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6.4 A numerical Boltzmann problem example

For this example we choose three energy levels (m = 3) so the state count is given by

$$\Omega(N_1,N_2,N_3) = \frac{g_1^{N_1}}{N_1!}\frac{g_2^{N_2}}{N_2!}\frac{g_3^{N_3}}{N_3!} \qquad \textit{(6.1.3)} \qquad (6.4.1)$$

and correspondingly (this uses the Stirling approximation),

$$f = \ln\Omega = \Sigma_{i=1}^{3} N_i\,[1 + \ln(g_i/N_i)]\,. \qquad \textit{(6.2.3)} \qquad (6.4.2)$$

Assume the three energy levels are ordered in this manner, where ε_1 is the lowest energy state,

$$\varepsilon_1 < \varepsilon_2 < \varepsilon_3\,. \qquad \text{and recall} \qquad u = U/M \quad \text{and } \varepsilon_1 \le u \le \varepsilon_3 \qquad (6.4.3)$$

We regard both N_1 and N_2 as functions of N_3 where, according to (6.3.1),

$$\begin{aligned} N_1 &= +(\varepsilon_2-\varepsilon_1)^{-1}[\,\varepsilon_2 M - U + (\varepsilon_3-\varepsilon_2)N_3] &&= N_1(N_3) \\ N_2 &= -(\varepsilon_2-\varepsilon_1)^{-1}[\,\varepsilon_1 M - U + (\varepsilon_3-\varepsilon_1)N_3] &&= N_2(N_3)\,. \end{aligned} \qquad \textit{(6.3.1)} \qquad (6.4.4)$$

It seems clear that one must have

$$\begin{aligned} &0 \le N_1 \le M \\ &0 \le N_2 \le M. \end{aligned} \qquad (6.4.5)$$

Using the expressions (6.4.4) in these inequalities and making use of (6.4.3) and the fact that $\varepsilon_1 \le u \le \varepsilon_3$, one finds that all four inequalities can be summarized as just two inequalities which we write as,

$$N_{3min} \le N_3 \le N_{3max}$$

$$N_{3min} = \max\left(\frac{u-\varepsilon_2}{\varepsilon_3-\varepsilon_2}M,\ 0\right)$$

$$N_{3max} = \min\left(\frac{u-\varepsilon_1}{\varepsilon_3-\varepsilon_1}M,\ M\right) = \frac{u-\varepsilon_1}{\varepsilon_3-\varepsilon_1}M \qquad \text{// since } u \le \varepsilon_3 \qquad (6.4.6)$$

To find the Lagrange multiplier β we must solve (6.2.17),

$$\Sigma_i\,[\,\varepsilon_i - u\,]\,g_i\,e^{-\beta\varepsilon_i} = 0\,. \qquad \textit{(6.2.17)} \qquad (6.4.7)$$

Then the other derived multiplier is then given by (6.2.14)

$$A = \frac{M}{\Sigma_i g_i\,e^{-\beta\varepsilon_i}} = \frac{M}{Z} \quad \text{where } Z \equiv \Sigma_i g_i e^{-\beta\varepsilon_i}\,. \qquad \textit{(6.2.14)} \qquad (6.4.8)$$

The components N_i of the solution vector are then given by

$$N_i = A\ g_i\ e^{-\beta\varepsilon_i}\ . \qquad (6.2.11) \qquad (6.4.9)$$

The curvature of f at its peak is given by

$$\frac{d^2f}{d^2N_3} = -\{\ \frac{1}{N_1}\ [\frac{\varepsilon_3-\varepsilon_2}{\varepsilon_2-\varepsilon_1}\ ]^2 + \frac{1}{N_2}[\ \frac{\varepsilon_3-\varepsilon_1}{\varepsilon_2-\varepsilon_1}\ ]^2 + \frac{1}{N_3}\ \} \qquad (6.3.8) \qquad (6.4.10)$$

The half-width of the Ω peak is then given by

$$dN_i = \sqrt{\frac{1.4}{|d^2f/d^2N_i|}} \qquad (6.3.13) \qquad (6.4.11)$$

For our specific Maple plots, we shall assume

$\varepsilon_3 = 3$	M = 1000 = number of particles	
$\varepsilon_2 = 2$	u = 1.5 = average energy	
$\varepsilon_1 = 1$	$g_1 = g_2 = g_3 = 5000$ = degeneracy	(6.4.12)

Here then is our Maple code. We first enter Ω,

```
restart; with(plots):
Omega := product(g[i]^N[i]/(N[i]!),i=1..3);
```

$$\Omega := \frac{g_1^{N_1}\ g_2^{N_2}\ g_3^{N_3}}{N_1!\ N_2!\ N_3!}$$

The quantities N_1 and N_2 are then replaced as in (6.4.4), [we use e_i in place of ε_i]

```
N[1] := (e[2]*M-U+(e[3]-e[2])*N[3])/(e[2]-e[1]);
```

$$N_1 := \frac{e_2 M - U + (e_3 - e_2) N_3}{e_2 - e_1}$$

```
N[2] := -(e[1]*M-U+(e[3]-e[1])*N[3])/(e[2]-e[1]);
```

$$N_2 := -\frac{e_1 M - U + (e_3 - e_1) N_3}{e_2 - e_1}$$

We next enter most of the data shown above and use it to compute N_{3min} and N_{3max}

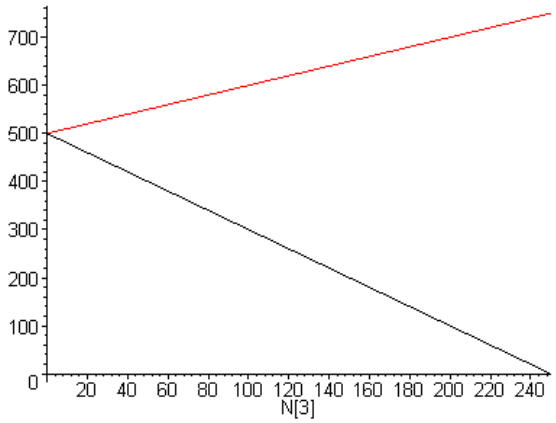
```
e[1] := 1: e[2] := 2: e[3] := 3: u := 1.5: M := 1000: U := M*u:
N3min := max(0,M*(u-e[2])/(e[3]-e[2]));
N3max := M*(u-e[1])/(e[3]-e[1]);
```

$$N3min := 0$$

$$N3max := 250.0000000$$

so the legal range of N_3 is (0,250). Here is a plot of N_1 (red) and N_2(black) versus N_3 :

```
plot([N[1],N[2]],N[3] = N3min..N3max, color = [red,black]);
```



(6.4.13)

We then enter the degeneracies and take a look at Ω in its numerical form,

```
g[1] := 5000: g[2] := 5000: g[3] := 5000:
Omega;
```

$$\frac{5000^{(500.0+N_3)}\ 5000^{(500.0-2N_3)}\ 5000^{N_3}}{(500.0+N_3)!\,(500.0-2N_3)!\,N_3!} \tag{6.4.14}$$

As is typical in statistical mechanics, at its peak the value of Ω is a *very* large number. Even with our relatively small number of particles M = 1000 and degeneracy g = 5000, the peak value is (see below)

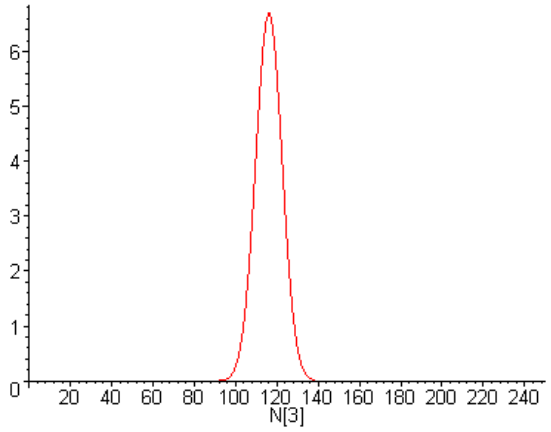
$$\Omega_{peak} = 6.71 \times 10^{1519} \tag{6.4.15}$$

Maple is uncomfortable plotting numbers larger than about 10^{40} so we pre-scale Ω down by 10^{1519} to make the scaled Ω be Maple-digestible. This scaling process in turn creates numbers smaller than 10^{-40} which are also rejected by the Maple plotter, so we use a Heaviside function to pin small numbers to 0 unless they are greater than the arbitrary value .01. Here then is a plot of $\Omega(N_3)$,

```
scale := 1e1519;
```

$$scale := .1\ 10^{1520}$$

```
OmegaScaled := (Omega/scale)*Heaviside(Omega/scale-.01):
xx := plot(  OmegaScaled,N[3] = N3min..N3max,numpoints=100  ):
display(xx);
```

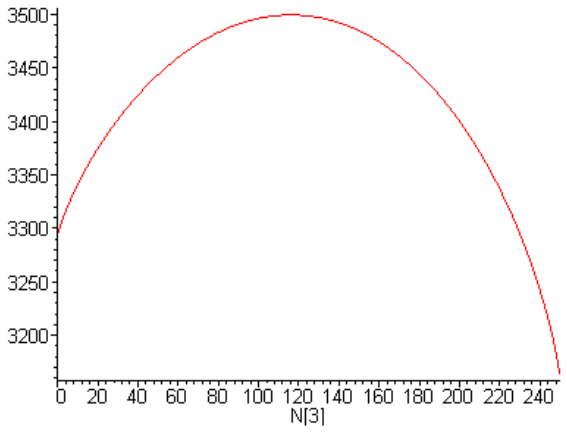


(6.4.16)

We broke the display command into two pieces: first create xx then plot xx. Replacing : with ; after the plot command gives one a list of numbers to be plotted, and from this list one can determine a reasonable scale factor. Once that is found, the plotting coordinates need not be displayed. The curve $\Omega(N_3)$ has the typical Gaussian (normal) shape which no doubt the energetic reader could show results from the central limit theorem.

A plot of $f = \ln(\Omega)$ has a much smoother and broader shape,

```
plot(ln(Omega),N[3] = N3min..N3max,numpoints=100 );
```



(6.4.17)

Recall from (6.3.8) that $\frac{d^2 f}{d^2 N_i}$ is everywhere negative, consistent with the cupping down seen in this plot.

Next, we have Maple solve (6.2.17) for the Lagrange multiplier β,

```
eq := sum((e[i]-u)*g[i]*exp(-beta*e[i]),i=1..3) = 0;
```

$$eq := -2500.\, e^{(-1.\,\beta)} + 2500.\, e^{(-2.\,\beta)} + 7500.\, e^{(-3.\,\beta)} = 0$$

```
s := solve(eq,beta);
```

$$s := .2644970943 - 3.141592654\, I,\ .8341151943$$

```
beta := s[2];
```

$$\beta := .8341151943$$

With $w = e^{-\beta}$ the above equation is $3w^2+w-1 = 0$ which has solutions $w = (-1 \pm \sqrt{13})/6$. The minus sign gives the complex β noted, while the plus sign gives the physical solution $\beta = - \ln[(-1 + \sqrt{13})/6] = .834$.

From this β value we compute the other Lagrange parameter A from (6.2.14)

```
Z := sum(g[i]*exp(-beta*e[i]),i=1..3);
```

$$Z := 99083.26914$$

```
A := M/Z;
```

$$A := .01009252126$$

Once these parameters are known, we use (6.2.11) to display the solution vector $\mathbf{N} = \{N_i\}$.

```
for i in [3,2,1] do N[i] := A*g[i]*exp(-beta*e[i]) od;
```

$$N_3 := 116.2040605$$

$$N_2 := 267.5918793$$

$$N_1 := 616.2040607$$

Since we set $u < \varepsilon_2$, we see here a normal distribution where higher energy states have fewer particles.

Our final task is to use (6.3.8) and (6.3.13) to determine the half-width of the Ω peak,

```
curve := (1/N[1])*((e[3]-e[2])/(e[2]-e[1]))^2 + (1/N[2])*((e[3]-e[1])/(e[2]-e[1]))^2 + 1/N[3]
```

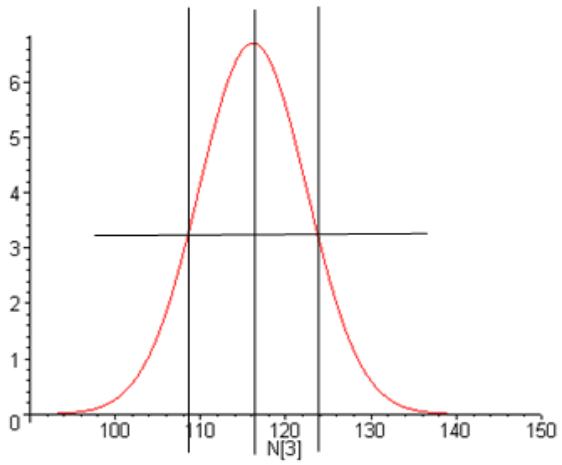
$$curve := .02517652703$$

```
dN3 := sqrt(1.4/curve);
```

$$dN3 := 7.457033725$$

which says $\Delta N \approx 7.5$. This width and the solution $N_3 = 616.2$ can be verified from this blowup plot of Ω,

```
xx := plot(  OmegaScaled,N[3] = 90..150,numpoints=100  ):
display(xx);
```



Notice that this Maple code does not use the Stirling approximation and provides a continuous interpolation of N! as Γ(N+1).

The peak value of Ω is found to be

```
evalf(Omega);
```

$$.6710572393\ 10^{1520}$$

In the above example we used u = 1.5 < ε_2 = 2. If we instead use u = 2.5 > ε_2 = 2, we find that the state populations are as shown above but in reverse order. Such a inverted situation corresponds to a negative absolute temperature T and cannot therefore arise in thermal equilibrium. It could arise in a laser medium which is driven by some power source.