

Расчет конфигурационного интеграла для реальных газов



$$Z_V = \int \int \int \dots_q e^{-\frac{\sum_{ij} U_{ij}}{kT}} dq \dots = \int \int \int \dots_q \left(\prod_{ij} e^{-\frac{U_{ij}}{kT}} \right) dq \dots \quad (1)$$

$$e^{-\frac{U_{ij}}{kT}} = 1 + f_{ij}$$

$$\begin{aligned} Z_V &= \int \int \int \dots_q \left(\prod_{ij} e^{-\frac{U_{ij}}{kT}} \right) dq \dots = \int \int \int \dots_q \left(\prod_{ij} (1 + f_{ij}) \right) dq \dots = \\ &= \int \int \int \dots_q \left(1 + \sum_{i,j} f_{ij} + \sum_{ij,kl} f_{ij} f_{kl} \dots \right) dq \dots \end{aligned} \quad (2)$$

$$Z_V \approx \int \int \int \dots_q \left(1 + \sum_{ij} f_{ij} \right) dq \dots$$

$$\begin{aligned} Z_V &= \int \int \int \dots_q \left(1 + \sum_{ij} f_{ij} \right) dq \dots = V^N + V^{N-2} \iint_q \sum_{ij} f_{ij} dq_i dq_j = \\ &V^N + V^{N-2} \frac{N^2}{2} \iint_q f_{ij} dq_i dq_j \end{aligned} \quad (3)$$

$$r_{ij} = q_j - q_i; \quad dr_{ij} = dq_j$$

$$\int \int \int_{q \dots} f_{ij} dq_{i,x} dq_{i,y} dq_{i,z} dq_{j,x} dq_{j,y} dq_{j,z} = V \int \int \int_r f_{ij} dr_{ij,x} dr_{ij,y} dr_{ij,z} \quad (4)$$

$$dr_{ij,x} dr_{ij,y} dr_{ij,z} = r^2 dr \sin \theta d\theta d\varphi$$

$$\int \int \int_r f_{ij} dr_{ij,x} dr_{ij,y} dr_{ij,z} = \int \int \int_{r,\theta,\varphi} f_{ij} r^2 dr \sin \theta d\theta d\varphi$$

$$r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi = 2 \times 2\pi r^2 dr = 4\pi r^2 dr$$

$$Z_V = V^N + V^{N-1} \frac{N^2}{2} \int_0^\infty f_{ij} 4\pi r^2 dr \quad (5)$$

$$Z_V = V^N + V^N \frac{N^2}{2V} \beta = V^N \left(1 + \frac{N^2}{2V} \beta \right) \quad (6)$$

$$\ln Z_V = N \ln V + \ln \left(1 + \frac{N^2}{2V} \beta \right) = N \ln V + \frac{N^2}{2V} \beta \quad (7)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{NkT}{V} - \frac{kTN^2\beta}{2V^2}; \quad (8)$$

$$\frac{pV}{RT} = 1 - \frac{N\beta}{2V}$$

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \dots$$

$$B(T) = -\frac{N\beta}{2} = -\frac{N}{2} \int_0^\infty f_{ij} 4\pi r^2 dr = 2\pi N \int_0^\infty \left(1 - e^{-\frac{U_{ij}}{kT}}\right) r^2 dr \quad (9)$$

$$U_{ij} = \infty \text{ при } 0 \leq r < r_0 \text{ и } U_{ij} = -c/r^6 \text{ при } r_0 \leq r < \infty \quad (10)$$

$$f_{ij} = \exp(-U_{ij}/kT) - 1 = \exp\left(\frac{c}{kT*r^6}\right) - 1 \text{ при } r_0 \leq r < \infty \quad (11)$$

$$f_{ij} = \frac{c}{kT*r^6}$$

$$0 \leq r < r_0; \int_0^{r_0} f_{ij} 4\pi r^2 dr = -\frac{4}{3} \pi r_0^3 \quad (12)$$

$$\begin{aligned}
r_0 \leq r < \infty; \int_{r_0}^{\infty} f_{ij} 4\pi r^2 dr &= \int_{r_0}^{\infty} \frac{c^* 4\pi r^2}{r^6 kT} dr = \frac{4\pi c}{kT} \int_{r_0}^{\infty} \frac{1}{r^4} dr = \\
&= -\frac{4\pi c}{kT} \frac{1}{3} \times \frac{1}{r^3} \Big|_{r_0}^{\infty} = \frac{4\pi c}{3kT} \times \frac{1}{r_0^3}
\end{aligned} \tag{13}$$

$$\beta = \int_0^{\infty} f_{ij}^* 4\pi r^2 dr = -\frac{4}{3} \pi r_0^3 + \frac{4\pi c}{3kT r_0^3} \tag{14}$$

$$\ln Z_V = N \ln V + \frac{N^2 * \left(-\frac{4}{3} \pi r_0^3 + \frac{4\pi c}{3kT r_0^3} \right)}{2V} \tag{15}$$

$$p = kT \left(\frac{\partial \ln Z_V}{\partial V} \right)_T = \frac{NkT}{V} - \frac{kTN^2 * \left(-\frac{4}{3} \pi r_0^3 + \frac{4\pi c}{3kT r_0^3} \right)}{2V^2} \tag{16}$$

$$\frac{pV}{RT} = 1 - \frac{N * \left(-\frac{4}{3} \pi r_0^3 + \frac{4\pi c}{3kT r_0^3} \right)}{2V} \tag{17}$$

$$B(T) = 2\pi N * \left(\frac{r_0^3}{3} - \frac{c}{3kT r_0^3} \right) = b_w - \frac{a_w}{RT} \tag{18}$$

$$b_w = \frac{2\pi N r_0^3}{3}; a_w = \frac{2\pi N^2 c}{3r_0^3} \quad (19)$$

$$\left(p + \frac{2\pi c N^2}{3r_0^3 V^2}\right) * \left(V - \frac{2\pi N r_0^3}{3}\right) = RT \quad (20)$$