Bull. Fac. Educ., Nagasaki Univ.: Natural Science No.76, 1~7 (2008. 3)

On the coefficients of the virial expansion of the state equation of an imperfect gas

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(Received October 31, 2007)

Abstract

After the review on the virial expansion of an imperfect gas, several combinatorial relations among the coefficients of the virial expansion are discussed.

1 Virial expansion of an imperfect gas

The state sum or partition function Z_N of an imperfect gas with N molecules in the classical approximation is given by the following:

$$Z_N := \sum_l e^{-E_l/kT} = \int_0^\infty e^{-E/kT}\Omega(E)dE.$$

Here the density function Ω is

$$\Omega(E)\Delta E := \frac{1}{N!h^{3N}} \int \cdots \int_{E-\Delta E \leq H \leq E} dp_1 \dots dp_N dq_1 \dots dq_N,$$

where $q_i = (x_i, y_i, z_i)$ is the coordinate of the i-th molecule with mass m, $p_i = (\dot{x}_i, \dot{y}_i, \dot{z}_i)$ is the momentum and $dq_i = dx_i dy_i dz_i$, $dp_i = d\dot{x}_i d\dot{y}_i d\dot{z}_i$. The

Hamiltonian H of an imperfect gas is of the form:

$$H = H(p,q) = \frac{1}{2m}\sum_{j=1}^{N} {p_j}^2 + U(q) = \frac{1}{2m}\sum_{j=1}^{N}({\dot{x}_j}^2 + {\dot{y}_j}^2 + {\dot{z}_j}^2) + U(q)$$

with potential of the interaction between 2 molecules:

$$U(q) = \sum_{1\le i<j\le N} u(r_{ij}), \quad r_{ij} = |q_i - q_j|.$$

Then

$$Z_N = \frac{1}{N!h^{3N}}\int\cdots\int e^{-H(p,q)/kT} dp_1 \dots dp_N dq_1 \dots dq_N$$

$$= \frac{1}{h^{3N}}\int\cdots\int e^{-\sum p_j^2/2mkT} dp_1 \dots dp_N \frac{1}{N!}\int\cdots\int e^{-U(q)/kT} dq_1 \dots dq_N$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \frac{Q_N}{N!}$$

where

$$Q_N = \int\cdots\int e^{-\beta U(q)} dq_1 \dots dq_N, \quad \beta = \frac{1}{kT}$$

is the configurational state sum. We will expand the configurational state sum after Ursell and Mayer-Mayer [4] as:

$$e^{-\beta U(q)} = \prod_{i<j} e^{-\beta u(r_{ij})} = \prod_{i<j}(1 + f_{ij}) = 1 + \sum f_{ij} + \sum f_{ij} f_{kl} + \cdots,$$

where we put $f_{ij} = f(r_{ij})$, $f(r) = e^{-\beta u(r)} - 1$ is the Mayer function. The last sums are looked upon running through all the graphs with N vertices. We can devide the concluding integrals according to the connected component, that is the cluster of molecules, of the graphs.

Introduce the cluster integral:

$$b_l' = Vb_l l! := \int\cdots\int {\sum}' \prod_{1\le i<j\le l} f_{ij}\; dq_1 \dots dq_l, \ (l > 1), \quad b_0 = 0, \ b_1 = 1$$

where V is the volume of the system and the sum $\sum'$ runs over all the connected graphs of vertices ①,...,ⓛ which are molecules, with edges f_{ij} which indicate the interactions. Then we have the Ursell expansion:

$$\frac{Q_N}{N!} = \frac{1}{N!}\sum_{\mu=(1^{m_1}2^{m_2}\dots)\vdash N} P(\mu)\prod_{l\ge1}(Vb_l l!)^{m_l} = \sum_{\mu=(1^{m_1}2^{m_2}\dots)\vdash N}\prod_{l\ge1}\frac{(Vb_l)^{m_l}}{m_l!}$$

where

$$P(\mu) = P(1^{m_1}, 2^{m_2}, \ldots) = \frac{N!}{\prod_{l\geq 1} l!^{m_l} m_l!} \quad (\mu = (1^{m_1}, 2^{m_2}, \ldots) \vdash N \ \therefore\ N = \sum_{l\geq 1} l m_l)$$

is the number of graphs of N vertices those have m_l clusters of l vertices ($l \geq 1$). The grand state sum ($T - \mu$ partition function) $\Xi := \sum_{N=0}^{\infty} \lambda^N Z_N$, $\lambda := e^{\mu/kT}$ is now calculated by

$$\begin{aligned}
\Xi &= \sum_{N=0}^{\infty} \lambda^N \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \sum_{\mu=(1^{m_1} 2^{m_2} \ldots)\vdash N} \prod_{l\geq 1} \frac{(Vb_l)^{m_l}}{m_l!} \\
&= \prod_{l=0}^{\infty} \sum_{m_l=0}^{\infty} \left(\lambda^l \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3l}{2}} Vb_l\right)^{m_l} \frac{1}{m_l!} \\
&= \prod_{l=0}^{\infty} \exp(Vb_l z^l) = \exp\left(V \sum_{l\geq 0} b_l z^l\right)
\end{aligned}$$

where $z := \lambda(2\pi mkT/h^2)^{3/2}$ is the fugacity. We get

$$\ln \Xi = V \sum_{l\geq 0} b_l z^l.$$

By thermodynamic identities:

$$N = kT \frac{\partial}{\partial \mu} \ln \Xi(T, V, \mu), \quad p = \frac{kT}{V} \ln \Xi,$$

we have 2 basic formula of an imperfect gas:

$$\frac{1}{v} := \frac{N}{V} = \sum_l l b_l z^l, \quad p = kT \sum_l b_l z^l.$$

Introduce the irreducible integral:

$$\beta_k' = V\beta_k k! := \int \cdots \int \sum' \prod_{1\leq i<j\leq k+1} f_{ij}\, dq_1 \ldots dq_{k+1}$$

where $\sum'$ runs over connected graphs with $k+1$ vertices ①,..., $\textcircled{k+1}$ those have no cut point. The irreducible integral β'_k is looked upon as more fundamental object than the cluster integral b_l, as so is block than a connected graph. Then Mayer-Mayer [4] and Husimi [1] showed the virial expansion:

$$p = \frac{kT}{v}\left(1 - \sum_{j=1}^{\infty} \frac{j}{j+1}\frac{\beta_j}{v^j}\right)$$

that is the equation of state of an imperfect gas, and relations between the cluster integral b_l and the irreducible integral β_k:

$$l^2 b_l = \sum_{(1^{m_1}2^{m_2}\ldots)\vdash l-1} \prod_{j\geq 1} \frac{(l\beta_j)^{m_j}}{m_j!}.$$

Present note gives further relations among the quantities by using the generating function of Husimi.

2 Relations

In order to deduce the above formula, Mayer-Mayer [4] gave a concrete combinatorial argument and Husimi [1] made use of generating function by showing the following identities:

$$z = \exp(-\varphi(w)), \quad \varphi(w) := \sum_{k\geq 1} \beta_k w^k, \quad w := \frac{1}{v} = \frac{N}{V}$$

from analogy of counting function of Cayley tree. A graph theoretical argument by the Prüfer code can also derive the formula(cf. [3]).

The relation between b_l and β_k is as above

$$l^2 b_l = \sum_{(1^{m_1}2^{m_2}\ldots)\vdash l-1} \prod_{j\geq 1} \frac{(l\beta_j)^{m_j}}{m_j!}.$$

Conversely the expression of β_k from b_l is given by

$$k\beta_k = \sum_{n=1}^{k} (-1)^{n+1} k^{\bar{n}} \sum_{\rho}{}' \prod_{l\geq 2} \frac{(lb_l)^{m_l}}{m_l!}, \quad k \geq 1,$$

where $k^{\bar{n}} := k(k+1)\cdots(k+n-1)$ and $\sum_\rho'$ takes over all the partitions of the form $\rho = (2^{m_2}, 3^{m_3}\ldots) \vdash k+n$ with length $l(\rho) = m_2 + m_3 + \cdots = n$.

We give a computation. By the Husimi's identity: $z = we^{-\varphi(w)}$, we have

$$\varphi(w) = \sum_{k\geq 1} \beta_k w^k = \ln w - \ln z.$$

Differentiating this,

$$\varphi'(w) = \sum_{k\geq 1} k\beta_k w^{k-1} = \frac{1}{w} - \frac{1}{z}\frac{dz}{dw}.$$

Denote by $[x^k]\phi(x)$ the coefficient of x^k in a series $\phi(x)$. Then by comparing the coefficient of w^{k-1} we get

$$k\beta_k = [w^{k-1}]\varphi'(w) = \frac{1}{2\pi i}\oint \frac{\varphi'(w)}{w^k}dw = \frac{1}{2\pi i}\oint \frac{dw}{w^{k+1}} - \frac{1}{2\pi i}\oint \frac{dz}{zw^k}$$

$$= \delta_{0k} - [z^0]\frac{1}{w^k} = -[z^0]\frac{1}{w^k}$$

since $k \geq 1$. By a basic identity: $w = \sum_{l\geq 1} lb_l z^l = z(1 + \sum_{l\geq 2} lb_l z^{l-1})$ and the binomial expansion: $(1+x)^\alpha = \sum_{n\geq 0}\binom{\alpha}{n}x^n$, we have

$$w^{-k} = z^{-k}\left(1 + \sum_{l\geq 2} lb_l z^{l-1}\right)^{-k} = z^{-k}\sum_{n\geq 0}\binom{-k}{n}\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n.$$

Since $\sum_{l\geq 2} lb_l z^{l-1} = O(z)$ we get

$$k\beta_k = -[z^0]w^{-k} = -[z^k]\sum_{n\geq 0}\binom{-k}{n}\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n = \sum_{n=0}^{k} -\binom{-k}{n}[z^k]\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n.$$

Expand

$$\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n = \sum_{l_1, l_2, \ldots, l_n \geq 2} l_1 b_{l_1} l_2 b_{l_2} \cdots l_n b_{l_n} z^{l_1 + l_2 + \cdots + l_n - n}.$$

Then we get

$$[z^k]\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n = \sum_{l_1, l_2 \ldots}{}' \prod_{i=1}^{n} l_i b_i$$

where the sum $\sum_{l_1,l_2\ldots}{}'$ runs over all $(l_1, l_2, \ldots, l_n) \in \mathbf{Z}^n$ with all $l_i \geq 2$ and $l_1+l_2+\cdots+l_n = k+n$. Put the partition $\rho = (l_1, l_2, \ldots, l_n) = (2^{m_2}, 3^{m_3}, \ldots) \vdash k+n$. Then its length is $l(\rho) = m_2 + m_3 + \cdots = n$ and

$$[z^k]\left(\sum_{l\geq 2} lb_l z^{l-1}\right)^n = \sum_{\rho=(2^{m_2}3^{m_3}\ldots)\vdash k+n,\ l(\rho)=n} C(\rho)\prod_{l\geq 2}(lb_l)^{m_l}$$

where $C(\rho) := \binom{n}{m_2, m_3, \ldots} = n!/\prod_{l\geq 2} m_l!$. Hence we obtain for $k \geq 1$, putting $a^{\underline{n}} = a(a-1)\cdots(a-n+1)$,

$$k\beta_k = \sum_{n=1}^{k} \frac{-(-k)^{\underline{n}}}{n!}\sum_{\rho}{}' \frac{n!}{\prod_{l\geq 2} m_l!}\prod_{l\geq 2}(lb_l)^{m_l} = \sum_{n=1}^{k}(-)^{n+1}k^{\bar{n}}\sum_{\rho}{}'\prod_{l\geq 2}\frac{(lb_l)^{m_l}}{m_l!}$$

as required.

Next we give a relation between the fugacity z and the numerical density $w = N/V$ of molecules. We know the basic identity:

$$w = \sum_{l\geq 1} lb_l z^l.$$

By reversing the series:

$$\begin{aligned} w &= z + 2b_2z^2 + 3b_3z^3 + 4b_4z^4 + \cdots \\ &= z + \beta_1 z^2 + \left(\frac{3}{2}\beta_1^2 + \beta_2\right) z^3 + \left(\frac{8}{3}\beta_1^3 + \beta_1\beta_2 + \beta_3\right) z^4 + \cdots, \end{aligned}$$

we get

$$\begin{aligned} z &= w - 2b_2w^2 + (8b_2^2 - 3b_3)w^3 - (40b_2^3 - 30b_2b_3 + 4b_4)w^4 + \cdots \\ &= w - \beta_1 w^2 + \left(\frac{\beta_1^2}{2} - \beta_2\right) w^3 - \left(\frac{\beta_1^3}{6} - \beta_1\beta_2 + \beta_3\right) w^4 + \cdots. \end{aligned}$$

The general coefficient $[w^l]z$ can be computed by the similar method using the identity: $z = we^{-\varphi(w)}$ or by the Lagrange inversion of series expansion. We give the result:

$$[w^l]z = \frac{1}{l}\sum_{n=1}^{l-1}(-1)^n l^{\bar{n}} \sum_{\rho=(2^{m_2}3^{m_3}\ldots)\vdash l+n-1,\ l(\rho)=n}\ \prod_{k\geq 2}\frac{(kb_k)^{m_k}}{m_k!}$$

$$= \sum_{(1^{n_1}2^{n_2}\ldots)\vdash l-1} \prod_{k\geq 1} \frac{(-\beta_k)^{n_k}}{n_k!}, \quad l \geq 1.$$

As observed in [4] these combinatorial relations among coefficients bear an arresting resemblance one another.

References

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