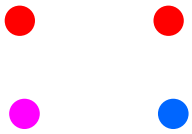
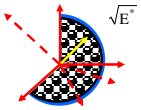
We shall now attempt to evaluate the number Ω.

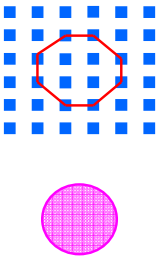
In this evaluation we shall explicitly assume the particles to be distinguishable, so that if a particle in state i gets interchanged with a particle in state j the resulting microstate is counted as distinct.



Consequently, the number Ω(N, V,E), or better $\Omega_N(E^*)$ is equal to the number of positive-integral lattice points **lying on** the surface of a 3N-dimensional sphere of radius $\sqrt{E^*}$.



Clearly, this number will be an extremely irregular function of E*, in that for two given values of E* which may be very close to one another the values of this number could be very different.



In contrast, the number $\Sigma_N(E^*)$, which denotes the number of positive-integral lattice points lying on or within the surface of a 3N-dimensional sphere of radius $\sqrt{E^*}$, will be much less irregular. In terms of our physical problem, this would correspond to the number, Σ(N, V, E), of microstates of the given system consistent with all macrostates characterized by the specified values of the parameters N and V but having energy less than or equal to E, i.e.

$$\Sigma(N, V, E) = \sum_{E' \le E} \Omega(N, V, E')$$

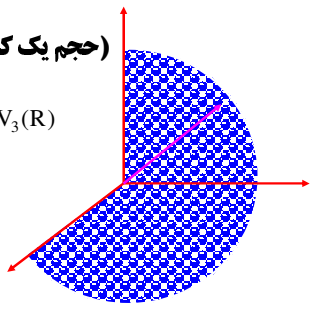
or

$$\Sigma_N(E^*) = \sum_{E^{*'} \le E^*} \Omega_N(E^{*'})$$

برای یک ذره در یک جعبه یک کره سه بعدی کافی است.

(حجم یک کره سه بعدی) ۱/۸

$$\frac{1}{8} \times \frac{4}{3} \pi R^3 = \frac{1}{8} \times V_3(R)$$



برای N ذره غیر برهمکنشی می توان نتیجه یک کره سه بعدی را بـه تـوان N رسانید. اما چون حتی برای یک ذره خود فرض کردن کره و محاسبه یک هشتم آن با تقریب همراه است، لذا به توان N رسانیدن آن با تقریب بیشتری همـراه خواهد شد. اگرچه در نظر گرفتن کره ^{3}N-بعدی نیز خود با تقریـب بـه دلیل پیوسته فرض کردن فضای گسسته همراه اسـت، امـا از دقـت بیشتری نسبت به قبل برخوردار است.

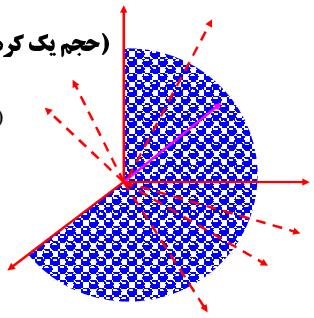
$$\frac{1}{2^{3N}}\times V_{3N}(R) \Longleftrightarrow \left(\frac{1}{8}\times\frac{4}{3}\pi R^{3}\right)^{N}=\left(\frac{1}{8}\times V_{3}(R)\right)^{N}$$

$$V_{3N}(R)=\frac{\pi^{3N/2}}{(3N/2)!}R^{3N} \neq \left[V_{3}(R)\right]^{N}=\left[\frac{4}{3}\pi R^{3}\right]^{N}=\left[\frac{4}{3}\pi\right]^{N}R^{3N}$$

اما برای N ذره یک کره 3N–بعدی دقت بیشتری دارد.

(حجم یک کره سه N بعدی) $1/2^{3N}$

$$\frac{1}{8}\times V_{3N}(R)$$



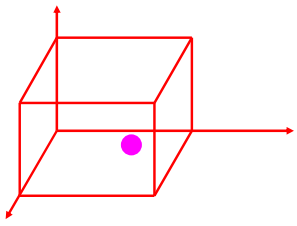
تمرین: حجم یک کره 3N بعدی را به دست آورید. (راهنمایی: ضمیمه کتاب پاتریا)

اما دقت شود همواره برای ذرات غیر برهمکنشی داریم که:

$$\Omega_N=[\Omega_1]^N$$

Of course, the number Σ will also be somewhat irregular; however, we expect that its asymptotic behavior, as $E^*\to\infty$ would be a lot smoother than that of Ω. We shall see in the sequel that the thermodynamics of the system follows equally well from the number Σ as from Ω.

To appreciate the point made here, let us digress a little to examine the behavior of the numbers $\Omega_1(\varepsilon^*)$ and $\Sigma_1(\varepsilon^*)$, which correspond to the case of a single particle confined to the given volume V.



The exact values of these numbers, for $\varepsilon^* < 10000$, can be extracted from a table compiled by Gupta (947).

تمرین: تعداد فوق را شمارش نمایید. راهنمایی: مرجع زیر را مطالعه نمایید:

Gupta, H. A947) Proc. Nat. Ins. Sci. India 13, 35.

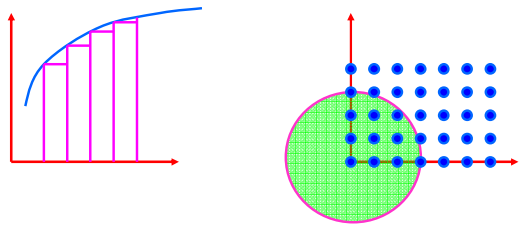
The **wild irregularities** of the number $\Omega_1(\varepsilon^*)$ can hardly be missed. The number $\Sigma_1(\varepsilon^*)$, on the other hand, exhibits a much **smoother asymptotic behavior**. From the geometry of the problem, we note that, asymptotically, $\Sigma_1(\varepsilon^*)$ **should be equal** to the volume of an **octant of a three-dimensional sphere of radius** $\sqrt{\varepsilon^*}$, i.e.

$$\lim_{\varepsilon^*\to\infty}\frac{\sum_1(\varepsilon^*)}{\frac{1}{8}\times\frac{4}{3}\pi\varepsilon^{*3/2}}=\lim_{\varepsilon^*\to\infty}\frac{\sum_1(\varepsilon^*)}{(\pi/6)\varepsilon^{*3/2}}=1$$

A more detailed analysis shows (see Pathria, 1966) that, to the next approximation,

$$\Sigma_1(\varepsilon^*)\approx\frac{\pi}{6}\varepsilon^{*3/2}\boxed{-\frac{3\pi}{8}\varepsilon^*}$$

the correction term arises from the fact that the volume of an octant somewhat overestimates the number of desired lattice points for it includes, partly though, some points with one or more coordinates equal to zero. Figure 1.2 shows a histogram of the actual values of $\Sigma_1(\varepsilon^*)$ for ε^* lying between 200 and 300; the theoretical estimate (15) is also shown. In the figure, we have also included a histogram of the actual values of the corresponding number of microstates, $\Sigma_1'(\varepsilon^*)$, when the quantum numbers n_x, n_y and n_z can assume the value zero as well. In the latter case, the volume of an octant somewhat underestimates the number of desired lattice points; we now have



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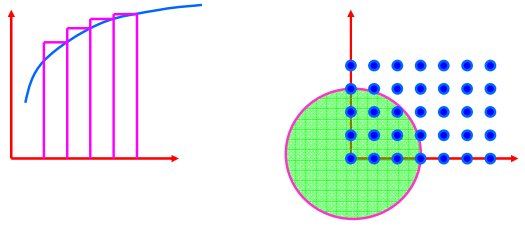
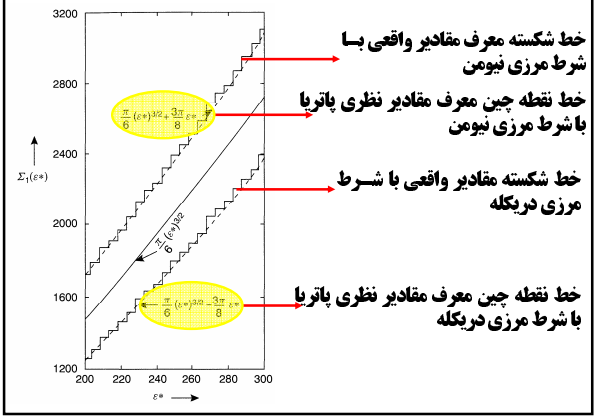
$$\Sigma_1'(\varepsilon^*)\approx\frac{\pi}{6}\varepsilon^{*3/2}\boxed{+\frac{3\pi}{8}\varepsilon^*}$$





تمرین: جملات تصحیحی معرفی شده را به دست آورید.

راهنمایی: از مرجع زیر استفاده نمایید:

Pathria, R. K. (966) Nuovo Cim. (Supp,), Ser. I, 4, 276.

Returning to the N-particle problem, the number $\Sigma_N(E^*)$ should be asymptotically equal to the "volume" of the "positive compartment" of a 3N-dimensional sphere of radius $\sqrt{E^*}$.

$$V_n(R)=\frac{\pi^{n/2}}{(n/2)!}R^n \longrightarrow S_n(R)=\frac{dV^n}{dR}=n\frac{\pi^{n/2}}{(n/2)!}R^{n-1}=$$

$$=\frac{2\pi^{n/2}}{(n/2-1)!}R^{n-1}$$

$$V_3(R)=\frac{\pi^{3/2}}{(3/2)!}R^3 \qquad S_3(R)=\frac{2\pi^{3/2}}{(3/2-1)!}R^2$$

$$\Gamma(n+1)=n!=\int_0^\infty e^{-x}x^n dx \longrightarrow \Gamma(1/2)=\int_0^\infty e^{-x}x^n dx=\sqrt{\pi}$$

$$V_3(R)=\frac{\pi^{3/2}}{(3/2)(1/2)\Gamma(1/2)}R^3 \qquad S_3(R)=\frac{2\pi^{3/2}}{(1/2)\Gamma(1/2)}R^2$$

$$V_3(R)=\frac{\pi^{3/2}}{(3/4)\sqrt{\pi}}R^3 \qquad S_3(R)=\frac{2\pi^{3/2}}{1/2\sqrt{\pi}}R^2$$

$V_3(R)=4/3\pi R^3$ ☺ $\qquad S_3(R)=4\pi R^2$ ☺

$$\sum_N(E^*)\approx\left(\frac{1}{2}\right)^{3N}\left\{\frac{\pi^{\frac{3N}{2}}}{(3N/2)!}\right\}E^{*3N/2}$$

$$\left\{\left(\frac{1}{2}\right)^3\left[\frac{4}{3}\pi E^{*3/2}\right]\right\}^N=\left(\frac{1}{2}\right)^{3N}\left(\frac{4}{3}\pi\right)^N E^{*3N/2}=\left(\frac{1}{2}\right)^{3N}\left\{\frac{\pi^N}{(3/2)!}\right\}E^{*3N/2}$$

$$\sum_{r=1}^{3N}n_r^2=\frac{8mV^{2/3}}{h^2}=E^*$$

$$\sum_N(E^*)\approx\left(\frac{1}{2}\right)^{3N}\left\{\frac{\pi^{\frac{3N}{2}}}{(3N/2)!}\right\}\left\{\frac{8mV^{2/3}}{h^2}\right\}^{3N/2}=\left(\frac{V}{h^3}\right)^N\frac{(2\pi mE)^{\frac{3N}{2}}}{(3N/2)!}$$

$$\sum_N(E^*)\approx\left(\frac{V}{h^3}\right)^N\frac{(2\pi mE)^{\frac{3N}{2}}}{(3N/2)!}$$

$$\mathrm{Ln}\left(\sum_N(E^*)\right)\approx\mathrm{Ln}\left\{\left(\frac{V}{h^3}\right)^N\frac{(2\pi mE)^{\frac{3N}{2}}}{(3N/2)!}\right\}=$$

$$N\mathrm{Ln}\left(\frac{V}{h^3}\right)+N\mathrm{Ln}(2\pi mE)^{\frac{3}{2}}-\mathrm{Ln}(3N/2)!=$$

$$N\mathrm{Ln}\left(\frac{V}{h^3}\right)+N\mathrm{Ln}(2\pi mE)^{\frac{3}{2}}-3N/2\,\mathrm{Ln}(3N/2)+3N/2=$$

$$N\mathrm{Ln}\left(\frac{V}{h^3}\right)+N\mathrm{Ln}(2\pi mE)^{\frac{3}{2}}-N\mathrm{Ln}(3N/2)^{3N/2}+3N/2=$$

$$\mathrm{Ln}\left(\sum_N(E^*)\right)\approx N\mathrm{Ln}\left(\frac{V}{h^3}\right)+N\mathrm{Ln}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}+3N/2$$

$$\mathrm{Ln}(n!)\approx n\mathrm{Ln}(n)-n$$

$$\mathrm{Ln}(n!)=\sum_{i=1}^{n}\mathrm{Ln}(i)$$

$$\mathrm{Ln}(n!)\approx\int_1^n\mathrm{Ln}(x)dx=[x\mathrm{Ln}(x)-x]_1^n=$$

$$=[n\mathrm{Ln}(n)-n]-[-1]$$

$$n\gg 1\Rightarrow \mathrm{Ln}(n)!\approx n\mathrm{Ln}(n)-n$$

For deriving the thermodynamic properties of the given system we must somehow fix the precise value of, or limits for, the energy of the system. In view of the extremely irregular nature of the function $\Omega(N, V, E)$, the specification of a precise value for the energy of the system cannot be justified on physical grounds, for that would never yield well-behaved expressions for the thermodynamic functions of the system. From a practical point of view, too, an absolutely isolated system is too much of an idealization. In the real world, almost every system has some contact with its surroundings, however little it may be; as a result, its energy cannot be defined sharply.[12] Of course, the effective width of the range over which the energy may vary would, in general, be small in comparison with the mean value of the energy. Let us specify this range by the limits $(E-\frac{1}{2}\Delta)$ and $(E+\frac{1}{2}\Delta)$ where, by assumption, $\Delta \ll E$; typically, $\Delta/E = O(1/\sqrt{N})$. The corresponding number of microstates, $\Gamma(N, V, E; \Delta)$, is then given by

$$\Gamma(N,V,E;\Delta)\simeq\frac{\partial\Sigma(N,V,E)}{\partial E}\Delta\approx\frac{3N}{2}\frac{\Delta}{E}\Sigma(N,V,E)$$

$$\Gamma(N,V,E;\,\Delta) \simeq \frac{\partial \Sigma(N,V,E)}{\partial E}\Delta \approx \frac{3N}{2}\frac{\Delta}{E}\Sigma(N,V,E)$$

$$\Omega(E) = \Phi(E+\delta E) - \Phi(E) = \frac{d\Phi}{dE}\delta E$$

$$\delta E \equiv \Delta \qquad \Phi(E) \equiv \Sigma(N,E,V) \qquad \Omega(E) \equiv \Gamma(N,E,V;\Delta)$$

در واقع $\Omega(E)$ نه $\Omega(E;\ \delta E)$ چون دقیقا به E اشاره می کند ولی در طبیعت فقط می توان از $\Omega(E;\ \delta E)$ صحبت کرد.

$$\Gamma(N,V,E;\,\Delta) \simeq \frac{\partial \Sigma(N,V,E)}{\partial E}\Delta \approx \frac{3N}{2}\frac{\Delta}{E}\Sigma(N,V,E)$$

$$\sum_N(E) \approx \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{(3N/2)!}$$

$$\frac{\partial \Sigma}{\partial E} = \frac{3N}{2}\left(\frac{V}{h^3}\right)^N \frac{(2\pi m)E^{\frac{3N}{2}-1}}{(3N/2)!} = \frac{3N}{2}\frac{\Sigma(E)}{E}$$

$$\Gamma(N,V,E;\Delta) \cong \frac{3N}{2}\frac{\Sigma(E)}{E}\Delta = \frac{3N}{2}\frac{\Delta}{E}\Sigma(E)$$

$$\Gamma(N,V,E;\,\Delta) \simeq \frac{\partial \Sigma(N,V,E)}{\partial E}\Delta \approx \frac{3N}{2}\frac{\Delta}{E}\Sigma(N,V,E)$$

$$\mathrm{Ln}\Gamma(N,V,E;\Delta) \cong \mathrm{Ln}\Sigma(N,V,E) + \mathrm{Ln}\left(\frac{3N}{2}\right) + \mathrm{Ln}\left(\frac{\Delta}{E}\right)$$

$$\sum_N(E) \approx \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{\frac{3N}{2}}}{(3N/2)!}$$

$$\begin{aligned}
\mathrm{Ln}\Gamma(N,V,E;\Delta) &\cong \mathrm{NLn}\left[\frac{V}{h^3}(2\pi mE)^{\frac{3}{2}}\right] - \mathrm{Ln}\left(\left(\frac{3N}{2}\right)!\right) + \mathrm{Ln}\left(\frac{3N}{2}\right) + \mathrm{Ln}\left(\frac{\Delta}{E}\right) = \\
&= \mathrm{NLn}\left[\frac{V}{h^3}(2\pi mE)^{\frac{3}{2}}\right] - \frac{3N}{2}\mathrm{Ln}\left(\frac{3N}{2}\right) + \frac{3N}{2} + \mathrm{Ln}\left(\frac{3N}{2}\right) + \mathrm{Ln}\left(\frac{\Delta}{E}\right) \\
&= \mathrm{NLn}\left[\frac{V}{h^3}(2\pi mE)^{\frac{3}{2}}\right] - \mathrm{NLn}\left(\frac{3N}{2}\right)^{3/2} + \frac{3N}{2} + \left\{\mathrm{Ln}\left(\frac{3N}{2}\right) + \mathrm{Ln}\left(\frac{\Delta}{E}\right)\right\} \\
&= \mathrm{NLn}\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3N}{2} + \left\{\mathrm{Ln}\left(\frac{3N}{2}\right) + \mathrm{Ln}\left(\frac{\Delta}{E}\right)\right\}
\end{aligned}$$

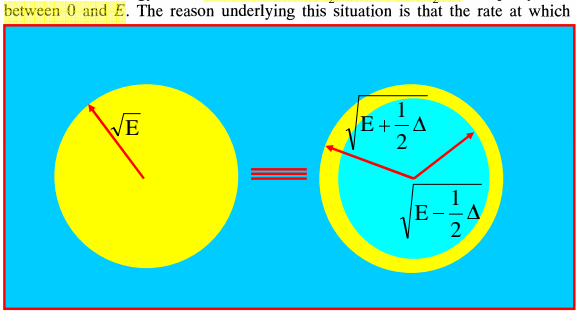
whence

$$\ln\Gamma(N,V,E;\,\Delta) \approx N\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}N + \left\{\ln\left(\frac{3N}{2}\right) + \ln\left(\frac{\Delta}{E}\right)\right\}$$

Now, for $N \gg 1$, the first term in the curly bracket is negligible in comparison with any of the terms outside this bracket, for $\lim_{N\to\infty}(\ln N)/N = 0$. Furthermore, for any reasonable value of Δ/E, the same is true of the second term in this bracket.[13] Hence, for all practical purposes,

$$\mathrm{Ln}(\Gamma(N,V,E;\Delta)) \approx \mathrm{NLn}\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}\right] + \frac{3N}{2}$$

Thus, we arrive at the baffling result that, for all practical purposes, the actual width of the range allowed for the energy of the system does not make much difference; the energy could lie between $(E - \frac{1}{2}\Delta)$ and $(E + \frac{1}{2}\Delta)$ or equally well between 0 and E. The reason underlying this situation is that the rate at which



The stage is now set for deriving the thermodynamics of our system. First of all, we have

$$S = k\ln\Gamma(N,V,E) = Nk\ln\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}} + \frac{3}{2}Nk$$

$$S - \frac{3}{2}Nk = NK\ln\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}$$

$$\frac{S}{Nk} - \frac{3}{2} = \ln\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}}$$

$$\exp\left\{\frac{S}{Nk} - \frac{3}{2}\right\} = \frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}} = \left(\frac{V^{2/3}}{h^2}\frac{4\pi mE}{3N}\right)^{3/2}$$

$$\exp\left\{\frac{2S}{3Nk} - 1\right\} = \frac{V^{2/3}}{h^2}\frac{4\pi mE}{3N}$$

$$E = \frac{h^2}{V^{2/3}}\frac{3N}{4\pi m}\exp\left\{\frac{2S}{3Nk} - 1\right\}$$

$$E = \frac{h^2}{V^{2/3}} \frac{3N}{4\pi m} \exp\left\{\frac{2S}{3Nk} - 1\right\}$$

$$dE = TdS - PdV + \mu dN$$

$$T = \frac{\partial E}{\partial S}\Big)_{V,N} = \frac{2}{3Nk} E$$

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT$$

$$E = \frac{h^2}{V^{2/3}} \frac{3N}{4\pi m} \exp\left\{\frac{2S}{3Nk} - 1\right\}$$

$$P = -\frac{\partial E}{\partial V}\Big)_{S,N} = \frac{2}{3}\frac{1}{V} E$$

$$E = \frac{3}{2} PV \qquad E = \frac{3}{2} NkT = \frac{3}{2} nRT$$

$$PV = \frac{2}{3}\frac{3}{2} NkT = NkT = nRT$$

$$PV = NkT = nRT$$

$$E = \frac{3}{2} NkT = \frac{3}{2} nRT$$

$$C_V = \frac{\partial E}{\partial T}\Big)_{V,N} = \frac{3}{2} Nk = \frac{3}{2} nR$$

$$C_P = \frac{\partial H}{\partial T}\Big)_{P,N} = \frac{\partial}{\partial T}(E + PV)_{P,N} =$$

$$= \frac{\partial}{\partial T}\left(\frac{3}{2} NkT + NkT\right)_{P,N}$$

$$= \frac{5}{2} NK = \frac{5}{2} nR$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2} nR}{\frac{3}{2} nR} = \frac{5}{3}$$

حال می خواهیم دو حالت ترمودینامیکی را بررسی کنیم:

1) The isothermal change of states

$$T = Const;\ E = \frac{3}{2} NKT \rightarrow E = Const$$

این حالت را از هر دو روش آماری و ترمودینامیک بررسی می کنیم:

الف) روش آماری

$$E_f = E = \frac{3Nh^2}{4\pi m V_f^{\frac{2}{3}}} \exp\left(\frac{2S_f}{3NK} - 1\right) \qquad E_i = E = \frac{3Nh^2}{4\pi m V_i^{\frac{2}{3}}} \exp\left(\frac{2Si}{3NK} - 1\right)$$

با تقسیم دو رابطه خواهیم داشت:

$$1 = \left(\frac{V_f}{V_i}\right)^{\frac{2}{3}} \exp\left(\frac{2}{3NK}(S_i - S_f)\right) \rightarrow \left(\frac{V_f}{V_i}\right)^{\frac{2}{3}} = \exp\left(\frac{2}{3NK}(S_f - S_i)\right)$$

$$\rightarrow \frac{2}{3} \ln\frac{V_f}{V_i} = \frac{2}{3NK}(S_f - S_i) \rightarrow S_f - S_i = NK \ln\frac{V_f}{V_i}$$

ب) روش ترمودینامیکی

$$dE = TdS - pdV + \mu dN \rightarrow TdS = pdV$$

برای گاز ایده آل $PV = NkT \rightarrow TdS = \frac{NkT}{V} dV$

$$\int_{S_i}^{S_f} dS = \int_{S_i}^{S_f} NK \frac{dV}{V} \rightarrow S_f - S_i = NK \ln\frac{V_f}{V_i}$$

این همان نتیجه ای است که از روش آماری به دست آورده بودیم.

2) The adiabatic change of states

S= Constant, N= Constant

الف) روش آماری

$$E_i = \frac{3Nh^2}{4\pi m V_i^{\frac{2}{3}}} \exp\left(\frac{2S}{3NK} - 1\right), \quad E_f = \frac{3Nh^2}{4\pi m V_f^{\frac{2}{3}}} \exp\left(\frac{2S}{3NK} - 1\right)$$

$$\frac{E_i}{E_f} = \left(\frac{V_f}{V_i}\right)^{\frac{2}{3}} \rightarrow E_i V_i^{\frac{2}{3}} = E_f V_f^{\frac{2}{3}} \quad \rightarrow EV^{\frac{2}{3}} = Const\,;\, E = \frac{3}{2}NKT$$

$$\rightarrow \frac{3}{2}NKTV^{\frac{2}{3}} = Const \rightarrow TV^{\frac{2}{3}} = Const \rightarrow TV^{\gamma-1} = Const$$

ب) روش ترمودینامیک

$$dE = Tds - pdV + \mu dN \rightarrow dE = pdV$$

$$\begin{cases} PV = NkT \\ E = \frac{3}{2}NkT \end{cases} \rightarrow PV = \frac{2}{3}E \rightarrow P = \frac{2}{3}\frac{E}{V}$$

$$dE = -\frac{2}{3}\frac{E}{V}dV \rightarrow \int_{E_I}^{E_f} \frac{dE}{E} = -\frac{2}{3}\int_{v_i}^{v_f} \frac{dV}{V}$$

$$\ln\frac{E_f}{E_i} = -\frac{2}{3}\ln\frac{V_f}{V_i} \rightarrow \ln\frac{E_f}{E_i} = \ln\left(\frac{V_i}{V_f}\right)^{\frac{2}{3}}$$

$$\rightarrow \frac{E_f}{E_i} = \left(\frac{V_i}{V_f}\right)^{\frac{2}{3}} \rightarrow E_i V_i^{\frac{2}{3}} = E_f V_v^{\frac{2}{3}} = EV^{\frac{2}{3}} \rightarrow EV^{\frac{2}{3}} = Const$$

$$\rightarrow PV^{\gamma} = Const \rightarrow TV^{\gamma-1} = Const$$

با سازگاری نتایج ترمودینامیکی و آماری به نظر می رسد که محاسبه جگـالی حالت ها را درست انجام داده ایم ولی تمام این محاسبات اشکال اساسی دارد.