Virial Coefficients

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A fluid is a large collection of small particles. The simplest model for fluids in D-dimensional space gives rise to the ideal gas law

$$\frac{P}{\kappa T}=\rho$$

where P is pressure, T is temperature, ρ is density and κ is Boltzmann's constant. A more general model takes interparticle interactions of all orders into consideration. It features the virial series expansion

$$\frac{P}{\kappa T}=\rho+\sum_{n=2}^{\infty}B_{n,D}\,\rho^{n}$$

where coefficients $B_{n,D}$ depend on the choice of potential function. We will focus on the hard core potential

$$\begin{cases}\infty & \text{if } r\leq 1,\\ 0 & \text{if } r>1\end{cases}$$

which implies that two particles have no interaction if their distance >1 and they are prohibited from approaching a distance ≤ 1. The particles are called hard rods if $D=1$, hard disks if $D=2$ and hard spheres if $D=3$. A more realistic potential

$$\begin{cases}\infty & \text{if } r\leq 1,\\ -\varepsilon & \text{if } 1<r\leq 1+\delta,\\ 0 & \text{if } r>1+\delta\end{cases}$$

includes a region of attraction as well as a repulsive hard core; this is called the square-well potential. Other choices exist.

If $D=1$, then [1, 2, 3]

$$\frac{P}{\kappa T}=\frac{\rho}{1-\rho}$$

that is, $B_{n,1}=1$ for all $n\geq 1$, corresponding to a fluid of hard rods. For $D\geq 2$, we need to discuss nonseparable graphs on n vertices, building on material covered in [4, 5]. The number of such graphs is 1, 1, 3, 10 for $2\leq n\leq 5$. Figure 1 exhibits the 15 graphs so far mentioned and symbols representing each [6, 7]. English letters

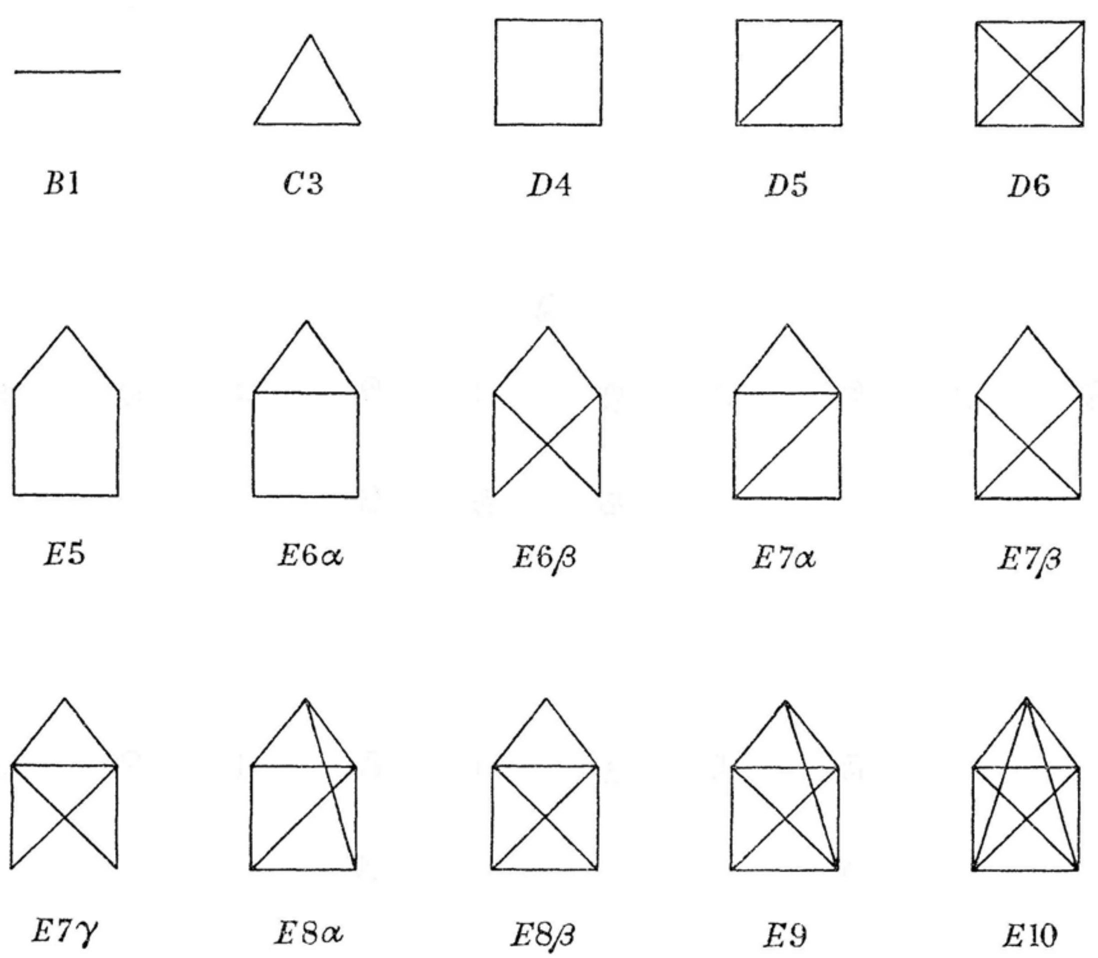

Figure 1: 15 unlabeled nonseparable graphs on ≤ 5 vertices.

correspond to the number of vertices; integers correspond to the number of edges; Greek letters will be explained shortly. The number of *labeled* nonseparable graphs is 1, 1, 10, 238 for $2 \leq n \leq 5$. Our interest is in the labeled case. For $n = 4$, there are 3 graphs of type $D4$, 6 graphs of type $D5$ and 1 graph of type $D6$. For $n = 5$, there are 12 graphs of type $E5$, 70 graphs of type $E6$, 100 graphs of type $E7$, 45 graphs of type $E8$, 10 graphs of type $E9$ and 1 graph of type $E10$. Further refinement is needed for three cases:

$$70\ E6 \text{ graphs} \;=\; 60\ E6\alpha \text{ graphs} \;+\; 10\ E6\beta \text{ graphs},$$

$$100\ E7 \text{ graphs} \;=\; 60\ E7\alpha \text{ graphs} \;+ 30\ E7\beta \text{ graphs} \;+\; 10\ E7\gamma \text{ graphs},$$

$$45\ E8 \text{ graphs} \;=\; 15\ E8\alpha \text{ graphs} \;+\; 30\ E8\beta \text{ graphs}.$$

Let us now illustrate what is called the Mayer formalism for representing virial coefficients $B_{n,D}$ for $2 \leq n \leq 5$ and $D \geq 2$. Given n points $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$, ..., $\vec{r}_n$ in $\mathbb{R}^D$ with $\vec{r}_1 = \vec{0}$ by convention, define $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and

$$f(r) = \begin{cases} -1 & \text{if } r \leq 1, \\ 0 & \text{if } r > 1. \end{cases}$$

We abuse notation and allow graph symbols to serve as shorthand for certain integrals:

$$B_{2,D} = -\frac{1}{2}\int\limits_{\mathbb{R}^D} f(r_{12})d\vec{r}_2 = -\frac{1}{2}\frac{1}{1!}B1,$$

$$B_{3,D} = -\frac{1}{3}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{12})f(r_{23})f(r_{31})d\vec{r}_2\, d\vec{r}_3 = -\frac{2}{3}\frac{1}{2!}C3,$$

$$B_{4,D} = -\frac{3}{4}\frac{1}{3!}\left(3D4 + 6D5 + D6\right)$$

where

$$D4 = \int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{12})f(r_{23})f(r_{34})f(r_{41})d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4,$$

$$D5 = \int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{12})f(r_{23})f(r_{34})f(r_{41})f(r_{13})d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4,$$

$$D6 = \int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{12})f(r_{23})f(r_{34})f(r_{41})f(r_{13})f(r_{24})d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4.$$

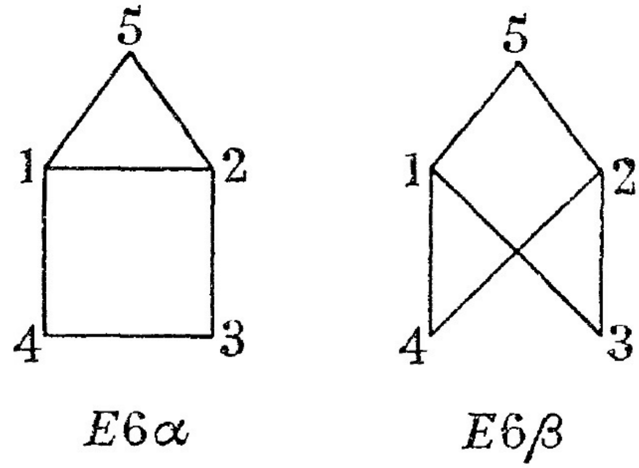

Figure 2: Selected labeled nonseparable graphs on 5 vertices.

Continuing,

$$B_{5,D} = -\frac{4}{5}\frac{1}{4!}\left(12E5 + 60E6\alpha + 10E6\beta + 60E7\alpha + 30E7\beta + 10E7\gamma + 15E8\alpha + 30E8\beta + 10E9 + E10\right)$$

where, for example,

$$E6\alpha = \int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{12})f(r_{14})f(r_{15})f(r_{23})f(r_{25})f(r_{34})d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4\, d\vec{r}_5,$$

$$E6\beta = \int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D}\int\limits_{\mathbb{R}^D} f(r_{13})f(r_{14})f(r_{15})f(r_{23})f(r_{24})f(r_{25})d\vec{r}_2\, d\vec{r}_3\, d\vec{r}_4\, d\vec{r}_5$$

and we have used the helpful labels in Figure 2.

From these formulas, we deduce that [8, 9, 10, 11, 12, 13, 14, 15, 16, 17]

$$B_{2,D} = \frac{\pi^{D/2}}{2\Gamma\left(1+D/2\right)} = \begin{cases} \pi/2 & \text{if } D=2, \\ 2\pi/3 & \text{if } D=3; \end{cases}$$

$$\frac{B_{3,D}}{B_{2,D}^2} = \frac{4\Gamma\left(1+D/2\right)}{\sqrt{\pi}\Gamma\left((1+D)/2\right)}\int\limits_0^{\pi/3}\sin(\theta)^D d\theta = \begin{cases} 4/3-\sqrt{3}/\pi & \text{if } D=2, \\ 5/8 & \text{if } D=3; \end{cases}$$

$$\frac{B_{4,D}}{B_{2,D}^3} = \begin{cases} 2-(9/2)\left(\sqrt{3}/\pi\right)+10/\pi^2 & \text{if } D=2, \\ 2707/4480+(219/2240)\left(\sqrt{2}/\pi\right)-(4131/4480)\left(\operatorname{arcsec}(3)/\pi\right) & \text{if } D=3; \end{cases}$$

$$\frac{B_{5,D}}{B_{2,D}^4} = \begin{cases} 0.33355604... & \text{if } D=2, \\ 0.110252... & \text{if } D=3. \end{cases}$$

Elaborating on $B_{5,D}$ for $D=3$:

$$\frac{E5}{B_2^4} = -\frac{40949}{10752}, \qquad \frac{E6\alpha}{B_2^4} = \frac{68419}{26880}, \qquad \frac{E6\beta}{B_2^4} = \frac{82}{35},$$

$$\frac{E7\alpha}{B_2^4} = -\frac{34133}{17920}, \qquad \frac{E7\beta}{B_2^4} = -\frac{18583}{5376}+\frac{33291}{9800}\frac{\sqrt{3}}{\pi}, \qquad \frac{E7\gamma}{B_2^4} = -\frac{73491}{35840},$$

$$\frac{E8\beta}{B_2^4} = -\frac{35731}{6720}+\frac{1458339}{627200}\frac{\sqrt{2}}{\pi}-\frac{33291}{9800}\frac{\sqrt{3}}{\pi}+\frac{683559}{35840}\frac{\operatorname{arcsec}(3)}{\pi}$$

but exact expressions for

$$\frac{E8\alpha}{B_2^4} \approx 2(0.56965), \qquad \frac{E9}{B_2^4} \approx 3(-0.30490) \qquad \frac{E10}{B_2^4} \approx 30(0.02369)$$

remain open. Even less is known about $B_{5,D}$ for $D=2$:

$$\frac{E6\beta}{B_2^4} = 16-\frac{116}{\pi^2}, \qquad \frac{E7\gamma}{B_2^4} = -16+\frac{16\sqrt{3}}{\pi}+\frac{196}{3\pi^2}-\frac{117\sqrt{3}}{2\pi^3}.$$

Numerical integration is evidently required for the remaining subcases. For example [14, 16],

$$\begin{aligned} E6\alpha &= 4\pi^2\int_0^1\int_0^{1-r} A(r)A(s)r\,s\,ds\,dr + 4\pi\int_0^1\int_{1-r}^{1+r} A(r)A(s)\arccos\left(\frac{r^2+s^2-1}{2r\,s}\right) r\,s\,ds\,dr \\ &\approx (4.46966949)B_2^4 \approx \frac{1}{2}(8.93933899)B_2^4, \end{aligned}$$

$$\begin{aligned} E7\alpha &= -4\pi^2\int_0^1\int_0^{1-r} A(r)A(s)r\,s\,ds\,dr - 4\pi\int_0^1\int_{1-r}^{1} A(r)A(s)\arccos\left(\frac{r^2+s^2-1}{2r\,s}\right) r\,s\,ds\,dr \\ &\approx (-3.61831477)B_2^4 \approx \frac{1}{2}(-7.23662954)B_2^4, \end{aligned}$$

$$\begin{aligned} E5 &= -E6\alpha - 4\pi \int_{1}^{2} \int_{-1+r}^{2} A(r)A(s) \arccos\left(\frac{r^2+s^2-1}{2r\,s}\right) r\,s\,ds\,dr \\ &\approx (-5.97307832)B_2^4 \approx \frac{5}{2}(-2.38923133)B_2^4 \end{aligned}$$

where

$$A(r) = 2\arccos\left(\frac{r}{2}\right) - \frac{r}{2}\sqrt{4-r^2}$$

is the area of the intersection of two overlapping disks, each of unit radius, with distance r between their centers. Other symbols require evaluation of trivariate integrals or worse; computational difficulty seems to increase with the number of edges in the graph. A remarkable breakthrough was achieved recently [18, 19], giving $E10$ for $D = 2$ solely in terms of bivariate integrals and hence to high accuracy:

$$\frac{E10}{B_2^4} = 1.8090652427... = 5(0.3618130485...) = 30(0.0603021747...)$$

Details of this computation are still forthcoming. Analogous estimates for the other unsolved contributions to $B_{5,2}$ are unavailable; the corresponding difficulties for $B_{5,3}$ are insurmountable.

A different normalization for virial coefficients often appears:

$$\tilde{B}_{n,D} = \frac{B_{n,D}}{(\omega_D/2^D)^{n-1}}$$

where $\omega_D = \pi^{D/2}/\Gamma(1 + D/2)$, the volume enclosed by the unit sphere in $\mathbb{R}^D$. Thus $\tilde{B}_{2,2} = 2$, $\tilde{B}_{2,3} = 4$, $\tilde{B}_{3,2} = 16/3 - 4\sqrt{3}/\pi$ and $\tilde{B}_{3,3} = 10$. We merely mention challenging research for $n > 5$ and $D > 3$, which is beyond the scope of his essay [20, 21, 22, 23, 24, 25, 26, 27, 28, 29].

0.1. Addendum. An expression for the area of the intersection I of three overlapping disks, each of unit radius, is found in [30]. Let the centers be $(-r/2, 0)$, $(r/2, 0)$ and (x, y), where $0 < r < 2$ and the third point is assumed to be inside the intersection J of the first two disks. Assume further that a nonempty arc of ∂J lies outside of the third circle, that is, I is nondegenerate. Let

$$d_{12} = r, \qquad d_{13} = \sqrt{(x+r/2)^2 + y^2}, \qquad d_{23} = \sqrt{(x-r/2)^2 + y^2},$$

$$x_{12} = d_{12}/2, \qquad x'_{13} = d_{13}/2, \qquad x''_{23} = d_{23}/2,$$

$$y_{12} = \sqrt{1 - d_{12}^2/4}, \qquad y'_{13} = -\sqrt{1 - d_{13}^2/4}, \qquad y''_{23} = \sqrt{1 - d_{23}^2/4},$$

$$\lambda' = \frac{d_{12}^2 + d_{13}^2 - d_{23}^2}{2d_{12}d_{13}}, \qquad \mu' = \sqrt{1-\lambda'^2}, \qquad \lambda'' = -\frac{d_{12}^2 + d_{23}^2 - d_{13}^2}{2d_{12}d_{23}}, \qquad \mu'' = \sqrt{1-\lambda''^2},$$

$$x_{13} = x'_{13}\lambda' - y'_{13}\mu', \qquad y_{13} = x'_{13}\mu' + y'_{13}\lambda',$$

$$x_{23} = x''_{23}\lambda'' - y''_{23}\mu'' + d_{12}, \qquad y_{23} = x''_{23}\mu'' + y''_{23}\lambda'',$$

$$c_1 = \sqrt{(x_{12}-x_{13})^2 + (y_{12}-y_{13})^2}, \qquad c_2 = \sqrt{(x_{12}-x_{23})^2 + (y_{12}-y_{23})^2},$$

$$c_3 = \sqrt{(x_{13}-x_{23})^2 + (y_{13}-y_{23})^2}.$$

Then the desired area is

$$\begin{aligned}\aleph(x,y,r) &= \frac{1}{4}\sqrt{(c_1+c_2+c_3)(-c_1+c_2+c_3)(c_1-c_2+c_3)(c_1+c_2-c_3)} + \\ &\quad \sum_{k=1}^{3}\left[\arcsin\left(\frac{c_k}{2}\right) - \frac{c_k}{4}\sqrt{4-c_k^2}\right].\end{aligned}$$

Define also

$$u(x,r) = \sqrt{1-x^2} - \sqrt{1-r^2/4}, \qquad v(x,r) = \sqrt{1-(x+r/2)^2},$$

$$w(r) = \frac{1}{4}\left(-r + \sqrt{3}\sqrt{4-r^2}\right);$$

exact formulas for

$$\theta(r) = A(r)\int_0^{r/2}\int_0^{u(x,r)} dy\,dx,$$

$$\varphi(r) = A(r)\int_0^{w(r)}\int_0^{u(x,r)} dy\,dx, \qquad \psi(r) = A(r)\int_{w(r)}^{1-r/2}\int_0^{v(x,r)} dy\,dx$$

exist but are omitted for brevity's sake. Two additional symbols for $D = 2$ are therefore [14]

$$\begin{aligned}E8\beta &= 8\pi\left[\int_0^1 \theta(r)A(r)\,r\,dr + \right. \\ &\quad \int_0^1\int_{r/2}^{w(r)}\int_0^{-u(x,r)} A(d_{13})\,A(r)\,r\,dy\,dx\,dr + \int_0^1\int_{w(r)}^{1-r/2}\int_0^{v(x,r)} A(d_{13})\,A(r)\,r\,dy\,dx\,dr + \\ &\quad \left.\int_0^1\int_0^{r/2}\int_{u(x,r)}^{v(x,r)} \aleph(x,y,r)A(r)\,r\,dy\,dx\,dr + \int_0^1\int_{r/2}^{w(r)}\int_{-u(x,r)}^{v(x,r)} \aleph(x,y,r)A(r)\,r\,dy\,dx\,dr\right] \\ &\approx (2.810839)B_2^4,\end{aligned}$$

$$
\begin{aligned}
E7\beta &= -E8\beta - 2\pi \int_{\sqrt{3}}^{2} A(r)^3 r\,dr - \\
&\quad 8\pi \left[\int_{1}^{\sqrt{3}} \varphi(r)A(r)\,r\,dr + \int_{1}^{\sqrt{3}} \psi(r)A(r)\,r\,dr + \int_{1}^{\sqrt{3}} \int_{0}^{w(r)} \int_{u(x,r)}^{v(x,r)} \aleph(x,y,r)A(r)\,r\,dy\,dx\,dr \right] \\
&\approx (-3.202747)B_2^4.
\end{aligned}
$$

We have not attempted to independently evaluate [16]

$$
\frac{E8\alpha}{B_2^4} \approx 2.529628 \approx 2(1.264814), \qquad \frac{E9}{B_2^4} \approx -2.160499 \approx 3(-0.720166)
$$

except to verify that a certain identity

$$
E6\beta + E7\gamma + 3(E7\beta + E8\alpha + E8\beta) + 4E9 + E10 = 0
$$

is satisfied.

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