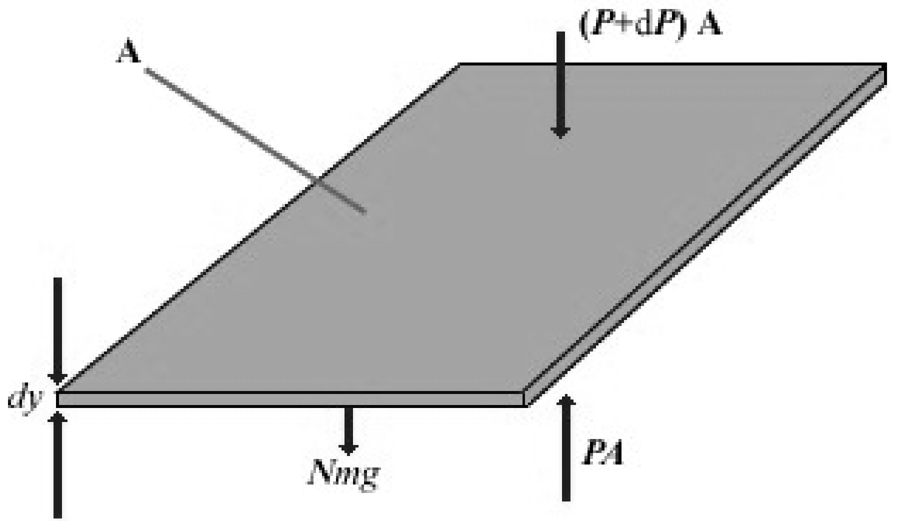
# Law of atmospheres

**Assume that temperature does not depend on the height**

**$PV = Nk_BT$**

The number of particles per unit volume of gas, $\mathbf{n_V = N/V}$.

Determine how $\mathbf{n_V}$ changes in atmosphere.



$P = n_V kBT$. Thus, if the number density $n_V$ is known, we can find the pressure and vice versa.

Consider an atmospheric layer of thickness **dy** and the cross-sectional area **A**.

Because the air is in static **equilibrium**, the upward force on the bottom of this layer, **PA**, must exceed the downward force on the top of the layer, **(P + dP)A**, by an amount equal to the weight of gas in this thin layer.

If the mass of gas molecule in the layer is m, and the area a total of N molecules in the layer, then the weight of the layer is **mgN = mgnVAdy**.

Thus $PA - (P + dP)A = mgn_V Ady$, which reduces to

$$dP = - mgn_V dy$$

Because $P = n_V k_B T$, and **T** is assumed to remain **constant**, therefore

$$dP = k_B T \, dn_V.$$

$$n_V k_B T \, dn_V = - mg n_V dy$$

$$\frac{dn_v}{n_v} = -\frac{mg}{k_B T} dy$$

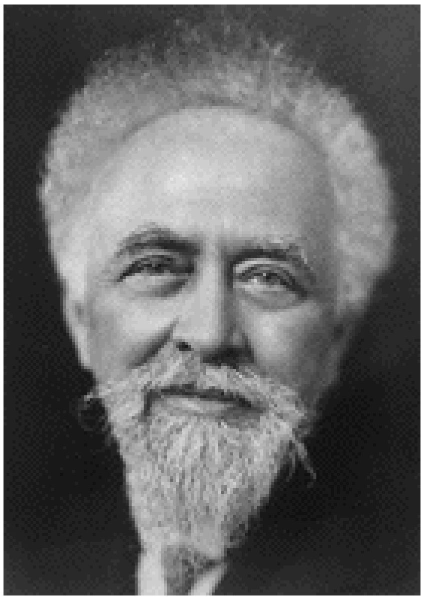
$$n(y) = n_0 e^{-mgy/k_B T}$$

This equation predicts that the **number density** of our atmosphere **decreases exponentially** with increasing altitude and the **pressure** varies according to the expression:

$$\mathbf{P = P_0 \text{ ´ } exp(-mg\mathit{y}/k_BT)}$$

Where $\mathbf{P_0 = n_0k_B\ T}$ **and** $\mathbf{n_0}$ » **2.7 ´ 10$^{25}$** molecules/m$^3$ **at sea level.**

*"Either as a gas or in solution, the same number of any kind of molecules whatever, enclosed in the same volume at the same temperature, exert the same pressure on the walls that confine them."*



***Jean-Baptiste Perrin***

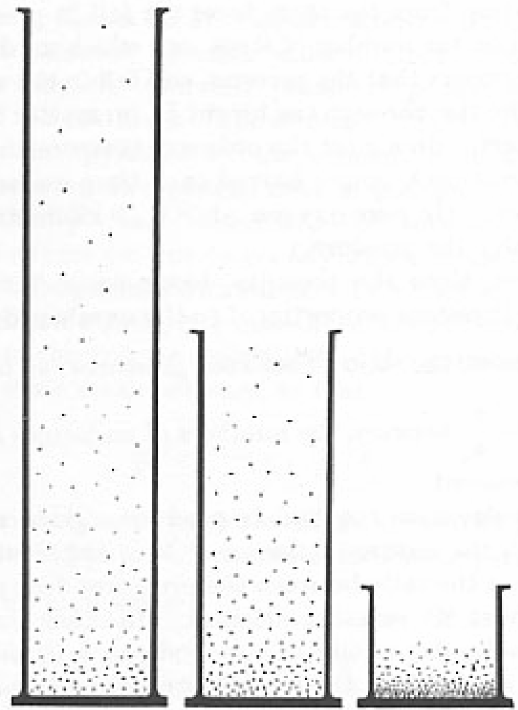


FIG. 3.

***"Is it now conceivable that even visible particles might still obey them accurately, so that a granule agitated by the Brownian movement would count neither more nor less than an ordinary molecule with respect to the effect of its impact upon a partition that stops it?"***

The law of atmosphere provides the expression for the number density of gas molecules in gravitational field.

It can be represented in another form if we take into account that the **gravitational potential energy** of molecule at height ***y*** is ***U = mgy***. Then

$$\mathbf{n_V = n_0\ ´\ exp(\,-\mathit{U}/k_B T)}$$

# Boltzmann Distribution Law

- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
  - Typically at a rate of a billion times per second
- The **number density** $n_V(E)$
  - Is called a **distribution function**
  - **It is defined so that $n_V(E)\,dE$ is the number of molecules per unit volume with energy between $E$ and $E + dE$**

# Boltzmann Distribution Law

- From statistical mechanics, the number density is

$$\boldsymbol{n_V(E) = n_o e^{-E/k_B T}}$$

- This equation is known as the **Boltzmann distribution law**
- It states that the **probability** of finding the molecule in a particular energy state **varies exponentially** as the energy divided by $k_B T$

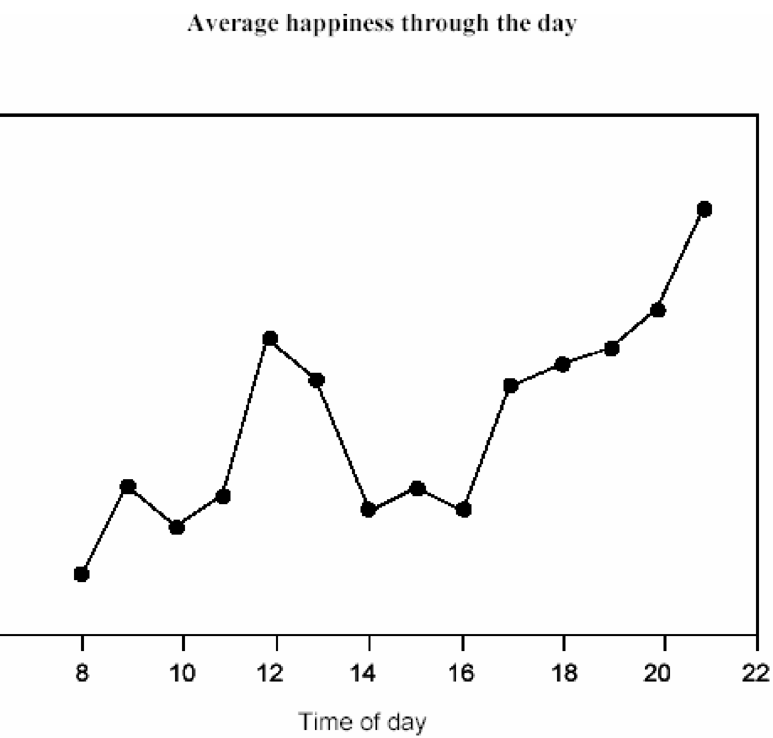
The conditions for the Boltzmann distribution law to be valid are :

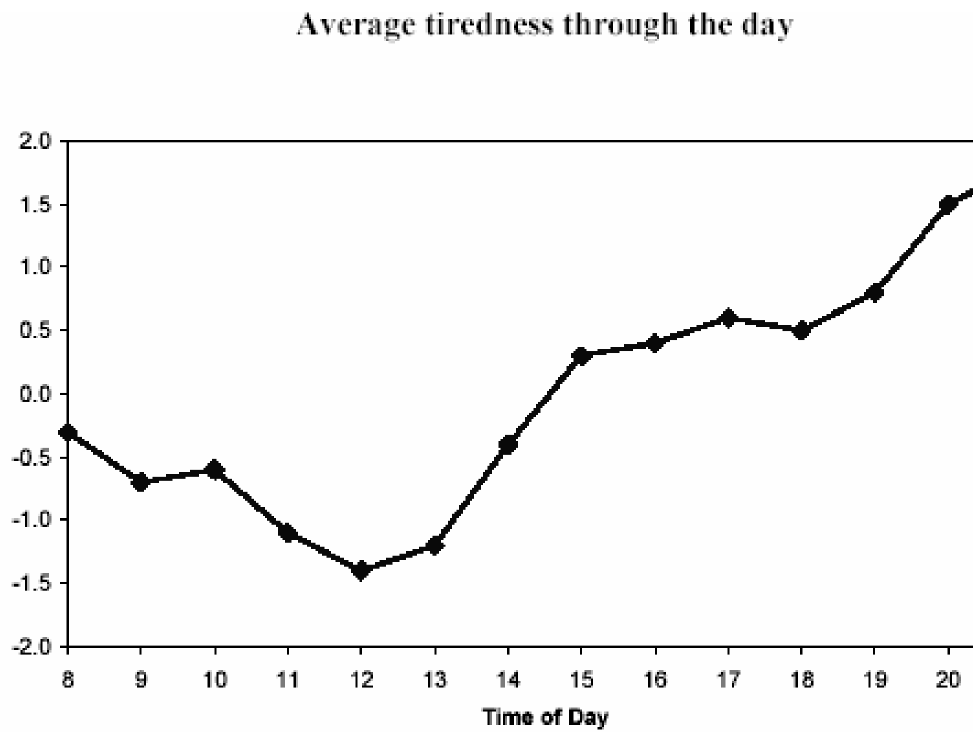
- The **number of particles** in the system **is constant**.

- The **total energy** of the system **is constant**. Nevertheless, energy can be exchanged between the particles, e.g. in collisions. But the system as a whole is thermally isolated.

Particles tend to distribute their energy among all possible states. **But, since the total energy is a constant in time, the particles can only exchange energy without producing or consuming energy.**

# Distribution of happiness through the day



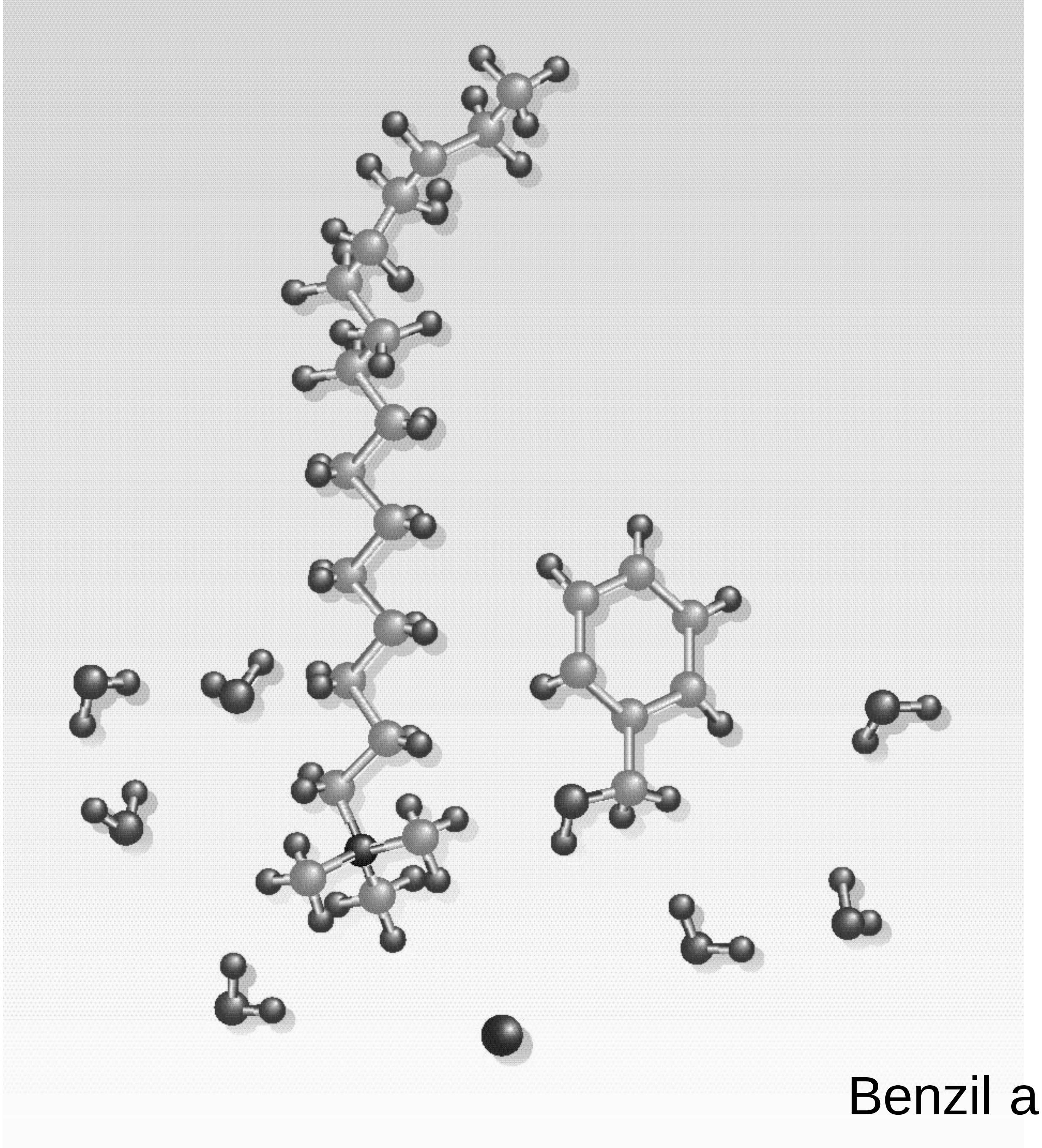




From a study of around 1000 working women in Texas. They were asked to divide the previous day into episodes, like a film. Typically they identified about 15 episodes. They then said what they were doing in each episode, and who they were doing it with. Finally they also asked how they felt in each episode, along twelve dimensions which were then combined into a single index of feeling.

**From the lecture by Richard Layard, LSE, 2003**

# Complex Molecules

- For molecules with more than two atoms, the vibrations are more complex
- The number of degrees of freedom is larger
- The more degrees of freedom available to a molecule, the more “ways” there are to store energy



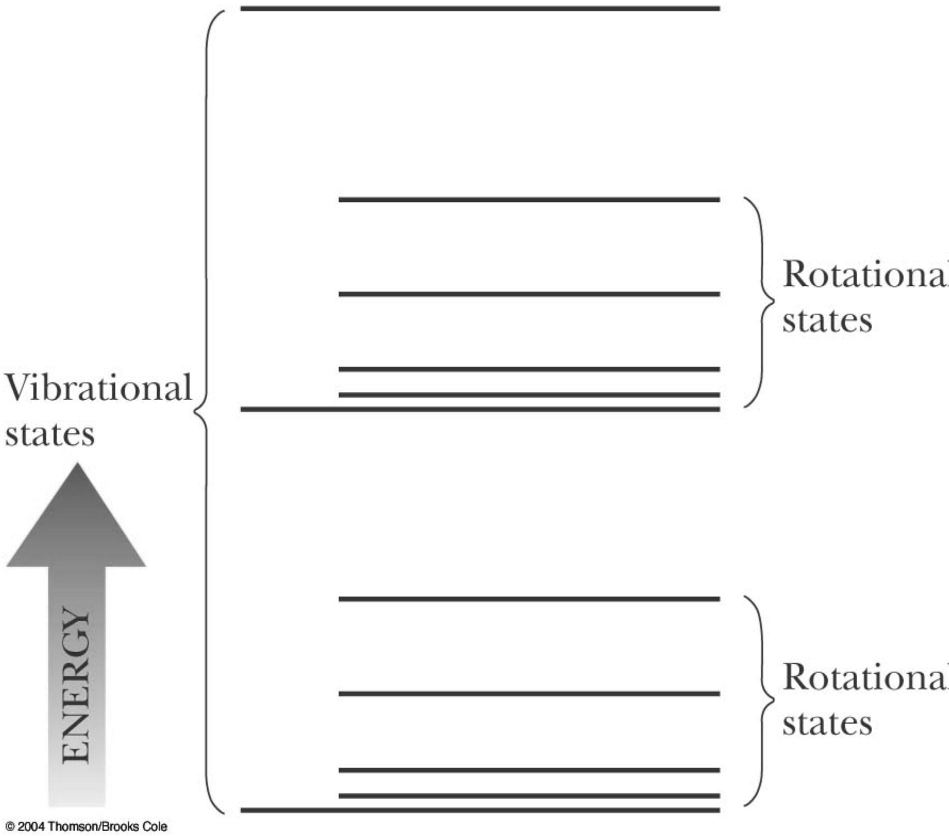
Benzil alcohol molecule

# Quantization of Energy

- In quantum mechanics, the energy is proportional to the frequency of the wave representing the frequency
- The energies of atoms and molecules are quantized

# Quantization of Energy

- This energy level diagram shows the rotational and vibrational states of a diatomic molecule
- The lowest allowed state is the **ground state**



# Population of levels according to their energy

The Boltzmann distribution law gives the number of particles per state at one energy $E_i$ compared to that at another energy $E_j$ as

$$\mathbf{N_i/N_j = \exp´\{-(E_i - E_j)/k_BT\}}$$

**So the relative population depends only on the ratio of energy difference between levels to $k_BT$.**