<u>The Free Boson Gas and Bose-Einstein Condensation</u>

• *Starting point:* For non-interacting bosons the grand partition function and mean occupation numbers are

$$Z_{\rm g} = \prod_\alpha \frac{1}{1-{\rm e}^{-(\epsilon_\alpha-\mu)\beta}}\;, \qquad \bar N_\alpha = \frac{1}{{\rm e}^{\beta(\epsilon_\alpha-\mu)}-1} = \frac{1}{{\rm e}^{\beta\epsilon_\alpha}z^{-1}-1}\;,$$

where the single-particle energy is $\epsilon_\alpha = \hbar^2k_\alpha^2/2m$ for massive particles, cp_α for massless particles, and the value of the chemical potential μ or fugacity $z := {\rm e}^{\beta\mu}$ are to be determined from the condition that a sum over all 1-particle states gives $\sum_\alpha \bar N_\alpha = N$. What we can say in general is that, from the fact that $\bar N_\alpha$ is positive and finite even for the smallest ϵ_α we obtain that ${\rm e}^{-\beta\mu} > 1$, or $0 < z < 1$; in particular, $\mu < 0$.

• *Goal:* Study the properties of this gas at low T. We'll see that there is a phase transition at some $T = T_{\rm c}$, below which the gas has two components, and look at the behavior of thermodynamical quantities there.

Density of States

• *Idea:* Overall quantities such as $\bar N$ and $\bar E$ are obtained as sums over 1-particle states of the system but can be converted into sums, possibly approximated by integrals, over energy levels ϵ_α, provided we know their degeneracies $g(\epsilon_\alpha)$, or the density of states $g(\epsilon)$ giving the number $g(\epsilon)\,{\rm d}\epsilon$ of states in the energy interval ${\rm d}\epsilon$.

• *Approximating the sum over states:* A general sum $\sum_\alpha f(\epsilon_\alpha)$ over states is well approximated by an integral if f varies slowly with ϵ, and in that case $g(\epsilon)$ is the function such that $\sum_\alpha f(\epsilon_\alpha) \approx \int_0^\infty {\rm d}\epsilon\, g(\epsilon)\, f(\epsilon)$. If the label $\alpha \leftrightarrow (\vec k, \gamma)$, where $k_i = 2\pi n_i/L_i$, $n \in \mathbf{Z}$, and γ is an internal parameter with g_s possible values,

$$\sum_\alpha f(\epsilon_\alpha) \approx \sum_\gamma \int_{{\rm I\!R}^3} {\rm d}^3n\, f(\epsilon(n)) = \frac{g_sV}{8\pi^3}\int_{{\rm I\!R}^3}{\rm d}^3k\, f(\epsilon(k)) = \frac{g_sV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty {\rm d}\epsilon\,\sqrt{\epsilon}\, f(\epsilon)\;,$$

where in the last step we have used the fact that for free massive particles $\epsilon = \hbar^2k^2/2m$. We conclude that

$$g(\epsilon) = \frac{g_sV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon} \equiv 2\pi\, g_sV\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\epsilon}\;.$$

Relating Chemical Potential to Temperature

• *Particle number as a sum over states:* If we replace the sum $\bar N = \sum_\alpha \bar N_\alpha$ over particle states by an integral over all energies using the density of states and set $\bar N = N$, we get that N is approximately given by

$$N \approx \int_0^\infty {\rm d}\epsilon\, g(\epsilon)\,\bar N(\epsilon) = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{\epsilon}\,{\rm d}\epsilon}{{\rm e}^{\beta\epsilon}z^{-1}-1} = \frac{2\,V}{\sqrt{\pi}}\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{x}\,{\rm d}x}{{\rm e}^xz^{-1}-1}\;,$$

where $x := \beta\epsilon$ and we have set $g_s = 1$ for simplicity. This last integral is an example of Bose-Einstein function

$$g_l(z) := \frac{1}{\Gamma(l)}\int_0^\infty \frac{x^{l-1}\,{\rm d}x}{{\rm e}^xz^{-1}-1} = \frac{z}{\Gamma(l)}\int_0^\infty \frac{{\rm e}^{-x}\,x^{l-1}\,{\rm d}x}{1-z\,{\rm e}^{-x}} = \sum_{n=1}^\infty \frac{z^n}{\Gamma(l)}\int_0^\infty {\rm d}x\, x^{l-1}\,{\rm e}^{-nx} = \sum_{n=1}^\infty \frac{z^n}{n^l}\;,$$

with $l = \frac32$. Then, if we define $\lambda := \sqrt{h^2/2\pi mk_{\rm B}T}$ as usual and using $\Gamma(l) = (l-1)\,\Gamma(l-1)$, $\Gamma(\frac12) = \sqrt{\pi}$,

$$N = V\lambda^{-3}\, g_{3/2}(z) \qquad [\text{or } \delta := \rho\,\lambda^3 = g_{3/2}(z)]\;.$$

Some relevant properties of $g_l(z)$, defined for $0 < z < 1$, are that it is a monotonically increasing function of z, which attains a finite maximum value in this range at $z = 1$ where $g_l(1) = \zeta(l)$, and that $g_l'(z) = z^{-1}\,g_{l-1}(z)$. Therefore, the maximum value of $g_{3/2}(z)$ is $g_{3/2}(1) \approx 2.612$, while its slope $g_l'(z)$ is infinite there. [Add plot.]

• *Decreasing the temperature:* As T decreases, to keep the value of $N = V\lambda^{-3}\,g_{3/2}(z)$ constant $g_{3/2}(z)$ must increase, which implies that z must increase towards 1 (or $\mu \to 0$). But $g_{3/2}(z)$ cannot increase beyond $g_{3/2}(1)$ while λ^{-3} keeps decreasing with T, so there is a finite T below which the condition $N = V\lambda^{-3}\,g_{3/2}(z)$ cannot be satisfied. The problem arose from the way we treated the $\vec k = 0$ state, since $\bar N_0 \to \infty$ as $z \to 1$.

• *Better approximation:* Treat the contribution to $\sum_{\vec k}\bar N_{\vec k}$ from the $\vec k = 0$ state, which blows up, separately:

$$N = \bar N_0 + \sum_{\vec k\neq\vec 0}\bar N_{\vec k} = \frac{z}{1-z} + \frac{2\,V}{\sqrt{\pi}}\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{x}\,{\rm d}x}{{\rm e}^xz^{-1}-1} = \frac{z}{1-z} + \frac{V}{\lambda^3}\,g_{3/2}(z)\;.$$

Bose-Einstein Condensation

• *Idea:* The expression for N/V we get from the above result has a lowest-energy contribution $\bar{N}_0/V$ and a "normal" contribution $\bar{N}_{\rm n}/V$. The latter is at most equal to the value one gets using $z = 1$. But this means that as T decreases or N increases, at some point the normal term will not be able to accommodate all N particles, and particles start condensating in the ground state. This is an example of phase transition.

• *Critical temperature:* Bose-Einstein condensation sets in at a $T_{\rm c}$ such that

$$\frac{N}{V} = \lambda^{-3}\, g_{3/2}(1) = \zeta(\tfrac{3}{2})\, \lambda^{-3}\ , \qquad \text{which gives} \qquad T_{\rm c} \approx \frac{3.31\, \hbar^2}{m k_{\rm B}}\, \rho^{2/3}.$$

To determine the behavior of thermodynamical quantities we start with the mean energy.

• *Mean Energy:* The mean number of particles $\bar{N}_\alpha$ in each state was obtained from $Z_{\rm g} = \prod_\alpha [1-{\rm e}^{-(\epsilon_\alpha-\mu)\beta}]^{-1}$, from which we can also get $\bar{E} = -\partial \ln Z_{\rm g}/\partial\beta|_{\beta\mu}$. Alternatively, we can calculate the mean energy using

$$\bar{E} = \sum_\alpha \epsilon_\alpha\, \bar{N}_\alpha \approx \int_0^\infty {\rm d}\epsilon\, g(\epsilon)\, \epsilon\, \bar{N}(\epsilon) = \int_0^\infty {\rm d}\epsilon\, g(\epsilon)\, \frac{\epsilon}{{\rm e}^{\beta\epsilon} z^{-1} - 1}$$

(notice that now we can replace the sum with an integral without running into a problem with the $k = 0$ term) and, introducing again the variable $x := \beta\epsilon$,

$$\bar{E} = \frac{V}{\sqrt{2}\pi^2} \Big(\frac{m k_{\rm B} T}{\hbar^2}\Big)^{3/2} k_{\rm B} T \int_0^\infty \frac{x^{3/2}\, {\rm d}x}{{\rm e}^x z^{-1} - 1} = \frac{3}{2}\, \lambda^{-3}\, k_{\rm B} T\, V\, g_{5/2}(z)\ .$$

• *Heat capacity:* According to the definition $C_V = \partial\bar{E}/\partial T|_{V,N}$, but the energy expression above is of the form $\bar{E}(T,V,z) = \bar{E}(T,V,z(T,V,N))$, and varying T in it while keeping N constant means calculating

$$C_V = \frac{\partial\bar{E}}{\partial T}\Big|_{V,z} + \frac{\partial\bar{E}}{\partial z}\Big|_{T,V} \frac{\partial z}{\partial T}\Big|_{V,N}\ .$$

The pieces that go into the calculation are

$$\frac{\partial\bar{E}}{\partial T}\Big|_{V,z} = \frac{15}{4}\, \lambda^{-3} k_{\rm B} V\, g_{5/2}(z)\ , \qquad \frac{\partial\bar{E}}{\partial z}\Big|_{T,V} = \frac{3}{2}\, \lambda^{-3}\, k_{\rm B} T\, V\, z^{-1}\, g_{3/2}(z)\ ,$$
$$\frac{\partial z}{\partial T}\Big|_{V,N} = -\frac{3z}{2T}\, \frac{g_{3/2}(z)}{g_{1/2}(z)} \quad \text{(from differentiating } N = V \lambda^{-3} g_{3/2}(z),\ \text{for } T > T_{\rm c})\ ,$$

and substituting into the heat capacity we finally get that [add plots of $\bar{N}_0$, $\bar{N}_{\rm n}$ and C_V]

$$C_V = \frac{3}{4}\, \lambda^{-3} k_{\rm B} V \left(5\, g_{5/2}(z) - 3\, \frac{g_{3/2}^2(z)}{g_{1/2}(z)}\right)\ .$$

It is easy to check that in the $T \to 0$ limit ($\lambda \to \infty$, $z \to 1$), $\partial z/\partial T|_{V,N} \approx 0$ and $C_V \approx \partial\bar{E}/\partial T|_{V,z}$ vanishes as $T^{\,3/2}$, consistently with the third law; and as $T \to \infty$ ($\lambda \to 0$, $z \to 0$), when all $g_l(z) \approx z + \mathcal{O}(z^2)$ with $z \approx \rho\, \lambda^3$, the heat capacity approaches $\frac{3}{2}\, k_{\rm B} N$, consistently with the principle of equipartition.

• *Applications:* Well-known ones are related to liquid-He superfluidity and superconductivity, phenomena in which particles (He atoms and Cooper pairs) condense in the ground state and the systems exhibit zero viscosity and electrical resistivity, respectively. Each of those systems has interesting features of its own, as ^{3}He behaves differently from ^{4}He and those fluids are not ideal gases. Applications to cosmology include proposals for dark matter and dark energy.

Reading

• *Course textbook:* Kennett, §§ 9.1–9.3.
• *Other textbooks:* Halley, pp 74–78; Mattis & Swendsen, §§ 5.8–5.10; Pathria & Beale, Chapter 7; Plischke & Bergersen, § 11.1; Schwabl, § 4.4.