

درس پدیده‌های بحرانی

تمرینات سری اول

زمان تحویل: ۹۷/۷/۲۴

۱- با محاسبه تعداد حالت‌ها در فضای فاز در حضور تبهگنی برای سه نوع ذره کلاسیکی، فرمیونی و بوزونی نشان دهید در دمای بالا داریم:

$$\Omega^{FD} = \Omega^{BE} \rightarrow \Omega^{MB}$$

۲- برای یک سیستم بدون برهمکنش که شامل ذرات تمیزناپذیر است، احتمال یافتن n_i ذره در تراز i ام تک‌ذره‌ای، $P_i(n_i, T, \mu)$ ، متوسط ذرات، $\langle n_i \rangle$ و افت و خیز در عدد اشغال، $\langle (n_i - \langle n_i \rangle)^2 \rangle$ ، را برای آمارهای ماکسول-بولتزمن، بوز-اینشتین و فرمی-دیراک بیابید و نتایج را تحلیل کنید.

۳- طیف تابش یک جسم دلخواه در d بُعد را با فرض اینکه ضریب جذب به صورت $\omega^2 kT(d+1)$ تغییر می‌کند، محاسبه نموده و وابستگی انرژی کل تابش شده در تمام فرکانس‌ها را به دما و بُعد سیستم تعیین کنید. فرض کنید که شارش توسط عبارت $R = \frac{1}{4} n \langle v \rangle$ داده شود.

۴- فرض کنید در حدود ۱۰۰ ثانیه پس از انفجار اولیه در عالم معادله حالت گاز به صورت $U = 3PV$ باشد از طرفی با توجه به انتقال انرژی، داریم $U = \sigma VT^4$.

الف: آنترופی را محاسبه کنید.

ب: با توجه به انبساط کیهان به صورت بی‌دررو، وابستگی دما به فاکتور مقیاس که به صورت $a = \frac{r}{R}$ تعریف می‌شود در همان زمان بدست

آورید. (r فاصله اجسام از یکدیگر و R مقداری ثابت می‌باشد)

۵- با کمک قضیه ویربال معادله حالت و انرژی درونی یک سیستم بس-ذره‌ای برهمکنشی با جمله برهمکنش $U(|\vec{r}_i - \vec{r}_j|)$ را محاسبه کنید.

۶- حد ترمودینامیک را برای انرژی الکترواستاتیک ذخیره شده در یک کره با اندرکنشی به صورت $U(r) = \frac{A}{r^\sigma}$ در d بُعد بررسی نمایید.

۷- تمرین ۲ فصل اول کتاب Goldenfeld

موفق باشید

موحد

تَحَصَّلُ عِلْمٍ وَدَانِشِ مَائِمِي تَقْوِيَّتْ وَتَأْيِيْدُ عَقْلِ آدَمِيَّاسْت. "حضرت علی(ع)"

	Microcanonical $\Omega(E, V, N)$	Canonical $Z(T, V, N)$	Grand canonical $Z(T, V, \mu)$
$\frac{S}{k}$	$\ln \Omega$	$\left(\frac{\partial(T \ln Z)}{\partial T}\right)_{V, N}$	$\left(\frac{\partial(T \ln Z)}{\partial T}\right)_{V, \mu}$
F	$E - kT \ln \Omega$	$-kT \ln Z$	$kT \mu^2 \left(\frac{\partial(\mu^{-1} \ln Z)}{\partial \mu}\right)_{T, V}$
U	Fixed (=E)	$kT^2 \left(\frac{\partial(\ln Z)}{\partial T}\right)_{V, N}$	$-\left(\frac{\partial(\ln Z)}{\partial \beta}\right)_{\beta \mu, V}$
N	Fixed	Fixed	$kT \left(\frac{\partial(\ln Z)}{\partial \mu}\right)_{T, V}$
kT	$\left(\frac{\partial(\ln \Omega)}{\partial E}\right)_{V, N}^{-1}$	Fixed	Fixed
$\frac{\mu}{kT}$	$-\left(\frac{\partial(\ln \Omega)}{\partial N}\right)_{E, V}$	$-\left(\frac{\partial(\ln Z)}{\partial N}\right)_{T, V}$	Fixed
P	$kT \left(\frac{\partial(\ln \Omega)}{\partial V}\right)_{E, N}$	$kT \left(\frac{\partial(\ln Z)}{\partial V}\right)_{T, N}$	$\frac{kT}{V} \ln Z$
$\frac{C_V}{k}$	$-\beta^2 \left(\frac{\partial^2(\ln \Omega)}{\partial E^2}\right)_{V, N}^{-1}$	$\beta^2 \left(\frac{\partial^2(\ln Z)}{\partial \beta^2}\right)_{V, N}$	$T \left(\frac{\partial^2(T \ln Z)}{\partial T^2}\right)_{V, \mu}$
$(\Delta N)^2$	0	0	$\left(\frac{\partial^2(\ln Z)}{\partial(\beta \mu)^2}\right)_{\beta, V}$
$(\Delta E)^2$	0	$\left(\frac{\partial^2(\ln Z)}{\partial \beta^2}\right)_{V, N}$	$\left(\frac{\partial^2(\ln Z)}{\partial \beta^2}\right)_{\beta \mu, V}$

$$\int_0^\infty dx x^n e^{-\alpha x} = \frac{n!}{\alpha^{n+1}}$$

$$\left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2} \exp\left[-\frac{\sigma^2 k^2}{2}\right]$$

$$\lim_{N \rightarrow \infty} \ln N! = N \ln N - N$$

$$\langle e^{-ikx} \rangle = \sum_{n=0}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle$$

$$\ln \langle e^{-ikx} \rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c$$

$$\cosh(x) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots$$

$$\sinh(x) = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$$

Surface area of a unit sphere in d dimensions

$$S_d = \frac{2\pi^{d/2}}{(d/2-1)!}$$

$$\sum_k \rightarrow \frac{l^d}{(2\pi)^d} \int d^d k \rightarrow \int g(\varepsilon) d\varepsilon$$

$$V_d = \frac{R^d \pi^{d/2}}{2 \Gamma\left(\frac{d}{2}\right)} \quad B_j(y) = \left(1 + \frac{1}{2j}\right) \coth\left(\left[1 + \frac{1}{2j}\right]y\right) - \frac{1}{2j} \coth\left(\frac{y}{2j}\right)$$

$$\text{for } y \rightarrow 0 \quad B_j(y) \sim \frac{1}{3} \left(1 + \frac{1}{j}\right) y$$

$$\int_{-\infty}^\infty dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

$$\Gamma(t) = \int_0^\infty dx x^{t-1} e^{-x} = (t-1)\Gamma(t-1)$$

$$\Gamma(t)\Gamma(1-t) = \frac{\pi}{\sin \pi t}, \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

Answer to Exercise set 1

1- For **Boltzmann** gas we know that particles are distinguishable so for any interchange between them we have new microstate, so for n_i particles in cell number i with g_i sub cells that all belong to energy ε_i we can count all possible microstate:

$$W_{MB}\{n_i\} = \frac{N!}{n_1!n_2!\dots n_k!} g_1^{n_1} g_2^{n_2} \dots g_k^{n_k} = N! \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

However, $\Omega_{MB}\{n_i\}$ is defined to be $1/N!$ of the last quantity:

$$W_{MB}\{n_i\} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

This definition corresponds to the rule of "correct Boltzmann counting" and does not correspond to any physical property of the particles in system. It is just a rule that defines the mathematical model. The total phase space volume can be evaluate by this:

$$\Omega_{MB} = \sum_{\{n_i\}} W_{MB}\{n_i\}$$

For **Fermi** gas we have different situation because of first indistinguishably and second Pauli exclusion principle. Now particles can fill g_i level by occupation number (n_i) just zero and one. So we can write:

$$w_i = \binom{g_i}{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$W_{FD}\{n_i\} = \prod_i w_i = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

and finally:

$$\Omega_{FD} = \sum_{\{n_i\}} W_{FD}\{n_i\}$$

For **Bose** gas we have each level can be occupied by any number of particles. We have $g_i - 1$ partitions an n_i particles, we should count all possible microstate, we have:

$$w_i = \binom{n_i + g_i - 1}{n_i} = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$W_{BE}\{n_i\} = \prod_i w_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

and finally:

$$\Omega_{BE} = \sum_{\{n_i\}} W_{BE}\{n_i\}$$

To obtain the entropy $S = k \log \Omega(E)$ we need to sum $W\{n_i\}$ over $\{n_i\}$. This is a formidable task. For the Boltzmann gas it was explicitly done. As we might correctly

guess, however, $\Omega(E)$ is quite well approximated by $W\{\bar{n}_i\}$, where $\{\bar{n}_i\}$ is the set of occupation numbers that maximizes $W\{\bar{n}_i\}$. We adopt this approximation and verify its correctness by showing that the fluctuations are small. Accordingly the entropy is taken to be:

$$S = k \log \Omega(E) \approx k \log W\{\bar{n}_i\}$$

by Lagrange multiplier we can find distribution function for occupation numbers that maximize the entropy.

Let's attack our problem we should show that for high temperature we have:

$$\Omega_{BE} = \Omega_{FD} \longrightarrow \Omega_{MB}$$

In high temperature we have $g_i \gg n_i$ so for **Bose** gas we have:

$$W_{BE}\{\bar{n}_i\} = \frac{(\bar{n}_i + g_i - 1)!}{\bar{n}_i!(g_i - 1)!} = \frac{(\bar{n}_i + g_i - 1)(\bar{n}_i + g_i - 2) \dots (g_i)}{\bar{n}_i!} \approx \frac{g_i^{\bar{n}_i}}{\bar{n}_i!}$$

For **Fermi** gas we have:

$$W_{FD}\{\bar{n}_i\} = \frac{g_i!}{\bar{n}_i!(g_i - \bar{n}_i)!} = \frac{g_i(g_i - 1)g_i - 2) \dots (g_i - \bar{n}_i)}{\bar{n}_i!} \approx \frac{g_i^{\bar{n}_i}}{\bar{n}_i!}$$

Which is the same as **Maxwell-Boltzmann** phase space volume:

$$W_{MB}\{\bar{n}_i\} = \frac{(g_i)^{\bar{n}_i}}{\bar{n}_i!}$$

For general view of this question please see section 8.5 of Statistical Mechanics by Huang and 3.8 of Pathria third edition.

2- We begin with particles that is obey Maxwell-Boltzmann statistics. Number of microstate for such particles calculate with:

$$\Omega_{MB} = \sum_{\{n_i\}} W_{MB}\{n_i\}$$

We can approximate this summation with:

$$S = k \log \Omega_{MB} \approx k \log W\{\bar{n}_i\}$$

We have two important constrains:

$$\begin{aligned} \sum_i n_i &= N \\ \sum_i n_i \epsilon_i &= E \end{aligned} \quad (1)$$

We know that the volume in Γ space for Maxwell-Boltzmann is:

$$\Omega_{MB} \approx W_{MB}\{\bar{n}_i\} = \prod_i \frac{(g_i)^{\bar{n}_i}}{\bar{n}_i!}$$

Now we want to maximize Ω_{MB} with above two constrains and find maximum occupation number \bar{n}_i . We take logarithm and use Stirling's approximation we have:

$$\begin{aligned} \log \Omega_{MB} &= - \sum_{i=1}^K \log n_i! + \sum_{i=1}^K n_i \log g_i \\ \log \Omega_{MB} &= - \sum_{i=1}^K n_i \log n_i + \sum_{i=1}^K n_i \log g_i + \text{constant} \end{aligned}$$

K is number of cells. Now we use Lagrange multiplier and imply constrains, we have:

$$\begin{aligned} \delta \left(\log \Omega_{MB} \right) - \delta \left(\alpha \sum_{i=1}^K n_i + \beta \sum_{i=1}^K n_i \epsilon_i \right) &= 0 \quad (n_i = \bar{n}_i) \\ \sum_{i=1}^K \left[-(\log n_i + 1) + \log g_i - \alpha - \beta \epsilon_i \right] \delta n_i &= 0 \quad (n_i = \bar{n}_i) \end{aligned}$$

Finally:

$$\log \bar{n}_i = -1 + \log g_i - \alpha - \beta \epsilon_i$$

So:

$$\bar{n}_i = g_i e^{-\alpha - \beta \epsilon_i - 1}$$

For a gas without external potential we have:

$$P_i = C e^{-\beta \epsilon_i}$$

¹We can consider constant $N!$ in here or we can ignore it, because it is a constant and in differentiation it will be zero.

Now we can write similar above for Fermi-Dirac distribution, we know that number of states for fermions is:

$$\Omega_{FD} \approx W_{FD}\{\bar{n}_i\} = \prod_i \frac{g_i!}{\bar{n}_i!(g_i - \bar{n}_i)!}$$

use Stirling's approximation:

$$\begin{aligned} \log \Omega_{FD} &= \sum_{i=1}^K \left[\log g_i! - \log n_i! - \log(g_i - n_i)! \right] \\ &\approx \sum_{i=1}^K \left[g_i \log g_i - n_i \log n_i - (g_i - n_i) \log(g_i - n_i) \right] \end{aligned}$$

We differentiate of above and put our constrains in by Lagrange multiplier, so we have:

$$\begin{aligned} \delta \left[\log \Omega_{FD} - \alpha \sum_{i=1}^K n_i + \beta \sum_{i=1}^K n_i \varepsilon_i \right] &= 0 \quad (n_i = \bar{n}_i) \\ \sum_{i=1}^K \left[-\log n_i + \log(g_i - n_i) - \alpha - \beta \varepsilon_i \right] \delta n_i &= 0 \quad (n_i = \bar{n}_i) \end{aligned}$$

Finally:

$$-\log n_i + \log(g_i - n_i) - \alpha - \beta \varepsilon_i = 0$$

$$\bar{n}_i = \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} + 1}$$

Similarly we can write above for Bose-Einstein distribution and find:

$$\bar{n}_i = \frac{g_i}{e^{-\alpha + \beta \varepsilon_i} - 1}$$

For second approach we can calculate grand partition function. For classic ideal gas we can find grand partition function as:

$$\mathcal{Q}(z, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V, T) = e^{zV/\lambda^3} \quad (2)$$

Where $\lambda = h/(2\pi mkT)^{1/2}$ is thermal wavelength. In the Bose-Einstein and Fermi-Dirac cases grand partition functions is:

$$\mathcal{Q}(z, V, T) = \begin{cases} \prod_{\varepsilon} (1 - ze^{-\beta \varepsilon})^{-1} & \text{Bose-Einstein} \\ \prod_{\varepsilon} (1 + ze^{-\beta \varepsilon}) & \text{Fermi-Dirac} \end{cases}$$

We can summarize our results by define q-potential of system:

$$q(z, V, T) = \log \mathcal{Q}(z, V, T)$$

We can use above definition for summarize our results as below:

$$q(z, V, T) = \frac{1}{a} \sum_{\epsilon} \log(1 + aze^{-\beta\epsilon})$$

where $a = 1, +1,$ or $0,$ depending on the statistics governing the system. In particular, the classical case $a \rightarrow 0$ gives:

$$q_{MB}(z, V, T) = z \sum_{\epsilon} e^{-\beta\epsilon} = zQ_1$$

In agreement with equation 2 for one particle. Now we can calculate occupation number mean value we have:

$$\begin{aligned} \langle n_{\epsilon} \rangle &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \log Q(z, V, T) \\ &= -\frac{1}{\beta} \frac{\frac{\partial}{\partial \epsilon} Q(z, V, T)}{Q(z, V, T)} \\ &= -\frac{1}{\beta} \left(\frac{\partial q}{\partial \epsilon} \right)_{z, T, \text{all other } \epsilon} \\ &= \frac{1}{z^{-1}e^{\beta\epsilon} + a} \end{aligned} \quad (3)$$

We shall now examine statistical fluctuations in the variable n_{ϵ} , we know that:

$$\begin{aligned} \langle n_{\epsilon}^2 \rangle &= \frac{1}{Q} \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right)^2 Q \right]_{z, T, \text{all other } \epsilon} \\ \langle n_{\epsilon}^2 \rangle - \langle n_{\epsilon} \rangle^2 &= \frac{1}{Q} \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right)^2 Q \right]_{z, T, \text{all other } \epsilon} - \left[\frac{1}{Q} \left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right) Q \right]_{z, T, \text{all other } \epsilon}^2 \\ &= \left(-\frac{1}{\beta} \right)^2 \frac{1}{Q} \left[\frac{\partial^2 Q}{\partial \epsilon^2} - \frac{1}{Q} \left(\frac{\partial Q}{\partial \epsilon} \right)^2 \right]_{z, T, \text{all other } \epsilon} \\ &= \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right)^2 \log Q \right]_{z, T, \text{all other } \epsilon} \\ &= \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right) \langle n_{\epsilon} \rangle \right]_{z, T} \end{aligned}$$

Now put result of equation 3 in above we have:

$$\begin{aligned} \langle n_{\epsilon}^2 \rangle - \langle n_{\epsilon} \rangle^2 &= \left[\left(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon} \right) \frac{1}{z^{-1}e^{\beta\epsilon} + a} \right]_{z, T} \\ &= \frac{z^{-1}e^{\beta\epsilon}}{\left[z^{-1}e^{\beta\epsilon} + a \right]^2} \end{aligned}$$

We can write above in this way:

$$\frac{\langle n_{\epsilon}^2 \rangle - \langle n_{\epsilon} \rangle^2}{\langle n_{\epsilon} \rangle^2} = z^{-1}e^{\beta\epsilon} = \frac{1}{\langle n_{\epsilon} \rangle} - a$$

In the classical case ($a = 0$), the relative fluctuation is normal. In the Fermi–Dirac case, it is given by $1/\langle n_{\epsilon} \rangle - 1$, which is below normal and tends to vanish as $\ln \langle n_{\epsilon} \rangle \rightarrow 1$. In

the Bose- Einstein case, the fluctuation is clearly above normal.

For greater understanding of the statistics of the occupation numbers, we evaluate the quantity $p_\epsilon(n)$, which is the probability that there are exactly n particles in a state of energy ϵ , For Bose-Einstein case we have:

$$p_\epsilon(n)|_{BE} = (ze^{-\beta\epsilon})^n [1 + ze^{-\beta\epsilon}] = \left(\frac{\langle n_\epsilon \rangle}{\langle n_\epsilon \rangle + 1} \right)^n \frac{1}{\langle n_\epsilon \rangle + 1}$$

Where n can be any positive integer number. For Fermi-Dirac case we have:

$$p_\epsilon(n)|_{FD} = (ze^{-\beta\epsilon})^n [1 + ze^{-\beta\epsilon}]^{-1}$$

Where n can be 0 or 1, we have:

$$p_\epsilon(n)|_{FD} = \begin{cases} 1 - \langle n_\epsilon \rangle & \text{for } n = 0 \\ \langle n_\epsilon \rangle & \text{for } n = 1 \end{cases}$$

For Maxwell-Boltzmann case we have:

$$p_\epsilon(n)|_{MB} = \frac{(ze^{-\beta\epsilon})^n / n!}{\exp(ze^{-\beta\epsilon})} = \frac{\langle n_\epsilon \rangle^n}{n!} e^{-\langle n_\epsilon \rangle}$$

For more information read section 6-2 and 6-3 of Pathria.

3- We want to calculate energy that radiated from a d-dimension body with temperature T , we use relations of perfect black body with a multiplier that comes from absorption coefficient $\gamma(\omega)$ which is:

$$\gamma(\omega) = \omega^2 k T (d + 1)$$

So we evaluate below:

$$I_b(\omega, T) = \gamma(\omega) I_{bb}(\omega, T)$$

b means body and bb means blackbody. We know that:

$$I_{bb}(\omega, T) = \frac{c}{4} u(\omega, T)$$

Now we want number of photons that their energy is between $\hbar\omega$ and $\hbar(\omega + d\omega)$ this quantity is $d\langle n(\omega) \rangle / d\omega$, we can write above as:

$$I_{bb}(\omega, T) = \frac{c}{4} u(\omega, T) = \frac{c}{4} \hbar\omega \frac{d\langle n(\omega) \rangle}{d\omega} = \frac{c}{4} \hbar\omega g(\omega) \langle n(\omega) \rangle, \quad \langle n(\omega) \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

$\langle n(\omega) \rangle$ is average of number of photons that radiated from body per frequency and unit area, which obey from Bose-Einstein statistics, $g(\omega)$ is density of states. Number of modes that have wave vector smaller than k is:

$$\begin{aligned} N(k) &= \frac{V_d}{\left(\frac{2\pi}{L}\right)^d} = \left(\frac{L}{2\pi}\right)^d \frac{\pi^{d/2}}{(d/2)\Gamma(d/2)} k^d, \quad k = \frac{\omega}{c} \\ N(\omega) &= \left(\frac{L}{2\pi}\right)^d \frac{\pi^{d/2}}{(d/2)\Gamma(d/2)} \frac{\omega^d}{c^d} \\ g(\omega) &= \frac{N(\omega)}{d\omega} = \left(\frac{L}{2\pi}\right)^d \frac{\pi^{d/2}}{(d/2)\Gamma(d/2)} d \frac{\omega^{d-1}}{c^d} \end{aligned}$$

g_s is spin degree of freedom and L radius of our d-dimension body.

We have enough information so we can evaluate desired quantity of question, we have:

$$I_{bb}(\omega, T) = \frac{c}{4} \hbar\omega g(\omega) \langle n(\omega) \rangle = \frac{c}{4} \hbar\omega \left(\frac{L}{2\pi}\right)^d \frac{\pi^{d/2}}{(d/2)\Gamma(d/2)} d \frac{\omega^{d-1}}{c^d} \frac{1}{e^{\beta\hbar\omega} - 1}$$

Total amount of energy radiated from body is:

$$I_b(T) = \int_0^\infty d\omega I_b(\omega, T) = \int_0^\infty d\omega \gamma(\omega) I_{bb}(\omega, T)$$

Calculation is straight forward.

4- **First solution:** (a) We can write:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

We have:

$$PV = \frac{U}{3} = \frac{\sigma T^4}{3} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{4}{3}\sigma T^3$$

Now we want to evaluate:

$$dS = \frac{dU + PdV}{T} \quad (4)$$

We know:

$$dU = C_v dT + \left[\left(\frac{\partial U}{\partial T}\right)_V - P \right] dV$$

From question information we we have:

$$dU = \sigma T^4 dV + 4\sigma T^3 V dT = C_v dT + \left(\frac{4}{3}\sigma T^4 - \frac{1}{3}\sigma T^4 \right) dV, \quad C_v = 4\sigma VT^3 \quad (5)$$

From 4 and 5 we have:

$$\begin{aligned} dS &= \frac{C_v}{T} dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] dV \\ &= 4\sigma VT^2 dT + \frac{4}{3}\sigma T^3 dV \end{aligned}$$

(b) For adiabatic expansion we know $dS = 0$ so we have:

$$\frac{C_v}{T} dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] dV = 0 \Rightarrow \frac{dT}{T} = -\frac{1}{3} \frac{dV}{V} \Rightarrow T \propto V^{-1/3}$$

Volume is proportional to R^3 so we have $T \propto R^{-1}$.

Second solution: (a) We can find entropy by below relation:

$$s(T) = \left(\frac{\partial P}{\partial T}\right)_\mu = \frac{1}{3V} \left(\frac{\partial U}{\partial T}\right)_\mu = \frac{4}{3}\sigma T^3$$

(b) The density of the universe was high enough in this era, so the weak and electromagnetic interaction rates kept all these species in thermal equilibrium with one other. Therefore, as the universe expanded adiabatically, the entropy in a co-moving volume of linear size a remained constant as the volume expanded from some initial value a_0^3 to a final volume a_1^3 :

$$s_{total} T_0 a_0^3 = s_{total} T_1 a_1^3$$

Since the entropy density is proportional to T^3 , the temperature and length scale at time t are related by

$$T(t)a(t) = \text{const.}$$

This is the same relation that applies for a freely expanding photon gas, but here it arises from an adiabatic equilibrium process. The temperature of universe as a function of the age of the universe t during this era is

$$T(t) = 10^{10} K \sqrt{\frac{0.992s}{t}}$$

For more information read section 9-3 of Pathria third edition.

5- Virial theorem states that:

$$\mathcal{V} = -\left\langle \sum_i \mathbf{q}_i \cdot \dot{\mathbf{p}}_i \right\rangle = -\left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle = -3NkT$$

Now we want to derive equation of state for a non-interacting gas. The only force that act on gas molecule is come from gas container's wall. We can see this force (in average) as a pressure P that come from walls, so the force of this pressure is $-Pd\mathbf{A}$ (the negative sign appears because the force is directed inward while the vector $d\mathbf{S}$ is directed outward), we can find virial:

$$\mathcal{V}_0 = \left\langle \sum_i q_i F_i \right\rangle_0 = \oint_A (-Pd\mathbf{A}) \cdot \mathbf{r} = -P \oint_A \mathbf{r} \cdot d\mathbf{A}$$

Using divergence theorem ² we have:

$$\mathcal{V}_0 = -P \oint_A \mathbf{r} \cdot d\mathbf{A} = -P \oint_A \nabla \cdot \mathbf{r} dV = -P \oint_A \frac{1}{r^2} \left(\frac{\partial}{\partial r} r^3 \right) dV = -3PV \quad (6)$$

Now from virial theorem we can find ideal gas equation of state:

$$PV = NkT$$

For a system with a interacting Hamiltonian is

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i>j} U_{ij}$$

Now we want to calculate equation of state for a interacting gas with above Hamiltonian with virial theorem. Assuming the inter particle potential to be central and denoting it by the symbol $u(\mathbf{r})$, where $\mathbf{r} = |\mathbf{r}_i - \mathbf{r}_j|$, if we have two particles i and j , with position vectors \mathbf{r}_i and \mathbf{r}_j , we should calculate below:

$$\begin{aligned} \mathbf{r}_i \cdot \left(-\frac{\partial u}{\partial \mathbf{r}_i} \right) + \mathbf{r}_j \cdot \left(-\frac{\partial u}{\partial \mathbf{r}_j} \right) &= \mathbf{r}_i \cdot \left(-\frac{\partial u}{\partial |\mathbf{r}_i - \mathbf{r}_j|^2} \frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_i} \right) \\ &+ \mathbf{r}_j \cdot \left(-\frac{\partial u}{\partial |\mathbf{r}_i - \mathbf{r}_j|^2} \frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_j} \right) \\ &= -\frac{\partial u}{\partial |\mathbf{r}_i - \mathbf{r}_j|^2} \left[\mathbf{r}_i \cdot \left(\frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_i} \right) + \mathbf{r}_j \cdot \left(\frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_j} \right) \right] \\ &= -\frac{\partial u}{\partial r^2} \left[\mathbf{r}_i \cdot \left(\frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_i} \right) + \mathbf{r}_j \cdot \left(\frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_j} \right) \right] \end{aligned}$$

Now we should calculate below first:

$$\begin{aligned} \frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_i} &= \frac{\partial}{\partial \mathbf{r}_i} (r_i^2 + r_j^2 - 2r_i r_j \cos \theta_{ij}) \\ &= \nabla_i (r_i^2 + r_j^2 - 2r_i r_j \cos \theta_{ij}) \\ &= (2r_i - 2r_j \cos \theta_{ij}) \hat{\mathbf{r}}_i \end{aligned}$$

² $\iiint_V \nabla \cdot \mathbf{F} dV = \iint_A \mathbf{F} \cdot \mathbf{n} dA$

θ_{ij} means angle between \mathbf{r}_i and \mathbf{r}_j , and:

$$\nabla_i = \frac{\partial}{\partial r_i} \hat{\mathbf{r}}_i + \frac{1}{r_i} \frac{\partial}{\partial \theta_i} \hat{\boldsymbol{\theta}}_i + \frac{1}{r_i \sin \theta_i} \frac{\partial}{\partial \phi_i} \hat{\boldsymbol{\phi}}_i$$

Similarly we can find:

$$\frac{\partial |\mathbf{r}_i - \mathbf{r}_j|^2}{\partial \mathbf{r}_j} = (2r_j - 2r_i \cos \theta_{ij}) \hat{\mathbf{r}}_j$$

Finally

$$\begin{aligned} \mathbf{r}_i \cdot \left(-\frac{\partial u}{\partial \mathbf{r}_i} \right) + \mathbf{r}_j \cdot \left(-\frac{\partial u}{\partial \mathbf{r}_j} \right) &= -2 \frac{\partial u(r)}{\partial r^2} \left[r_i^2 + r_j^2 - 2r_i r_j \cos \theta_{ij} \right] \\ &= -\frac{2}{2r} \frac{\partial u(r)}{\partial r} r^2 \\ &= -r \frac{\partial u(r)}{\partial r} \end{aligned}$$

Now we can consider only pairs in system instead of particles, we have $N(N-1)/2$ pairs and if $N \gg 1$ this number goes to $N^2/2$, we have:

$$\frac{N^2}{2} \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle = -\frac{N^2}{2V} \int_0^\infty \left(r \frac{\partial u(r)}{\partial r} \right) g(r) 4\pi r^2 dr \quad (7)$$

Combining 6 and 7 we have:

$$PV = NkT \left[1 - \frac{2\pi n}{3kT} \int_0^\infty \left(r \frac{\partial u(r)}{\partial r} \right) g(r) r^2 dr \right]$$

The internal energy of the system can also be expressed in terms of the functions $u(r)$ and $g(r)$. Noting that the average kinetic energy is still given by the expression $\frac{3}{2}NkT$, we have for the total energy:

$$U = \frac{3}{2}NkT \left[1 + \frac{4\pi n}{3kT} \int_0^\infty u(r) g(r) r^2 dr \right]$$

For detail calculation please refer to Pathria book second edition section 3-7 page 63.

6- We should calculate total energy with this integral:

$$E(\mathbf{R}) = \frac{1}{2} \int_{\Omega} d^d r d^d r' \rho(\mathbf{r}) U(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r})$$

For uniform system, $\rho(\mathbf{r}) = \rho$ and the integral becomes:

$$E(\mathbf{R}) = A \frac{\rho^2}{2} \int_{\Omega} d^d r d^d r' \frac{1}{|\mathbf{r} - \mathbf{r}'|^\sigma}$$

Now we make the change of variable $\mathbf{r} = \mathbf{R}\mathbf{x}$; $\mathbf{r}' = \mathbf{R}\mathbf{y}$ and Ω becomes the unit sphere, we have:

$$\begin{aligned} E(\mathbf{R}) &= A \frac{\rho^2}{2} \int_{\Omega} R^d d^d x R^d d^d y \frac{1}{|\mathbf{R}\mathbf{x} - \mathbf{R}\mathbf{y}|^\sigma} \\ &= \frac{1}{2} A \rho^2 R^{2d-\sigma} \int d^d x d^d y \frac{1}{|\mathbf{x} - \mathbf{y}|^\sigma} \\ &\propto R^{2d-\sigma} \end{aligned}$$

Now we can calculate energy per volume of such system we have:

$$E_b \equiv \frac{E(\mathbf{R})}{V(\mathbf{R})} \propto \frac{R^{2d-\sigma}}{R^d} = R^{d-\sigma}$$

in limit $R \rightarrow \infty$ we see that the thermodynamic limit is only well defined if and only if $d > \sigma$.

For more information see page 27 of "Lectures on Phase Transitions and the Renormalization Group" by Goldenfeld.

7- <http://www.physics.ohio-state.edu/~braaten/statmech/goldenfeld-1.pdf>