\beta,\, N) = \sum_{\Omega} e^{-\beta E(\Omega)} = \int_0^{\infty} g(E, N) e^{-\beta E} dE. \qquad (2)$$

We introduce functions $f(k, E)$ - probability distributions that the considered system, having energy $E$ consists of $k$ disjoint clusters.

$$\sum_{k=1}^{N} f(k, E) = h(E) \equiv 1. \qquad (3)$$

## Bell polynomials

Incomplete Bell polynomials [3] are given by expression below

$$B_{N,k}(\{\phi_n(\beta)\}) = N! \sum \prod_{n=1}^{N-k+1} \frac{1}{c_n!} \left(\frac{\phi_n(\beta)}{n!}\right)^{c_n}, \qquad (4)$$

where the summation takes place over all integers $c_n \geq 0$, such that $\sum_n c_n = k$ and $\sum_n n c_n = N$. In fact this is the summation over all possible partitions of the set of $N$ elements into $k$ disjoint, non-empty clusters. It was shown [1] that

$$Z(\beta,\, N) = \sum_{k=1}^{N} \int_0^{\infty} f_N(k, E) g(E, N) e^{-\beta E} dE = \\ = \sum_{k=1}^{N} \frac{(-\beta)^k}{N!} B_{N,k}(\{\phi_n(\beta)\}).$$

## Theorem

Let us consider the canonical system of $N$ interacting particles, at the temperature $T$ ($\beta = \frac{1}{k_B T}$). We assume that one can distinguish in the system $1 \leqslant k \leqslant N$ non-interacting clusters, which may have different sizes. In such a configuration, with a given number of clusters $k$, the partition function of the system $Z_k(\beta,\, N)$ is given by

$$Z_k(\beta,\, N) = \frac{1}{N!} B_{N,k}(\{w_n(\beta)\}), \qquad (5)$$

where $w_n(\beta) = -\beta\phi_n(\beta)$, and $\phi_n(\beta)$ is $n$-th derivative of the grand thermodynamic potential.

## Proof

We prove Theorem by the induction with respect to $N$.The basis step for $N = 2$ holds

$$Z_1(\beta,\, 2) + Z_2(\beta,\, 2) = \frac{1}{2} B_{2,1}(\{w_n(\beta)\}) + \frac{1}{2} B_{2,2}(\{w_n(\beta)\}) = \\ = w_2(\beta) + w_1^2(\beta), \qquad (6)$$

where appropriate Bell polynomials are written out explicitly. On the other hand, note that the following equation is true

$$w_1^2(\beta) = \frac{1}{2} B_{2,2}(\{w_n(\beta)\}) = \frac{1}{2} (Z_1(\beta,\, 1))^2 = Z_2(\beta,\, 2), \qquad (7)$$

Eqs. (6) and (7) gives the basis step for $N = 2$.
The statement which we want to prove looks as follows

$$P(N): \quad \forall_{k=1,\dots,N} \quad Z_k(\beta,\, N) = \frac{1}{N!} B_{N,k}(\{w_n(\beta)\}). \qquad (8)$$

From the fact, that clusters do not interact, the partition function can be written as follows

$$Z_k(\beta,\, N) = \int_0^{\infty} f_N(k, E) g(E, N) e^{-\beta E} dE = \\ = \frac{1}{N!} B_{N,k}(\{Z_1(\beta,\, n)\}). \qquad (9)$$

## Proof - continuation

Using statements $P(m)$, for $m = 1, \dots, N-1$, one may rewrite Eq. (9) into the following form

$$Z_k(\beta,\, N) = \frac{1}{N!} B_{N,k}(\{Z_1(\beta,\, n)\}) = \qquad (10) \\ = \frac{1}{N!} B_{N,k}\left(B_{1,1}(\{w_n(\beta)\}), \dots, B_{N-1,1}(\{w_n(\beta)\}), Z_1(\beta,\, N)\right).$$

From the fact that that $B_{m,1}(\{x_n\}) = x_m$ one can obtain

$$Z_k(\beta,\, N) = \frac{1}{N!} B_{N,k}\left(\{w_1(\beta), \dots, w_{N-1}(\beta), Z_1(\beta,\, N)\}\right).$$

This proves the statement $P(N)$ for $k = 2, 3, \dots, N$.

$$Z_1(\beta,\, N) = \sum_{k=1}^{N} Z_k(\beta,\, N) - \sum_{k=2}^{N} Z_k(\beta,\, N) = \\ = \frac{1}{N!} \sum_{k=1}^{N} B_{N,k}(\{w_n(\beta)\}) - \frac{1}{N!} \sum_{k=2}^{N} B_{N,k}(\{w_n(\beta)\}),$$

Finally we get

$$Z_k(\beta,\, N) = \frac{1}{N!} B_{N,k}\left(w_1(\beta), w_2(\beta), \dots, w_{N-1}(\beta), w_N(\beta)\right),$$

for $k = 1, \dots, N$, which proves induction step $P(N)$. ■

## Example

Let us consider case $k = 1$ - there is only one cluster consisting of all $N$ particles which can interact each other.

$$Z(\beta,\, N) = Z_1(\beta,\, N) = \frac{(-\beta)}{N!} B_{N,1}(\{\phi_n(\beta)\}) = \\ = -\frac{\beta}{N!} \phi_N(\beta) = -\frac{\beta}{N!} \frac{\partial^N \Phi(\beta,\, z)}{\partial z^N}\bigg|_{z=0}.$$

## References


- Agata Fronczak, Phys. Rev. E, **86**, 041139-041145, (2012).
- Agata Fronczak, Phys. Rev. E, **87**, 022131-022138, (2013).
- Herbert S. Wilf, "Generatingfunctionology", Academic, New York, (1990).