and using

$$\int_0^\infty \frac{E^3 \, \mathrm{d}E}{z^{-1}\mathrm{e}^{\beta E} - 1} = (k_\mathrm{B}T)^4 \Gamma(4)\mathrm{Li}_4(z), \qquad (30.49)$$

and recognizing that $z = 1$ because $\mu = 0$ and hence $\mathrm{Li}_4(z) = \zeta(4) = \pi^4/90$, and using $\Gamma(4) = 3! = 6$, we have that

$$U = \frac{V\pi^2}{15\hbar^3 c^3}(k_\mathrm{B}T)^4, \qquad (30.50)$$

which agrees with eqn 23.37.

For Bose systems with a dispersion relation like $E = \hbar^2 k^2/2m$ (i.e. for a gapless dispersion, where the lowest–energy level, corresponding to $k = 0$ or infinite wavelength, is at zero energy), the chemical potential has to be negative. If it were not, the level at $E = 0$ would have infinite occupation. Thus $\mu < 0$, and hence the fugacity $z = \mathrm{e}^{\beta\mu}$ must lie in the range $0 < z < 1$. But what value will the chemical potential take?

Equation 30.45 can be rearranged to give

$$N = \frac{(2S+1)\,V}{\lambda_T^3} \cdot \mathrm{Li}_{3/2}(z)$$

$$\frac{n\lambda_\mathrm{th}^3}{2S + 1} = \mathrm{Li}_{3/2}(z), \qquad (30.51)$$

and here we hit an uncomfortable problem. The left-hand side can be increased if $n = N/V$ increases or if T decreases (because $\lambda_\mathrm{th} \propto T^{-1/2}$). We can plug numbers for n and T into the left-hand side and then read off a value for z from the graph in Fig. 30.3, which shows the behaviour of the function $\mathrm{Li}_{3/2}(z)$ (and also $\mathrm{Li}_{5/2}(z)$). As we raise n or decrease T, we make the left-hand side of eqn 30.51 bigger and hence z bigger, so that μ becomes less negative, approaching 0 from below. However, if

$$\frac{n\lambda_\mathrm{th}^3}{2S + 1} > \zeta(\tfrac{3}{2}) = 2.612, \qquad (30.52)$$

there is no solution to eqn 30.51. What has happened?

30.4   Bose–Einstein condensation (BEC)

The solution to the conundrum raised in the previous section is remarkably subtle, but has far-reaching consequences. As the chemical potential has become closer and closer to zero energy, approaching this from below, the lowest energy level has become macroscopically occupied. The reason our mathematics has broken down is that our usual, normally perfectly reasonable, approximation in going from a sum to an integral in evaluating our grand partition function is no longer valid.

In fact, we can see when this fails using a rearranged version of eqn 30.52. Failure occurs when we fall below a temperature T_c given by

$$k_\mathrm{B}T_\mathrm{c} = \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.612(2S+1)}\right)^{2/3}. \qquad (30.53)$$