$\phi \equiv 0°$ for trans conformation and G=T-120°, G'=T+120°. So more trans conformation gives larger second moment of end-to-end distance. The last term is greater than one. (See Lecture # 200 for energy level of T, G, and G')

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## 2.9 The Gaussian Chain

Freely jointed model (and other end-to-end distance model):

→gives idea of flexible, randomly oriented chains

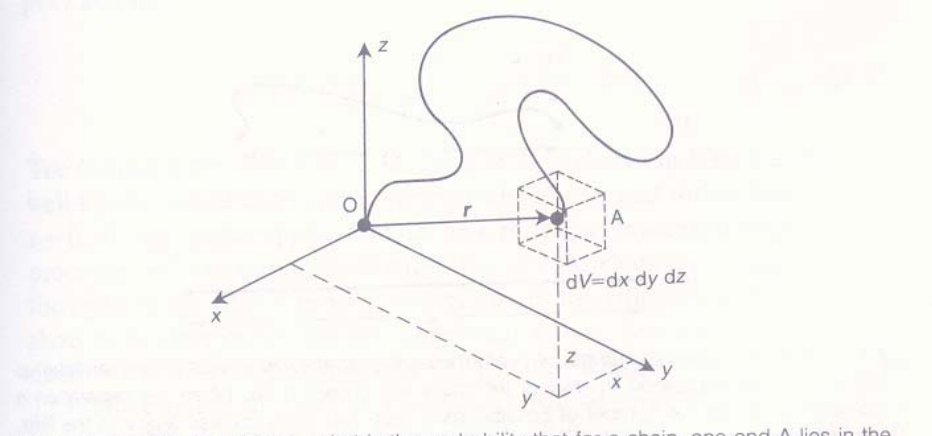
→doesn't lead to any further analysis.

Motivation

Consider a representative chain OA (Figure 2.16) with a coordinate system attached at one end.

The end-to-end vector be:

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \tag{2.13}$$

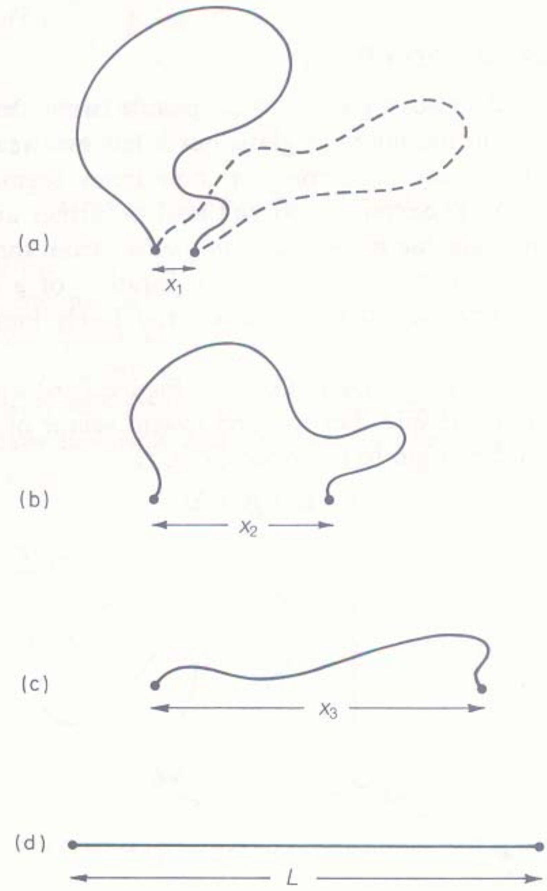



2.16 The statistical problem—what is the probability that for a chain, one end A lies in the volume element $dV = dx\,dy\,dz$ at $\mathbf{r}$ from the other end O?

Figure 2.16

The chain OA can take up an enormous number of different conformations, characterized by **r** → The probability that the other chain end lies within the volume element dV=dxdydz decreases as r increases!

See Figure 2.17 for one dimensional conformation.




**2.17** There are a certain number of conformations, or shapes, which the chain can take up with end-to-end separation $x_1$: two of the many are shown in (a). When the separation is increased to $x_2$ (b) the number of possibilities is less, and at $x_3$ (c) less again. In the limit, when the end-to-end distance equals the contour length $L$, there is only one conformation (d), the straight one.

Figure 2.17

For x = L (Contour length): Only one conformation exists→ The probability of occurrence is insignificant.

For x = 0 (O and A coincide): The greatest # of conformation → Probability of occurrence is greater than any other values of x.

For 0<x<L →Probability of occurrence is intermediate.

▶If $x_1$ can be achieved by $10^3$ times more than $x_2$, which is again

$10^3$ times more than $x_3$, then the occurrence of value

$$x_1/x_2/x_3=10^6/10^3/1$$

A function closely describe this behavior is the Gaussian function.

Gaussian chain (model):

End-to-end separation of a polymer follows Gaussian statistics.

One dimensional Gaussian function:

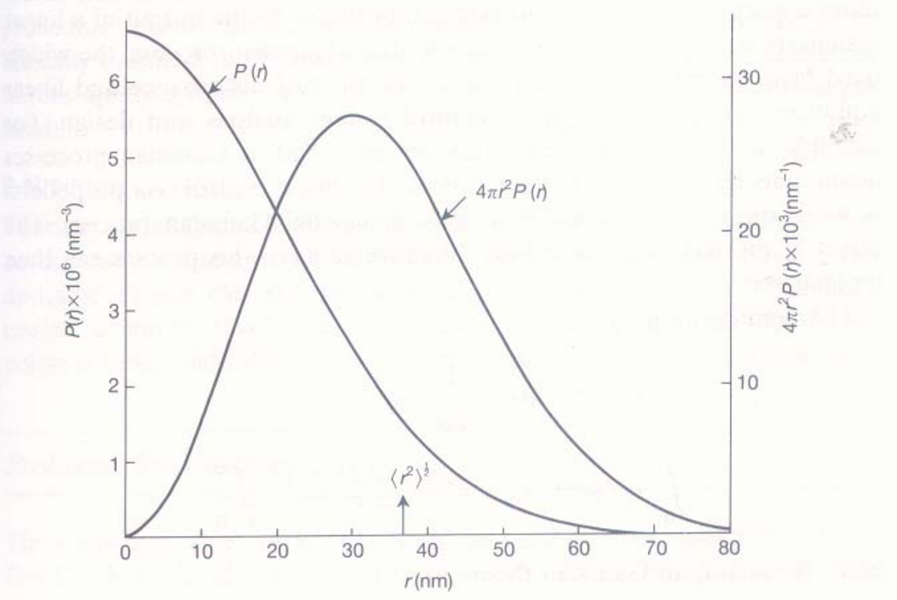
$$p(x) = \frac{\exp[-(x/\rho)^2]}{\sqrt{\pi}\,\rho} \qquad (2.14)$$

ρ = a representative length (a parameter)

The probability that the chain length lies between x and x+dx is linearly proportional to the magnitude of dx. The probability of the end-to-end length lying between x and x+dx to be the product of p(x) and dx:

$$p(x)dx = \frac{\exp[-(x/\rho)^2]}{\sqrt{\pi}\,\rho}dx \qquad (2.15)$$

See Gaussian function at Figure 2.23.

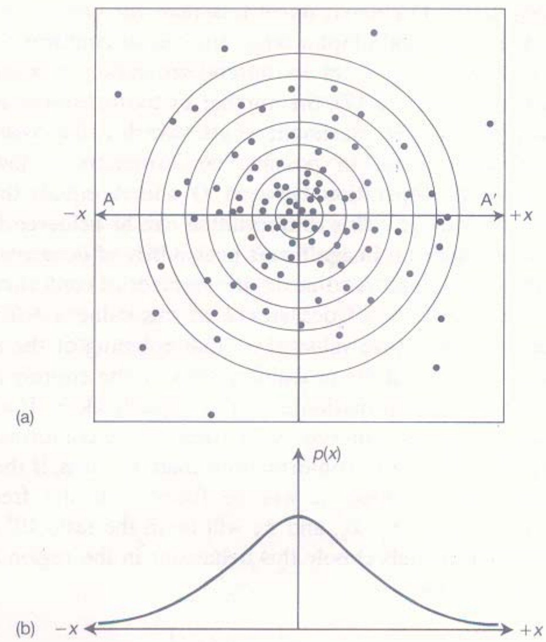



**2.23** The Gaussian distribution functions of the end-to-end vector $\boldsymbol{r}$, $P(r) = (\sqrt{\pi}\rho)^{-3}\exp[-(r/\rho)^2]$ and $4\pi r^2 P(r)$ (see eqn 2.N.7.2) plotted against $r$ for a polymer chain with $\rho = 30$ nm.

Figure 2.23.

▶Bell type, symmetrical about, and with a maximum at $x=0$.

The function is applicable for any random processes such as the distribution of rifle shots on a target (Figure 2.18).




**2.18** (a) The distribution of shots on a target. (b) The density of shots along a line such as AA′ is proportional to $p(x)$, the Gaussian function (see eqn 2.14).

Figure 2.18

▶The distribution of shots (# of shot per unit length) along line A-A is described by eq 2.14.

▶The # of shot in a length dx will be given by eq 2.15.

<u>Three dimensional Gaussian model</u>

The probability that chain end A lies between x~x+dx, y~y+dy, and z~z+dz to be

$$P(x,y,z)dxdydz = p(x)p(y)p(z)dxdydz$$

$$= \frac{\exp-[(x^2+y^2+z^2)/\rho^2)}{(\sqrt{\pi}\,\rho)^3}dxdydz \qquad (2.16)$$

$$= \frac{\exp[-(r/\rho)^2]}{(\sqrt{\pi}\,\rho)^3}dxdydz \qquad (2.17)$$

---

Gauss 함수의 조작(2N7)

$$P(r)=\frac{\exp-(r/\rho)^2}{(\sqrt{\pi}\rho)^3} \qquad (2.N.7.1)$$

∴ 확률은

$$P(r)dV=\frac{\exp-(r/\rho)^2}{(\sqrt{\pi}\rho)^3}\times 4\pi r^2 dr \qquad (2.N.7.2)$$

$$=\frac{4\pi}{(\sqrt{\pi}\rho)^3}r^2\exp[-(r/\rho)^2]dr$$

- most probable value of r

$$\frac{d}{dr}(P(r)dV)=0$$

$$\frac{d}{dr}(P(r)dV)=\frac{4\pi}{(\sqrt{\pi}\rho)^3}[2r\exp-(r/\rho)^2+r^2(-\frac{2r}{\rho^2})\exp-(r/\rho)^2=0$$

$$2r=r^2(\frac{2r}{\rho^2})\Rightarrow\frac{r}{\rho}=1\Rightarrow\rho=r$$

- 제곱값 평균(mean square value of r)

$$<r^2>=\frac{\int_0^\infty r^2P(r)4\pi r^2dr}{\int_0^\infty P(r)4\pi r^2dr} \qquad (2.N.7.4)$$

$$=\frac{4\pi}{(\sqrt{\pi}\rho)^3}\int_0^\infty r^4\exp[-(r/\rho)^2]dr$$

$$=\frac{3}{2}\rho^2 \qquad \text{(a)} \qquad (2.N.7.5)$$

(공식)

$$\int_0^\infty x^{2n}e^{-ax^2}dx=\frac{1.3.5...(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}} \qquad \text{(b)}$$

from (a) and (b)

$$x=r, n=2, a=\frac{1}{\rho^2}$$

$$\therefore [\int_0^\infty r^4e^{-(r/\rho)^2}dr=\frac{1.3}{2^{2+1}(\frac{1}{\rho^2})^2}\sqrt{\rho^2\pi}]\times\frac{4\pi}{(\sqrt{\pi}\rho)^3}=\frac{3}{2}\rho^2$$

So, $< r^2 > = \frac{3}{2}\rho^2$ (2.18)

from 자유사슬 modul

$$< r^2 > = nl^2 \qquad (2.10,\ 2.19)$$

(18)+(19)

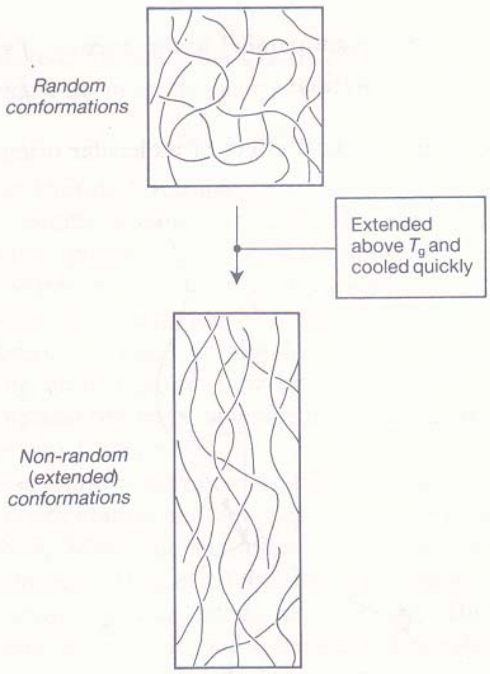
$$\rho = (\frac{2n}{3})^{\frac{1}{2}} l \qquad (2.21)$$

## 2.10 분자배향(Molecular Orientation)

분자배향은 고의적으로 혹은 본의 아니게 가공과정ㅇ서 일어남(Fig.2.19)

$$\text{고분자용융체} \xrightarrow[extruder\,injection]{\text{성형장치}} \text{분자배향} \xrightarrow{\text{냉각}} \text{배향고정} \rightarrow \text{이방성}$$

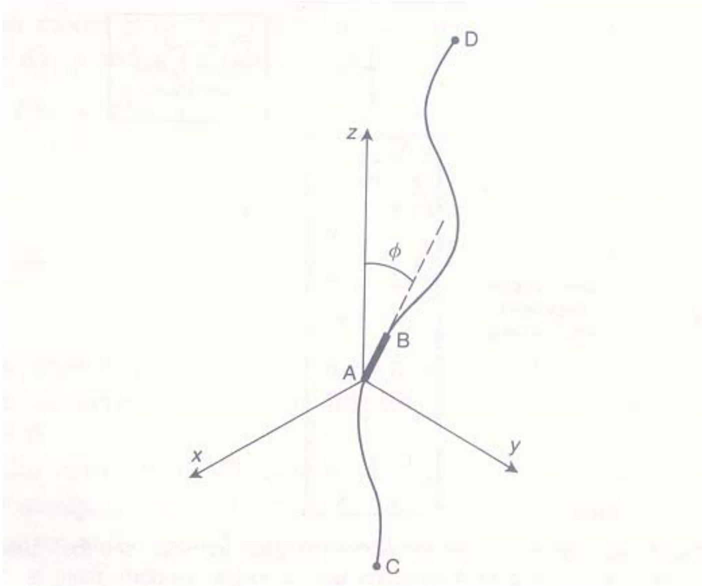
배향의 측도 혹은 측정 (Fig. 2.20)




**2.19** An amorphous polymer is extended above the glass transition and then quenched to the glassy state. The resulting conformations are no longer random: there is 'frozen-in' molecular orientation, which remains when stress is removed.

Figure 2.19

Figure 2.20



2.20 Section AB of molecule CD is inclined at angle $\phi$ to the $z$-axis.

분자 (1)의 segment(혹은 functional group) AB (Z축과 각Φ)
평균배향 …… $\cos^2\Phi$ (sample 內의 全 segment에 대한 평균)
배향인자 = f (orientation factor, Herman)

$$f = \frac{3\cos^2\Phi - 1}{2} \qquad (2.22)$$

for

$\Phi = 0°$, $f = \frac{3-1}{2} = 1$ perfect orientation along Z-axis

$\Phi = 90°$, $f = \frac{-1}{2}$ per endicular to Z-axis

How about random orientation ?

배향과 물성의 이방성
 배향방향 : 공유결합적인 성질
 강직성↑, 강도↑, 열팽창계수↓
 수직방향 : 2차결합 성질(van der Waals)
 강직성↓, 강도↓, 열팽창↑

배향 vs 굴절율