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Classical Statistical Mechanics (Gibbs, 1902; Einstein, 1902-04)

Let $(q_1, \ldots, q_n, p_1, \ldots, p_n)$ = phase space coordinates for a classical system of n degrees of freedom. Let $z = (q_1, \ldots, q_n, p_1, \ldots, p_n)$ stand for these coordinates collectively.

Let N = # of particles in a thermodynamic system; usually N is very large, $N \gg 1$. Ignoring internal degrees of freedom, for such a system we have

$$z = (\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N), \qquad n = 3N = \#\ \text{d.o.f.}$$

For a <u>single particle</u>, the phase space has coordinates $z = (\vec{r}, \vec{p})$, $n=3$. This is called the <u>μ-space</u> (or single-particle phase space). The dynamics is not autonomous on the μ-space unless the particles are noninteracting.

For the entire <u>N-particle system</u>, $z = (\vec{r}_1, \ldots, \vec{r}_N, \vec{p}_1, \ldots, \vec{p}_N)$ as above, $n = 3N$, and the phase space is called the <u>Γ-space</u> (or multi-particle phase space).

We postulate a <u>probability distribution</u> $\rho(z,t)$ on the Γ-space. This corresponds to an imaginary set of systems (in imagination, an infinite number), distributed throughout Γ-space. Each system is represented by a single point in Γ-space. ρ is normalized,

$$\int d^{2n}z \ \rho(z,t) = 1 \qquad \text{where } n = 3N.$$

The eqn. of evolution for ρ is the Liouville eqn,

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

where H is the Hamiltonian for the whole system. For example, we might have

$$H = \sum_{\alpha=1}^{N} \frac{|\vec{p}_\alpha|^2}{2m_\alpha} + V(\vec{r}_1, \dots, \vec{r}_N).$$

<u>Equilibrium</u> means $\frac{\partial \rho}{\partial t} = 0$. A sufficient condition for this is that ρ should be a function of the constants of motion of the system. We will assume that the Hamiltonian (the energy) is the only constant of motion, and we will take $\rho = \rho(H)$.

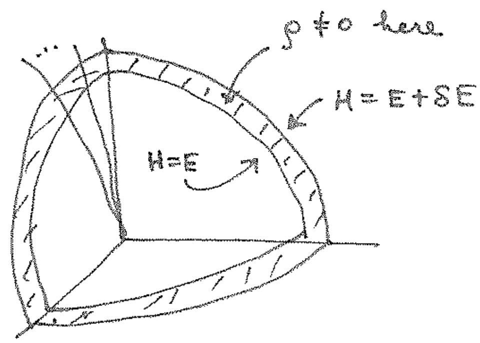
Suppose the system is isolated (so energy is conserved) and the energy is known to lie in an interval $[E, E+\delta E]$, where E is small. Then we take

$$\rho(z) = \frac{1}{A} \begin{cases} 1, & \text{if } E \le H(z) \le E + \delta E, \\ 0, & \text{otherwise} \end{cases} \qquad \delta E = \text{small}.$$

where A is a normalization. This is called the <u>microcanonical ensemble</u>. It means that all states in a given energy range are equally probable. If we took $\delta E \to 0$, we would get the distribution, $\rho(z) = \text{const} \times \delta(E - H(z))$. We will keep δE at a small but nonzero value to avoid mathematical troubles with δ-functions.

In the $6N$-dimensional phase space (Γ-space), ρ is constant and nonzero inside the <u>energy shell</u>, a thin layer between the two $(6N-1)$-dimensional surfaces $H = E$ and $H = E + \delta E$.

$\rho = 0$ everywhere else.



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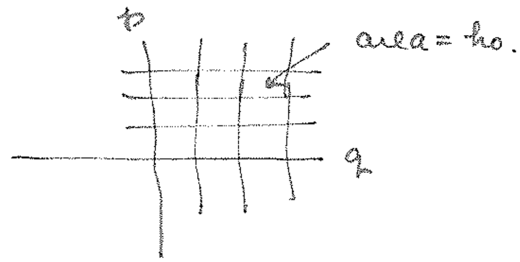
We will be interested in counting states. In classical mechanics, this requires us to discretize phase space into cells. In one d.o.f ($n=1$) we do this by introducing a grid that divides the phase plane into cells of area h_0.



h_0 has units of length × momentum = action, the same as h = Planck's constant. This is classical mechanics, so we don't assume $h_0 = h$. We will see what physics (if any) depends on h_0. For higher degrees of freedom ($n>1$) we have phase space cells of volume h_0^n.

Return to the Γ-space and the microcanonical ensemble.

Define

$$\nu(E) = \begin{pmatrix} \#\text{ of states (cells) with} \\ \text{energy} \le E \end{pmatrix} = \int_{H(z)<E} \frac{d^{2n}z}{h_0^n}.$$

$$= \int \frac{d^{2n}z}{h_0^n}\, \Theta(E-H(z))$$

where in the last integral we integrate over all of phase space. Also define

$$\Omega(E,\delta E) = \begin{pmatrix} \#\text{ of states (cells) with} \\ \text{energy between } [E, E+\delta E] \end{pmatrix} = \nu(E+\delta E) - \nu(E)$$

$$= \frac{d\nu}{dE}\,\delta E \qquad \text{if} \quad \delta E \text{ small enough.}$$

$$= \omega(E)\,\delta E,$$

where

$$\omega(E) = \frac{d\nu}{dE} = \int \frac{d^{2n}z}{h_0^n}\, \delta(E - H(z)).$$

We call $\omega(E)$ the <u>density of states</u>.

Finally, the normalization constant for ρ can be ~~written~~ derived,

$$1 = \int d^{2n}z\ \rho(z) = \frac{h_0^n}{A}\int \frac{d^{2n}z}{h_0^n}\left[\Theta(E+\delta E - H) - \Theta(E-H)\right]$$

$$= \frac{h_0^n}{A}\ \Omega(E,\delta E),$$

or,

$$\boxed{\rho = \frac{1}{h_0^n\, \Omega(E,\delta E)}\left[\Theta(E+\delta E-H) - \Theta(E-H)\right].} \qquad n = 3N$$

(microcanonical prob. distn).

Let's work this out for an ideal gas, of N identical particles, to see if it makes sense. We use the Hamiltonian,

$$H = \sum_{\alpha=1}^{N} \frac{|\vec{p}_\alpha|^2}{2m}.$$

The potential is zero, except at the walls of a container of volume V, where it rises to ∞. First we compute $\Omega(E,\delta E)$, which we get from $\omega(E)$, which we get from $\nu(E)$.

$$\nu(E) = \int d^3\vec{r}_1 \ldots d^3\vec{r}_N \int \frac{d^3\vec{p}_1 \ldots d^3 p_N}{h_0^{3N}}\ \Theta\left(E - \sum_{\alpha=1}^{N} \frac{p_\alpha^2}{2m}\right)$$

$$= \frac{V^N}{h_0^{3N}} \int_{\sum_{\alpha=1}^{N}|\vec{p}_\alpha|^2 \le 2mE} d^3\vec{p}_1 \ldots d^3\vec{p}_N.$$

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The final integral is the volume of a sphere in 3N-dimensional space of radius $\sqrt{2mE}$.

(Digression)#1. How to compute the volume of a sphere in n-dimensional space. Change notation for digression. Let R = radius of sphere.

(where $\sum_i x_i^2 = r^2$)

$$\text{vol.} = \int_{\sum_{i=1}^{n} x_i^2 \le R^2} dx_1 \dots dx_n = \int_0^R r^{n-1} dr \, d\Omega_{(n-1)} = \frac{R^n}{n} \int d\Omega_{(n-1)}.$$

where $d\Omega_{(n-1)}$ is the $(n-1)$-dimensional solid angle in n-dimensional space (e.g., $n=3$, $d\Omega_2 = \sin\theta \, d\theta \, d\phi$). To compute $\int d\Omega_{(n-1)}$, consider the Gaussian integral, which we do in both rectangular and spherical coordinates:

$$\int dx_1 \dots dx_n \, e^{-\sum_i x_i^2} = \left(\int dx \, e^{-x^2}\right)^n = \pi^{n/2}$$

$$= \int_0^\infty r^{n-1} dr \int d\Omega_{(n-1)} \, e^{-r^2}.$$

But

$$\int_0^\infty dr \, r^{n-1} e^{-r^2} = \frac{1}{2} \int_0^\infty dt \, t^{\frac{n}{2}-1} e^{-t} \qquad (t = r^2)$$

$$= \frac{1}{2} \Gamma\left(\frac{n}{2}\right).$$

(Digression #2). The Gamma function.

Defn: $\Gamma(x) = \int_0^\infty dt \, t^{x-1} e^{-t}$.

Special values: $\Gamma(1) = 1$

$\Gamma(\frac{1}{2}) = \sqrt{\pi}$

Recursion: $\Gamma(x+1) = x\,\Gamma(x)$.

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If x = integer = n,

$$\Gamma(n) = (n-1)\Gamma(n-1) = (n-1)(n-2)\ldots 1\cdot\Gamma(1) = (n-1)!$$

If x = half-integer = $n+\frac{1}{2} = \frac{2n+1}{2}$,

$$\Gamma\left(\frac{2n+1}{2}\right) = \frac{2n-1}{2}\,\Gamma\left(\frac{2n-1}{2}\right) = \left(\frac{2n-1}{2}\right)\left(\frac{2n-3}{2}\right)\cdots\left(\frac{1}{2}\right)\sqrt{\pi}.$$

Stirling: $\Gamma(x) \approx x^x e^{-x}\sqrt{\frac{2\pi}{x}}$.

End digression #2.

So from above, $$\int d\Omega_{(n-1)} = \frac{\pi^{n/2}}{\frac{1}{2}\Gamma(\frac{n}{2})},$$

and
$$\begin{pmatrix}\text{vol. of sphere of radius } R\\ \text{in } n\text{-dim'l space}\end{pmatrix} = \frac{\pi^{n/2}}{\frac{1}{2}\Gamma(\frac{n}{2})}\frac{R^n}{n} = \boxed{\frac{\pi^{n/2}}{\Gamma(\frac{n}{2}+1)}R^n.}$$

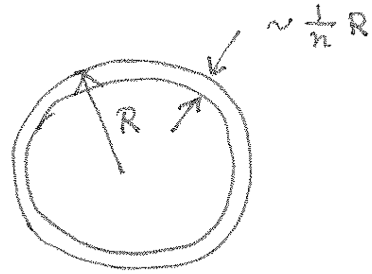
Note: when n is large, most of the volume lies near the surface, since R^n increases so rapidly. Let αR = radius inside of which the volume = $\frac{1}{2}$ of the volume at radius R. Since vol $\propto R^n$, we have

$$(\alpha R)^n = \frac{1}{2}R^n,$$

$$\alpha^n = \frac{1}{2}, \qquad \ln\alpha = -\frac{\ln 2}{n} = \text{small when } n \text{ large},$$

$$\alpha = e^{-\frac{\ln 2}{n}} \approx 1 - \frac{\ln 2}{n}.$$

Thus the fraction of the radius that contains most of the volume is $\sim\frac{1}{n}$ of total radius.



contains most of volume.

(End digression #1.)

So,

$$\nu(E) = \frac{V^N}{h_0^{3N}} \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)} \cdot (2mE)^{3N/2},$$

$$\omega(E) = \frac{3N}{2} \cdot 2m \cdot \frac{V^N}{h_0^{3N}} \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)} (2mE)^{\frac{3N}{2}-1}$$

note, $\dfrac{\frac{3N}{2}}{\Gamma(\frac{3N}{2}+1)} = \dfrac{1}{\Gamma(\frac{3N}{2})}$, so

$$\boxed{\Omega_N(E,\delta E) = 2m. \frac{V^N}{h_0^{3N}} \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2})} (2mE)^{\frac{3N}{2}-1} \delta E.}$$

Put N subscript on Ω to indicate number of particles.

Ok, this is just the normalization. Let's work out the probability distribution in phase space for a single particle. It doesn't matter which one, so let's take particle 1, and call the distribution $f(\vec{r}_1, \vec{p}_1)$. We get this by integrating ρ over all the other (2, 3, ..., N) particles.

$$f(\vec{r}_1, \vec{p}_1) = \int d^3\vec{r}_2 \ldots d^3\vec{r}_N \, d^3\vec{p}_2 \ldots d^3\vec{p}_N \quad \rho(z)$$

$$= \frac{1}{h_0^{3N} \Omega_N(E,\delta E)} \int d^3\vec{r}_2 \ldots d^3\vec{r}_N \, d^3\vec{p}_2 \ldots d^3\vec{p}_N \left[\Theta(E+\delta E - H) - \Theta(E-H) \right].$$

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Now write $$H = \frac{|\vec{p}_1|^2}{2m} + \tilde{H},$$

where $$\tilde{H} = \sum_{\alpha=2}^{N} \frac{|\vec{p}_\alpha|^2}{2m},$$ so

$$f(\vec{r}_1, \vec{p}_1) = \frac{1}{h_0^{3N}\,\Omega_N(E,\delta E)} \cdot h_0^{N-1} \times$$

$$\int \frac{d^3\vec{r}_2 \ldots d^3\vec{r}_N \, d^3\vec{p}_2 \ldots d^3\vec{p}_N}{h_0^{3(N-1)}} \left[\Theta\left(E+\delta E - \frac{p_1^2}{2m} - \tilde{H}\right) - \Theta\left(E - \frac{p_1^2}{2m} - \tilde{H}\right)\right].$$

The final integral is $\Omega_{N-1}\left(E - \frac{p_1^2}{2m}, \delta E\right)$, so

$$f(\vec{r}_1, \vec{p}_1) = \frac{h_0^{3(N-1)}\,\Omega_{N-1}\left(E - \frac{p_1^2}{2m}, \delta E\right)}{h_0^{3N}\;\Omega_N\,(E,\,\delta E)}$$

$$= \frac{2m \cdot V^{N-1} \cdot \dfrac{\pi^{\frac{3}{2}(N-1)}}{\Gamma\left(\frac{3(N-1)}{2}\right)} \left[2m\left(E - \frac{p_1^2}{2m}\right)\right]^{\frac{3}{2}(N-1)-1} \delta E}{2m \; V^N \; \dfrac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)} \left(2mE\right)^{\frac{3N}{2}-1} \; \delta E}$$

Digression. Suppose $x \gg 1$. Then

$$\Gamma(x+1) = x\,\Gamma(x)$$

$$\Gamma(x+2) = (x+1)\,x\;\Gamma(x) \approx x^2\,\Gamma(x)$$

$$\Gamma(x+3) = (x+2)(x+1)\,x\;\Gamma(x) \approx x^3\,\Gamma(x), \quad \text{etc.}$$

neglecting terms of relative order $1/x$. So we have,

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$$\Gamma(x+a) \simeq x^a \Gamma(x), \qquad x \gg a.$$

This is true even when a is not an integer. So,

$$\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N}{2}-\frac{3}{2}\right)} \simeq \frac{1}{\left(\frac{3N}{2}\right)^{-3/2}} = \left(\frac{3N}{2}\right)^{3/2}.$$

So,

$$f(\vec{r}_1,\vec{p}_1) = \frac{1}{V}\,\frac{1}{\pi^{3/2}}\left(\frac{3N}{2}\right)^{3/2} \boxed{\frac{\left[2mE-p_1^2\right]^{\frac{3N}{2}-\frac{5}{2}}}{(2mE)^{\frac{3N}{2}-1}}}.$$

$$= \left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-1}\left(2mE-p_1^2\right)^{-3/2}$$

We are interested in the limit of this as $E\to\infty$, $N\to\infty$, while holding

$$\bar{\varepsilon} \equiv \frac{E}{N} = \text{fixed}.$$

Use the following:

$$\frac{\left(\frac{3N}{2}\right)^{3/2}}{\left(2mE-p_1^2\right)^{3/2}} = \frac{\left(\frac{3}{2}\right)^{3/2}}{\left(2m\bar{\varepsilon}-\frac{p_1^2}{N}\right)^{3/2}} \to \frac{(3/2)^{3/2}}{(2m\bar{\varepsilon})^{3/2}}.$$

Also use

$$\lim_{\substack{N\to\infty \\ E\to\infty}} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-1} = \lim_{N\to\infty} \left(1 - \frac{p_1^2}{2mN\bar{\varepsilon}}\right)^{\frac{3N}{2}-1}$$

$$= e^{-\frac{3}{2}\frac{p_1^2}{2m\bar{\varepsilon}}}.$$

Then,

$$\boxed{f(\vec{r}_1,\vec{p}_1) = \frac{1}{V}\left(\frac{3/2}{2\pi m\bar{\varepsilon}}\right)^{3/2} e^{-\frac{3}{2}\frac{p_1^2}{2m\bar{\varepsilon}}}.}$$

This expresses f in terms of N, E, V, the parameters of the problem. Is it right? We know for an ideal gas, $\bar{\varepsilon} = \frac{3}{2}kT$, so

$$f(\vec{r}_1,\vec{p}_1) = \frac{1}{V}\frac{1}{(2\pi mkT)^{3/2}} e^{-\frac{p_1^2}{2mkT}},$$

which is correct (Maxwellian distribution). This calculation leads us to believe the microcanonical ensemble gives correct answers.

One more test of the microcanonical ensemble. According to Boltzmann, $S = k\ln\Omega$. Let's try it with our $\Omega(E,\delta E)$, and see if it makes sense. We get:

$$S = k\Big\{ N\ln V - 3N\ln h_0 + \frac{3N}{2}\ln\pi - \ln\Gamma\left(\frac{3N}{2}\right) + \left(\frac{3N}{2}-1\right)\ln(2mE)$$
$$+ \ln(2m) + \ln\delta E \Big\}.$$

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Use Stirling's approx,

$$\ln\Gamma\left(\frac{3N}{2}\right) = \frac{3N}{2}\left(\ln\frac{3N}{2}-1\right) + \frac{1}{2}\ln(2\pi) - \frac{1}{2}\ln\left(\frac{3N}{2}\right).$$

Also, factor N out of S (which should be proportional to N), and we get

$$S = Nk\left\{\ln V - 3\ln h_0 + \frac{3}{2}\ln\pi - \frac{3}{2}\left(\ln\frac{3N}{2}-1\right) + \frac{3}{2}\ln(2mE) + \frac{1}{N}\left[-\frac{1}{2}\ln(2\pi) + \frac{1}{2}\ln\left(\frac{3N}{2}\right) - \ln(2mE) + \ln(2m) + \ln\delta E\right]\right\}$$

The final term [ ] is negligable as $N\to\infty$ (and it's dimensionless, too), so we drop it, and get

Notice that dependence on δE has dropped out.

$$S = Nk\left\{\ln V - 3\ln h_0 + \frac{3}{2}\ln\pi + \frac{3}{2}\ln\left(\frac{2mE}{\frac{3}{2}N}\right) + \frac{3}{2}\right\}.$$

The entropy is supposed to be extensive, that is, if $\left.\begin{matrix} N\to\alpha N \\ E\to\alpha E \\ V\to\alpha V\end{matrix}\right\}$ we should get $S\to\alpha S$. This formula does not satisfy this condition. This is called the Gibbs paradox. It is resolved by noting that the identical particles are indistinguishable, so we have over counted states by a factor of $N!$, so Ω should be divided by $N!$ and S should be corrected by $-k\ln N! = -kN(\ln N-1)$.

This gives

$$\boxed{S = Nk\left\{ \ln\left(\frac{V}{N}\right) - 3\ln h_0 + \frac{3}{2}\ln\pi + \frac{3}{2}\ln\left(\frac{2mE}{\frac{3}{2}N}\right) + \frac{5}{2}\right\}.}$$