

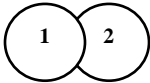
## **A DYNAMICAL DERIVATION OF THE EQUILIBRIUM** **VIRIAL EXPANSION**

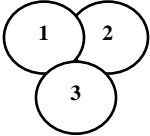
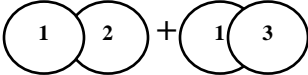
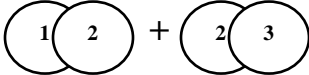
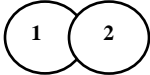
**1877**      Boltzmann:  $S = k \ln W$

**1910**      Einstein: “Usually,  $W$  is put equal to the number of complexions. “[However,] in order to calculate  $W$ , one needs a *complete* [deterministic] *molecular-mechanical theory* of the system under consideration.”

**The virial expansion of the pair distribution function in equilibrium for short-range particle interactions**

$$f_2^e(\mathbf{x}_1, \mathbf{x}_2; \beta) = f_2^e(\bar{\mathbf{q}}_1, \bar{\mathbf{p}}_1, \bar{\mathbf{q}}_2, \bar{\mathbf{p}}_2; \beta) =$$

$$= n^2 e^{-\beta \Phi_2(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_2)} f_1^e(\mathbf{p}_1; \beta) f_1^e(\mathbf{p}_2; \beta) +$$


$$+ n^3 \int_V d\bar{\mathbf{q}}_3 \left[ e^{-\beta \Phi_3(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_2, \bar{\mathbf{q}}_3)} - e^{-\beta \{\Phi_2(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_2) + \Phi_2(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_3)\}} - e^{-\beta \{\Phi_2(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_2) + \Phi_2(\bar{\mathbf{q}}_2, \bar{\mathbf{q}}_3)\}} + e^{-\beta \Phi_2(\bar{\mathbf{q}}_1, \bar{\mathbf{q}}_2)} \right] \bullet$$





$$\bullet f_1^e(\mathbf{p}_1; \beta) f_1^e(\mathbf{p}_2; \beta) f_1^e(\mathbf{p}_3; \beta) + O(n^4); n = \frac{N}{V}.$$

$$f_1^e(\mathbf{p}; \beta) = c e^{-\beta p^2 / 2m}, \text{ with } c = (2\pi m / \beta)^{-3/2}$$

**(Ursell expansion)**

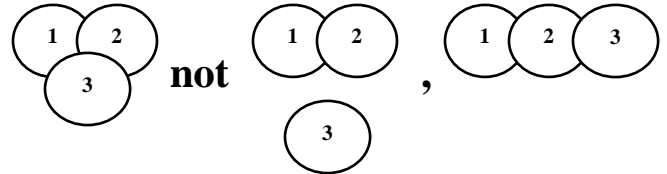
**Structure of inclusion-exclusion principle of set theory.**

Ad the integrand of  $n^3 \int_V d\vec{q}_3 [\dots]$ :

$$\left[ e^{-\beta\Phi_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)} - e^{-\beta\{\Phi_2(\vec{q}_1, \vec{q}_2) + \Phi_2(\vec{q}_1, \vec{q}_3)\}} - e^{-\beta\{\Phi_2(\vec{q}_1, \vec{q}_2) + \Phi_2(\vec{q}_2, \vec{q}_3)\}} + e^{-\beta\Phi_2(\vec{q}_1, \vec{q}_2)} \right]$$

1. This integrand has the *cluster property*, i.e., it *vanishes* for *separated* particle configurations, if not all three particles interact with each other.

2. Therefore, the integrand includes only *genuine* three-particle interactions or *overlaps*:



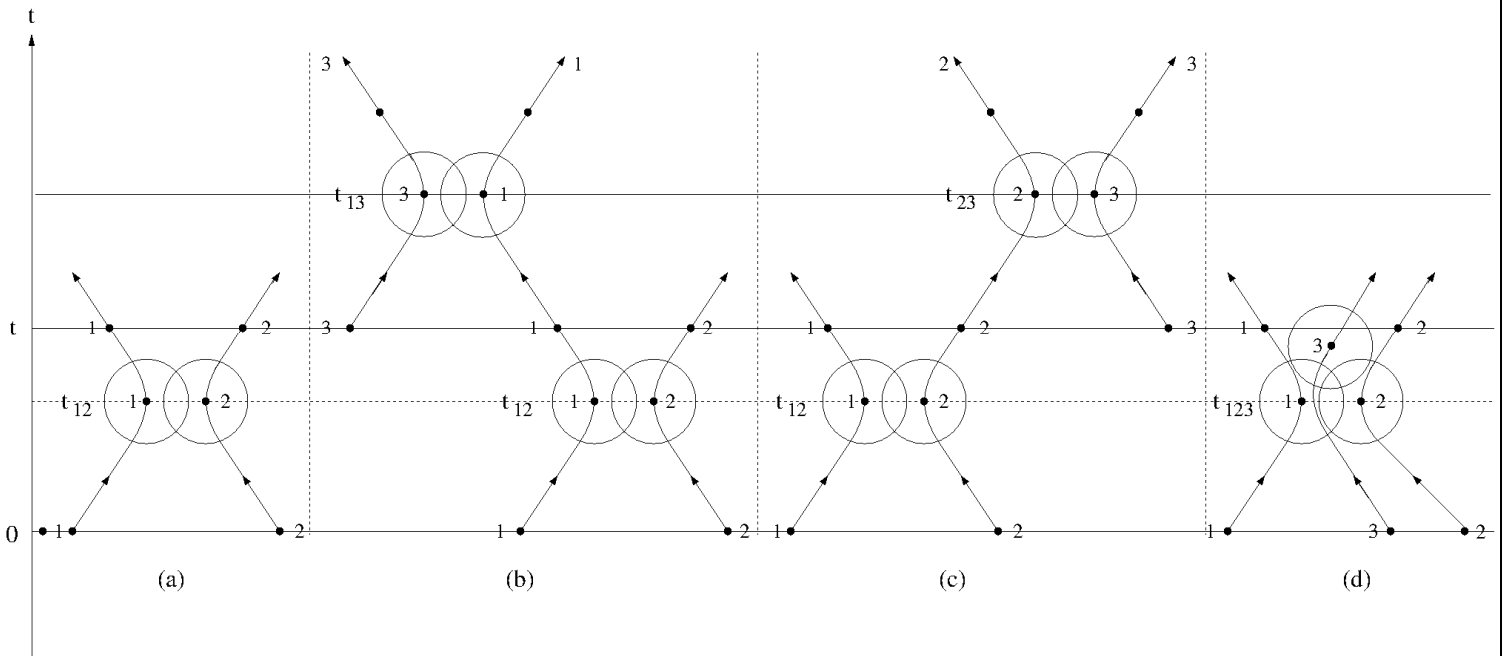
## The virial expansion of the pair distribution function in non-equilibrium

The density expansion of the *non-equilibrium* pair distribution function – i.e. the density to find in phase space two particles in the phases  $\mathbf{x}_1 = \bar{\mathbf{q}}_1, \bar{\mathbf{p}}_1$  and  $\mathbf{x}_2 = \bar{\mathbf{q}}_2, \bar{\mathbf{p}}_2$  – is for short-range forces:

$$f_2^{\text{ne}}(\mathbf{x}_1, \mathbf{x}_2; t) = n^2 S_{-t}(\mathbf{x}_1, \mathbf{x}_2) f_1^{\text{ne}}(\mathbf{x}_1; t) f_1^{\text{ne}}(\mathbf{x}_2; t) +$$

$$+ n^3 \int d\mathbf{x}_3 [S_{-t}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) - S_{-t}(\mathbf{x}_1, \mathbf{x}_2) S_{-t}(\mathbf{x}_1, \mathbf{x}_3) - S_{-t}(\mathbf{x}_1, \mathbf{x}_2) S_{-t}(\mathbf{x}_2, \mathbf{x}_3) + S_{-t}(\mathbf{x}_1, \mathbf{x}_2)] \cdot$$

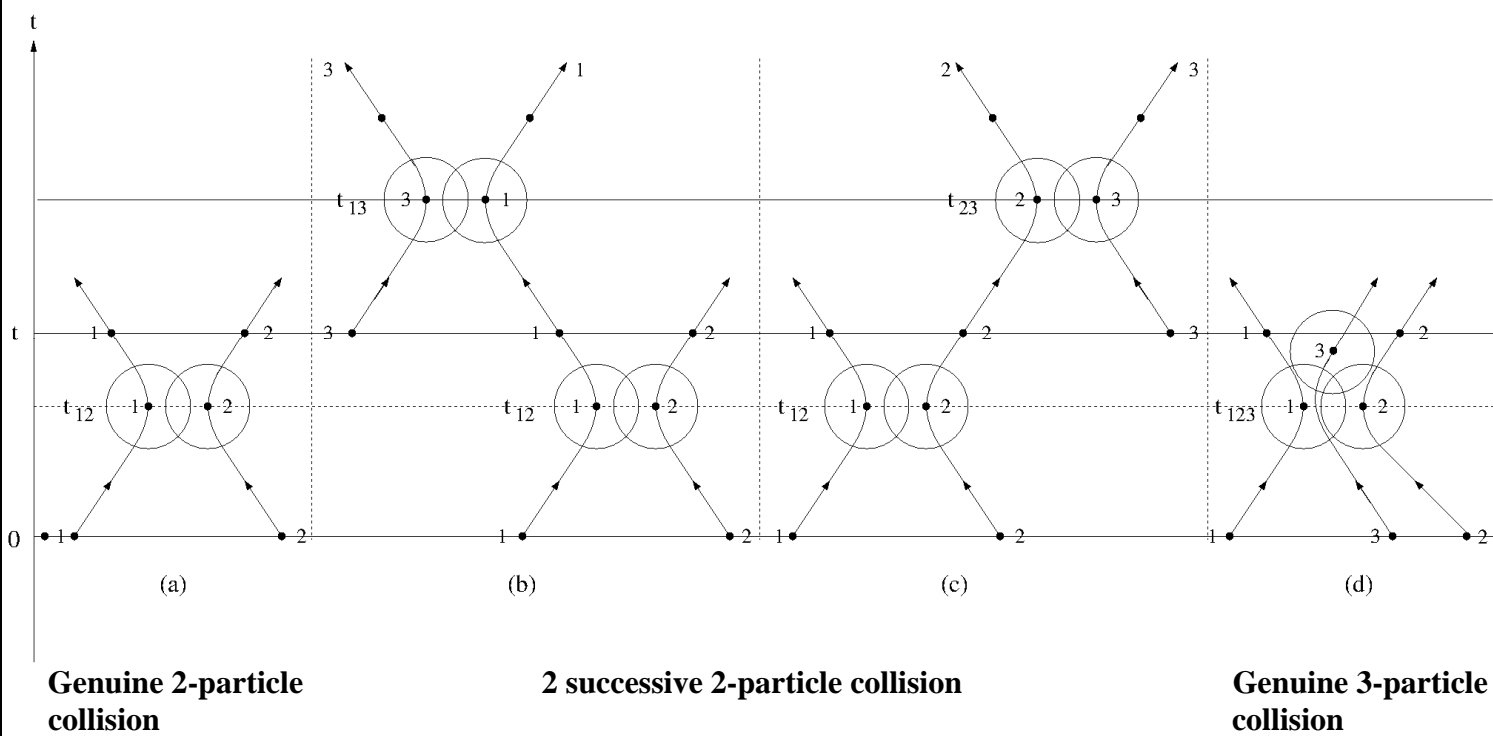
$$\cdot f_1^{\text{ne}}(\mathbf{x}_1; t) f_1^{\text{ne}}(\mathbf{x}_2; t) f_1^{\text{ne}}(\mathbf{x}_3; t) + O(n^4) \quad \text{with} \quad f_1^{\text{ne}}(\mathbf{x}_1; t) \equiv f_1^{\text{ne}}(\mathbf{x}_1(t)).$$



**Genuine 2-particle collision**

**2 successive 2-particle collision**

**Genuine 3-particle collision**



## Properties of the Streaming Operators

1. The streaming operator  $S_{-t}(x_1(t), \dots, x_s(t))$  transforms the phases  $x_i(t) \equiv (\bar{q}_i(t), \bar{p}_i(t))$  of  $s$ -particles at time  $t$ , into those at an *earlier* time  $t = 0$ ,  $S_{-t}(x_1(t), \dots, x_s(t)) = (x_1(0), \dots, x_s(0))$ .

2. The streaming operators in the 3-particle integrand have the same cluster property as the Boltzmann factors in equilibrium. Therefore, in general for  $s$ -particles, only *genuine*  $s$ -particle (dynamical) collisions contribute to the integral ( $s = 2, 3, \dots$ ).

3. At  $t = 0$ :  $f_s^{\text{ne}}(x_1, \dots, x_s; 0) = \prod_{i=1}^s f_1^{\text{ne}}(x_i; 0)$ , (no correlations).

(Generalizations of Boltzmann's Stoszahl Ansatz)

## Derivation of $f_2^e(x_1, x_2; \beta)$ from $f_2^{ne}(x_1, x_2; t)$

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**Four steps:**

$$1. \quad f_1^{ne}(\vec{q}, \vec{p}; t) \rightarrow f_1^e(p; \beta) ; f_s^{ne}(x_1, \dots, x_s; t) \rightarrow \prod_{i=1}^s f_1^e(p_i; \beta)$$

$$2. \quad \text{At } t = 0: \quad \prod_{i=1}^s f_1^e(p_i(0); \beta) \rightarrow c^s e^{-\beta T_s(p_1(0), \dots, p_s(0))}$$

$$\text{with } T_s(p_1(0), \dots, p_s(0)) = \sum_{i=1}^s \frac{p_i^2(0)}{2m} \quad (\text{separated configuration})$$

3. Use the cluster property: only genuine dynamical  
s-particle collisions contribute to  $f_2^{ne}(x_1, x_2; t)$ .

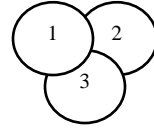
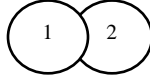
4. Conservation of initial kinetic energy for all  $t > 0$ .

In particular for  $t = t_{\text{coll}}$ :

$$\begin{aligned} T_s(p_1(0), \dots, p_s(0)) &\rightarrow T_s(p_1, \dots, p_s) + \Phi_s(\vec{q}_1, \dots, \vec{q}_s) \\ &= H_s(\vec{q}_1, \dots, p_s) \end{aligned}$$

a. One obtains then:

$$f_2^e(\mathbf{x}_1, \mathbf{x}_2; \beta) = n^2 c^2 e^{-\beta H_2(\mathbf{x}_1, \mathbf{x}_2)} + n^3 c^3 \int' d\mathbf{x}_3 e^{-\beta H_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)} + O(n^4),$$



where only *genuine* overlaps of the two or three particles are included, as indicated by the prime.

b. Here:  $H_2(\mathbf{x}_1, \mathbf{x}_2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \Phi_2(\vec{q}_1, \vec{q}_2)$

and  $H_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2m} + \Phi_3(\vec{q}_1, \vec{q}_2, \vec{q}_3)$

c. The general term is:  $n^s c^s \int' d\mathbf{x}_1, \dots, \int' d\mathbf{x}_s e^{-\beta H_s(\mathbf{x}_1, \dots, \mathbf{x}_s)}.$



**b. For a thermodynamic property, like the pressure  $p$ , one obtains the virial expansion:**

$$p = nkT \left[ 1 + n \int_V d\vec{q}_2 \left\{ e^{-\beta \Phi_2(\vec{q}_1, \vec{q}_2)} - 1 \right\} \right] + O(n^3) =$$

$$\int_V' d\vec{q}_2 e^{-\beta \Phi_2(\vec{q}_1, \vec{q}_2)}$$

**Here the cluster property follows for configurations, where**

$$r_{12} = |\vec{q}_1 - \vec{q}_2| > \text{range of the interparticle potential.}$$

**Ehrenfest would have said: “I told you so”, since he wrote:  
“If one has two different derivations of the same result, one can  
use two legs instead of one”, i.e. one walks instead of limps.**