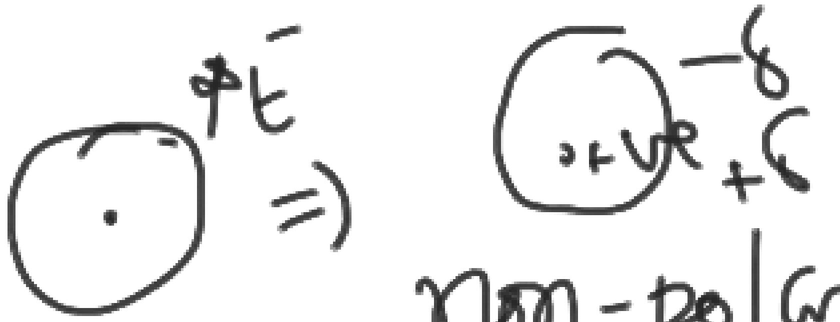
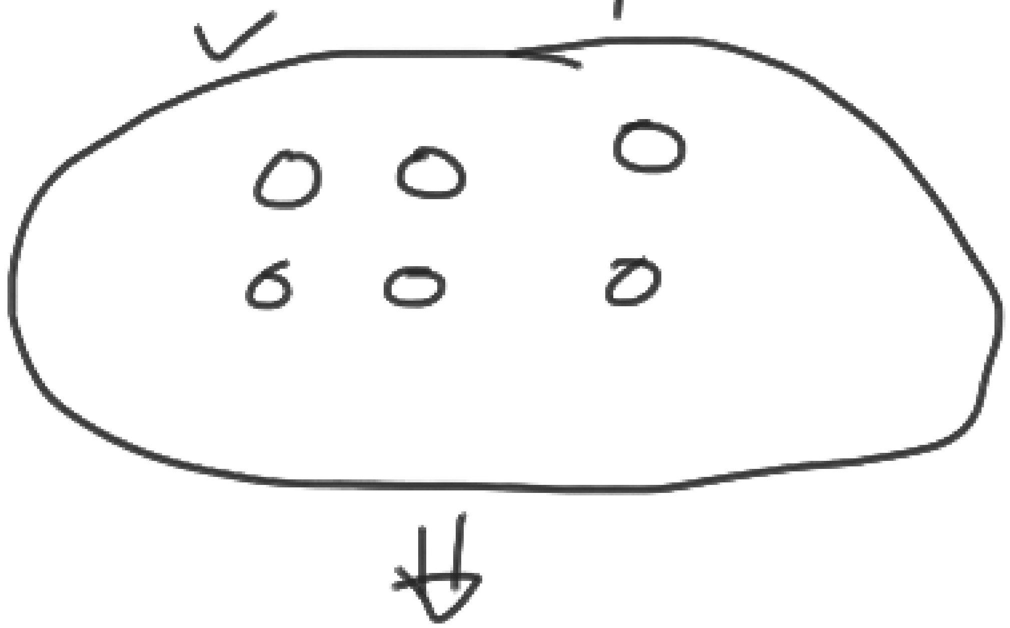


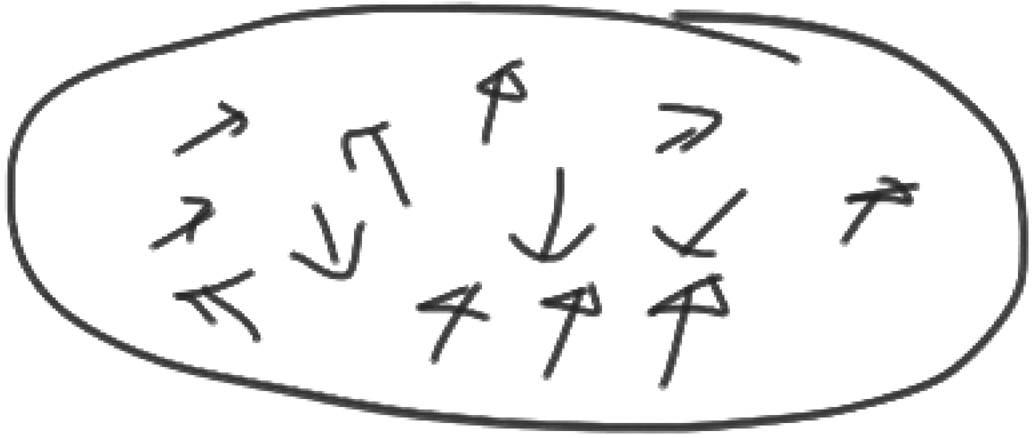
# BPT-401

Date - 06/04/2021

non-polar



Polar



## Polar dielectrics and the Langevin – Debye equation

Two mechanisms

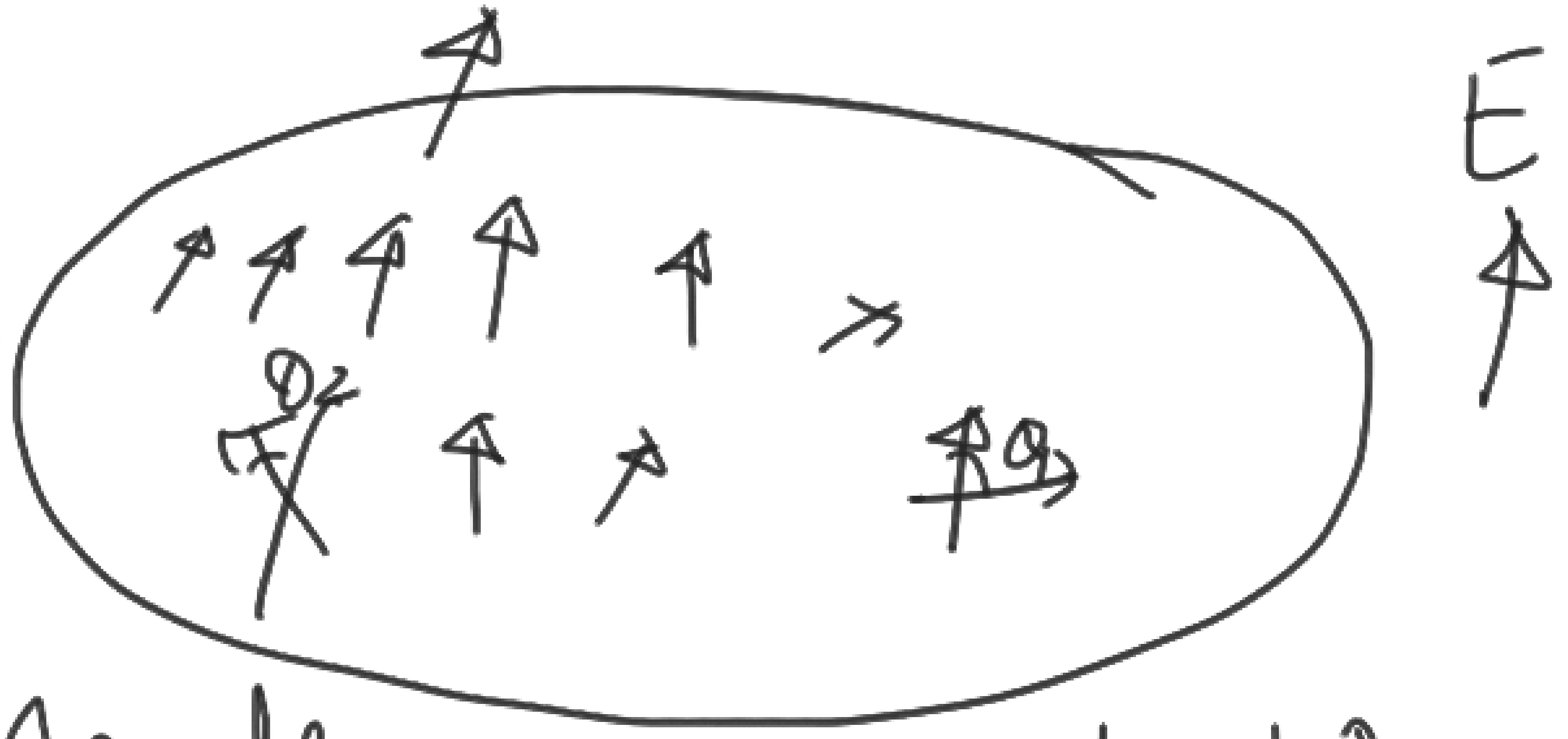
$\Rightarrow$ (i) Orientation of dipoles ~~towards~~ in the direction of $\vec{E}$

$\Rightarrow$ (ii) stretching of electron clouds $\Rightarrow$

$\alpha_0$

$N_A \sim 6.023 \times 10^{23}$

Principle of statistical mechanics,



in thermal equillibrium,

the probability of finding a molecule with P.E. 'U' is

$$\boxed{P(U) \propto e^{-U/k_BT}}$$

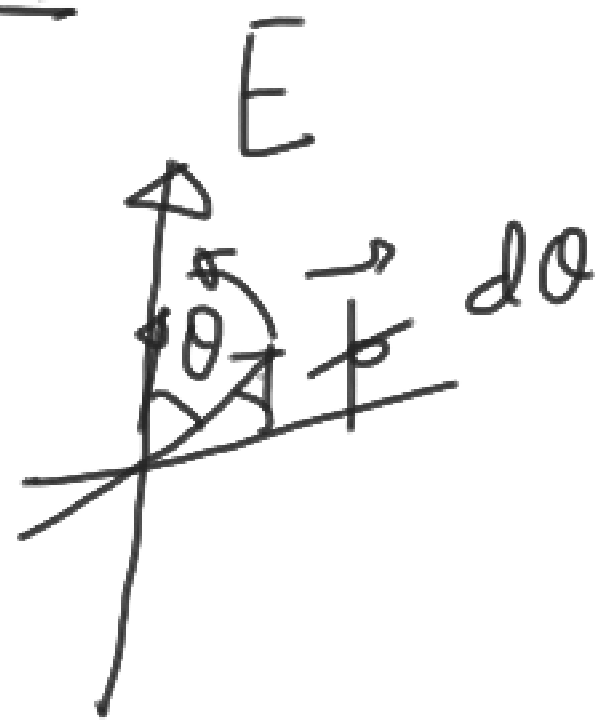
$$\propto e^{+pE\cos\theta/k_BT}$$

$k_B$ – Boltzman constant

$T$ – Absolute temperature.

P.E. of a dipole moment $\vec{p}$ in an electric field $\vec{E}$

$$U = -\vec{p}\cdot\vec{E} = -pE\cos\theta$$



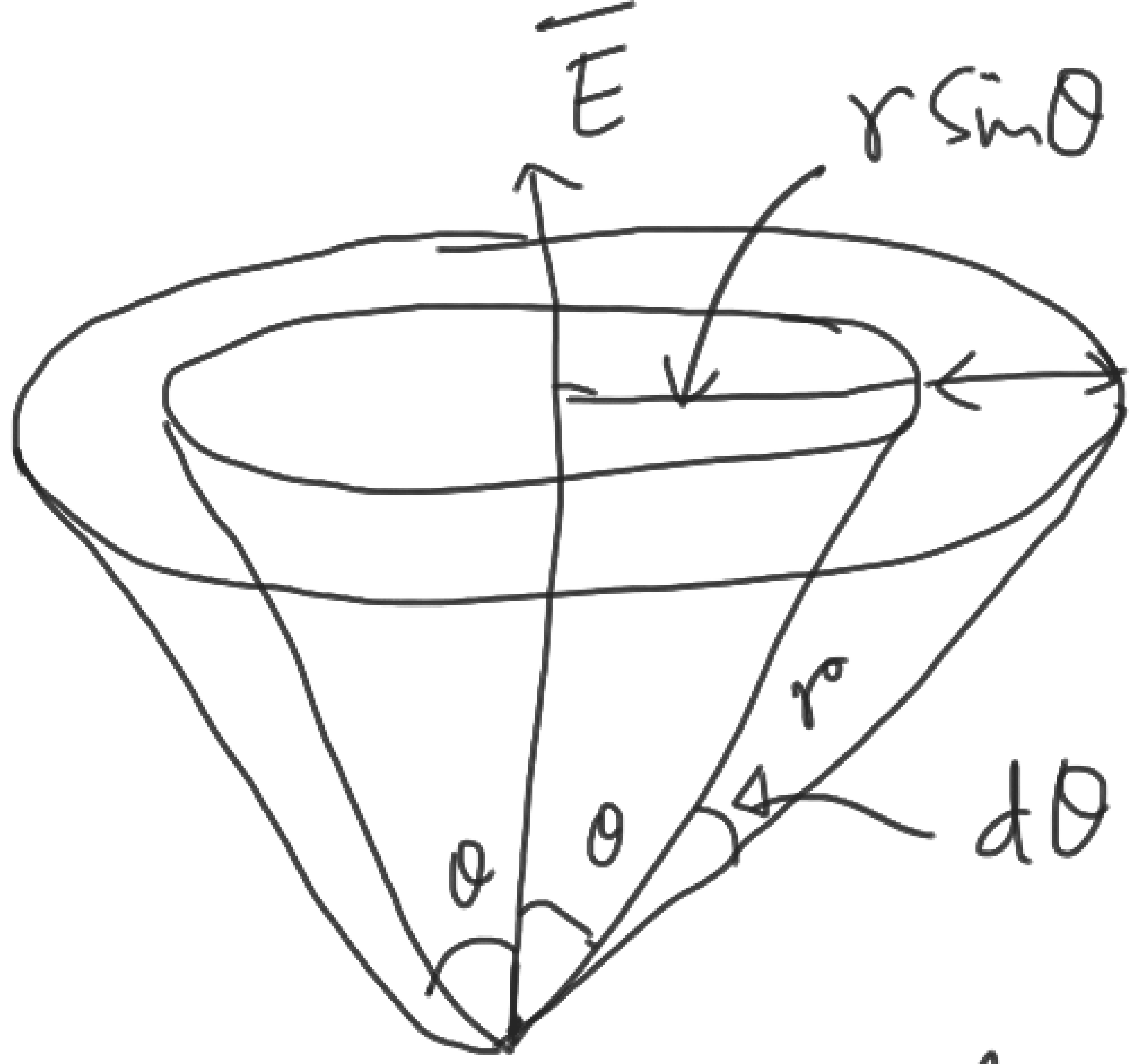

(Dilute)
In gasious phase, $\bar{E}_{avg} = \bar{E}_{local}$

$\simeq E_{external}$

$\theta$ & $\theta + d\theta$

So the probability that a dipole will have orientation $\theta$ w.r.t the field $\vec{E}$ is

$$P(\theta) \propto e^{pE\cos\theta/k_BT}$$



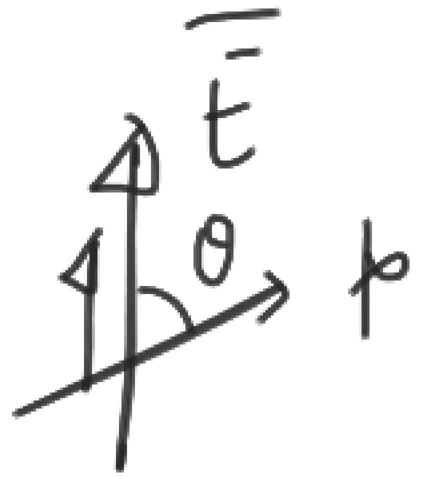

$\theta, \quad \theta + d\theta$

The probability that the axis of a dipole lies between the angles $\theta$ & $\theta + d\theta$, the conical solid angle

$$d\Omega = \frac{2\pi r \sin\theta . r d\theta}{r^2} = 2\pi \sin\theta d\theta$$

is proportional to $e^{pE\cos\theta / k_B T}$

The effective value of dipole moment is its along field $\vec{E}$ i.e, $p\cos\theta$




Now, its average value is

$$\langle p \rangle = \frac{\int (p\cos\theta)\left(e^{pE\cos\theta/k_BT}\right) d\Omega}{\int e^{pE\cos\theta/k_BT}\, d\Omega}$$

$$= \frac{p\int_0^{\pi} \cos\theta \; e^{pE\cos\theta/k_BT} \sin\theta\, d\theta}{\int_0^{\pi} e^{pE\cos\theta/k_BT} \sin\theta\, d\theta}$$

Let, $\frac{pE}{k_B T} = a$, and $\cos\theta = x$,

$dx = -\sin\theta \, d\theta$

| $\theta$ | $0$ | $\pi$ |
| --- | --- | --- |
| $x$ | $1$ | $-1$ |

$$\langle p \rangle = \frac{p \int_1^{-1} x e^{ax} \, dx}{\int_1^{-1} e^{ax} \, dx} = \frac{p \left[ \frac{x e^{ax}}{a} - \frac{e^{ax}}{a^2} \right]_1^{-1}}{\left[ \frac{e^{ax}}{a} \right]_1^{-1}}$$

$$= p \left[ \left( \frac{e^{a} + e^{-a}}{e^{a} - e^{-a}} \right) - \frac{1}{a} \right]$$

$$= p \left[ \coth a - \frac{1}{a} \right]$$

$$\Rightarrow \boxed{\frac{\langle p \rangle}{p} = \coth a - \frac{1}{a}}$$ Langevin - formula

where $a = \frac{pE}{k_B T}$

$\frac{\langle p \rangle}{p}$ as a function of $a = \frac{pE}{k_B T}$

If E is large or T is very small, $a \gg 1$

$$\frac{\langle p \rangle}{p} = 1$$

Typically, value of $p$ is such that
$a << 1$ at ordinary temperature.

$$\frac{\langle p \rangle}{p} \simeq \frac{a}{3} \approx \frac{1}{3}\frac{pE}{k_B T}$$

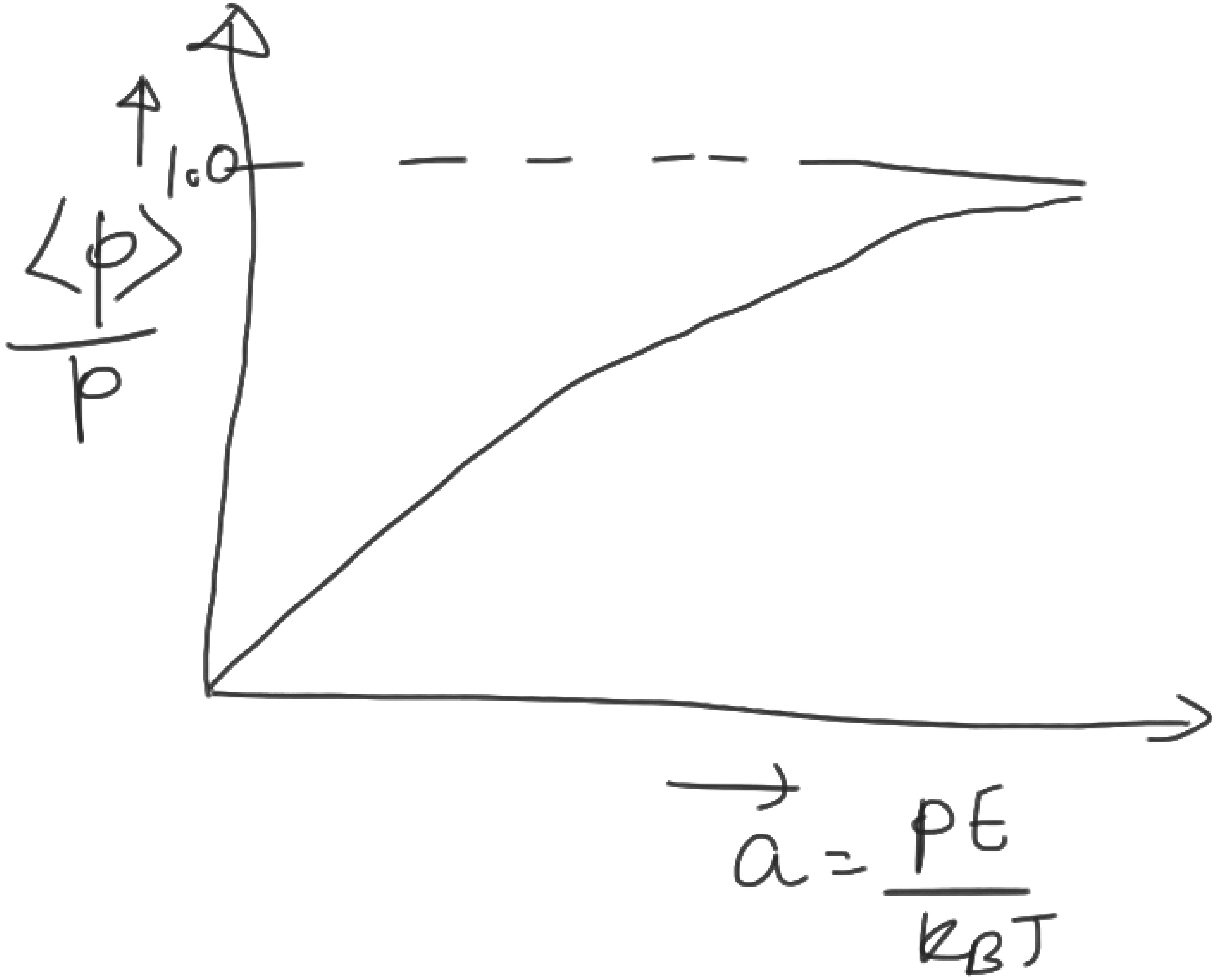
$$\langle p \rangle \simeq \frac{1}{3}\frac{p^2 E}{k_B T}$$

$$\boxed{\langle p \rangle \propto E}$$

$$e^a = 1 + a + \frac{a^2}{2!} + \frac{a^3}{3!} + \cdots$$

$$e^{-a} = 1 - a + \frac{a^2}{2!} - \frac{a^3}{3!} + \cdots$$

$$\coth a - \frac{1}{a} \approx \frac{a}{3}$$


$\frac{\langle p \rangle}{p}$
1.0
$a = \frac{pE}{k_B T}$

Now, Polarizability, $\alpha_{orient} = \frac{\langle p \rangle}{E}$

$$= \frac{1}{3}\frac{p^2}{k_B T}$$

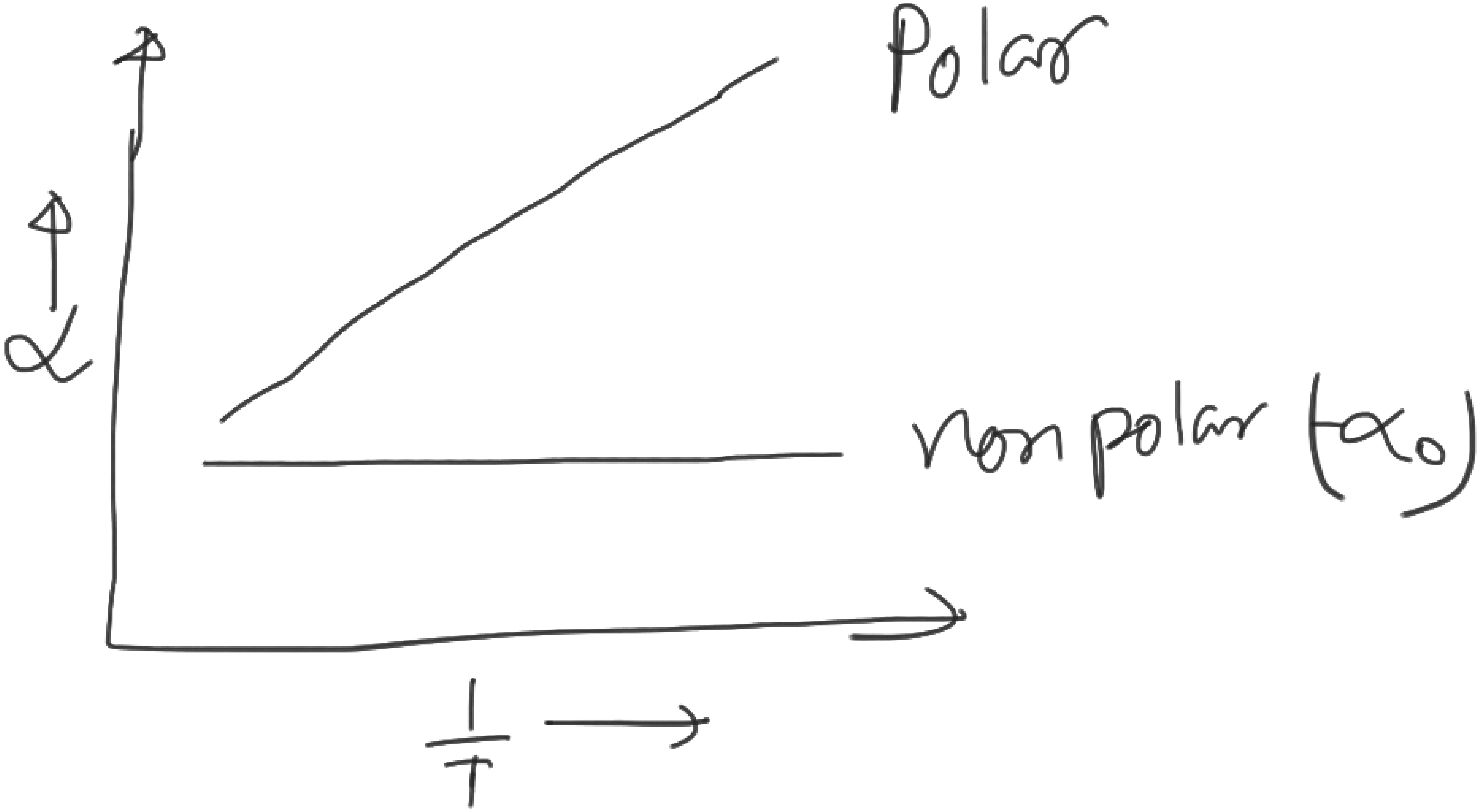
atomic Polarizability

$$\alpha = \alpha_0 + \alpha_{orient}$$

$$\boxed{\alpha = \alpha_0 + \frac{p^2}{3k_B T}}$$

Langevin-Debye equation

$$\alpha_{orient} \propto \left(\frac{1}{T}\right)$$




$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{n}{3\varepsilon_0}\left(\alpha_0 + \frac{p^2}{3k_BT}\right)$$

Debye equation