CONTENTS

PREFACE

This manual contains solutions to the problems in <u>Fundamentals of Statistical and Thermal Physics</u>, by F. Reif. The problems have been solved using only the ideas explicitly presented in this text and in the way a student encountering this material for the first time would probably approach them. Certain topics which have implications far beyond those called for in the statement of the problems are not developed further here. The reader can refer to the numerous treatments of these subjects. Except when new symbols are defined, the notation conforms to that of the text.

It is a pleasure to thank Dr. Reif for the help and encouragement he freely gave as this work was progressing, but he has not read all of this material and is in no way responsible for its shortcomings. Sincere thanks are also due to Miss Beverly West for patiently typing the entire manuscript.

I would greatly appreciate your calling errors or omissions to my attention.

<div align="right">R. F. Knacke</div>

CHAPTER 1

Introduction to Statistical Methods

1.1

There are $6 \cdot 6 \cdot 6 = 216$ ways to roll three dice. The throws giving a sum less than or equal to 6 are

Throw	1,1,1	1,1,2	1,1,3	1,1,4	1,2,2	1,2,3	2,2,2
No. of Permutations	1	3	3	3	3	6	1

Since there are a total of 20 permutations, the probability is $\frac{20}{216} = \frac{5}{54}$.

1.2

(a) Probability of obtaining one ace = (probability of an ace for one of the dice) × (probability that the other dice do not show an ace) × (number of permutations) = $(\frac{1}{6})(1 - \frac{1}{6})^5 \ (\frac{6!}{5!1!})$

$= (\frac{5}{6})^5 = .402$.

(b) The probability of obtaining at least one ace is one minus the probability of obtaining none, or

$$1 - (\frac{5}{6})^6 = .667$$

(c) By the same reasoning as in (a) we have

$$(\frac{1}{6})^2 (\frac{5}{6})^4 \frac{6!}{5!2!} = .040$$

1.3

The probability of a particular sequence of digits such that five are greater than 5 and five are less than 5 is $(\frac{1}{2})^5 (\frac{1}{2})^5$. Then multiplying by the number of permutations gives the probability irrespective of order.

$$\frac{10!}{5!5!} (\frac{1}{2})^5 (\frac{1}{2})^5 = .246$$

1.4

(a) To return to the origin, the drunk must take the same number of steps to the left as to the right. Thus the probability is

$$W \left(\frac{N}{2}\right) = \frac{N!}{(\frac{N}{2})! (\frac{N}{2})!} \ (\frac{1}{2})^N$$

where N is even.

(b) The drunk cannot return to the lamp post in an odd number of steps.

1

1.5

(a) $\left(\frac{5}{6}\right)^N$

(b) (Probability of being shot on the Nth trial) = (probability of surviving N-1 trials) × (probability of shooting oneself on the Nth trial) = $\left(\frac{5}{6}\right)^{N-1} \left(\frac{1}{6}\right)$.

(c) 6

1.6

$\bar{m} = \overline{m^3} = 0$ since these are odd moments. Using $\overline{n^r} = (p \frac{\partial}{\partial p})^r (p+q)^N$

and
$$\overline{m^2} = \overline{(2n - N)^2} = 4 \overline{n^2} - 4\bar{n}N + N^2$$

$$\overline{m^4} = \overline{(2n - N)^4} = 16 \overline{n^4} - 32 N\overline{n^3} + 24 N^2 \overline{n^2} - 8N^3\bar{n} + N^4$$

we find $\overline{m^2} = N$ and $\overline{m^4} = 3N^2 - 2N$.

1.7

The probability of n successes out of N trials is given by the sum

$$W(n) = \sum_{i=1}^{2} \sum_{j=1}^{2} \ldots \sum_{m=1}^{2} w_i w_j \ldots w_m$$

with the restriction that the sum is taken only over terms involving w_1 n times.

Then $W(n) = \sum_{i=1}^{2} w_i \sum_{j=1}^{2} w_j \ldots \sum_{m=1}^{2} w_m$. If we sum over all i ... m, each sum contributes (w_1+w_2) and

$$W'(n) = (w_1 + w_2)^N$$

$$W'(n) = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} w_1^n w_2^{N-n} \quad \text{by the binomial theorem .}$$

Applying the restriction that w_1 must occur n times we have

$$W(n) = \frac{N!}{n!(N-n)!} w_1^n w_2^{N-n}$$

1.8

We consider the relative motion of the two drunks. With each simultaneous step, they have a probability of 1/4 of decreasing their separation, 1/4 of increasing it, and 1/2 of maintaining it by taking steps in the same direction. Let the number of times each case occurs be n_1, n_2, and n_3, respectively. Then the probability of a particular combination in N steps is

$$W(n_1\ n_2\ n_3) = \frac{N!}{n_1!n_2!n_3!} \left(\frac{1}{4}\right)^{n_1} \left(\frac{1}{4}\right)^{n_2} \left(\frac{1}{2}\right)^{n_3} \quad \text{with } n_1+n_2+n_3 = N$$

The drunks meet if $n_1 = n_2$. Then the probability that they meet after N steps irrespective of the number of steps n_3 which leave their separation unchanged is

$$P = \sum_{n_3=0}^{N} \frac{N!}{n_1! n_2! n_3!} \left(\frac{1}{4}x\right)^{n_1} \left(\frac{1}{4x}\right)^{n_2} \left(\frac{1}{2}\right)^{n_3}$$

where we have inserted a parameter x which cancels if $n_1 = n_2$. We then perform the unrestricted sum over n_1 n_2 n_3 and choose the term in which x cancels. By the binomial expansion,

$$P' = \left(\frac{1}{4}x + \frac{1}{4x} + \frac{1}{2}\right)^N = \left(\frac{1}{2}\right)^{2N} \left(x^{1/2} + x^{-1/2}\right)^{2N}$$

Expansion yields
$$P' = \left(\frac{1}{2}\right)^{2N} \sum_{n}^{2N} \frac{(2N)!}{n!(2N-n)!} \left(x^{1/2}\right)^{n} \left(x^{-1/2}\right)^{2N-n}$$

Since x must cancel we choose the terms where $n = 2N-n$ or $n = N$

Thus
$$P = \left(\frac{1}{2}\right)^{2N} \frac{(2N)!}{(N!)^2}$$

1.9

(a) $\quad \ln(1-p)^{N-n} \approx -p(N-n) \approx -Np \qquad n \ll N \qquad\qquad$ thus $(1-p)^{N-n} \approx e^{-Np}$

(b) $\quad \frac{N!}{(N-n)!} = N(N-1) \cdots (N-n+1) \approx N^n \qquad\qquad$ if $n \ll N$

(c) $\quad W(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \approx \frac{N^n}{n!} p^n e^{-Np} = \frac{\lambda^n}{n!} e^{-\lambda}$

1.10

(a) $\qquad\qquad \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} e^{-\lambda} = e^{-\lambda} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} = e^{-\lambda} e^{\lambda} = 1$

(b) $\qquad\qquad \bar{n} = \sum_{n=0}^{\infty} \frac{n \lambda^n e^{-\lambda}}{n!} = \lambda e^{-\lambda} \frac{\partial}{\partial \lambda} \sum \frac{\lambda^n}{n!} = \lambda e^{-\lambda} e^{\lambda} = \lambda$

(c) $\qquad\qquad \overline{n^2} = \sum_{n=0}^{\infty} \frac{n^2 \lambda^n}{n!} e^{-\lambda} = e^{-\lambda} \left(\lambda \frac{\partial}{\partial \lambda}\right)^2 \sum \frac{\lambda^n}{n!} = \lambda^2 + \lambda$

$\qquad\qquad \overline{(\Delta n)^2} = \overline{n^2} - \bar{n}^2 = \lambda$

1.11

(a) The mean number of misprints per page is 1.

Thus
$$W(n) = \frac{\lambda^n}{n!} e^{-\lambda} = \frac{e^{-1}}{n!}$$

and
$$W(0) = e^{-1} = .37$$

3

(b)
$$P = 1 - \sum_{n=0}^{2} \frac{e^{-1}}{n!} = .08$$

1.12

(a) Dividing the time interval t into small intervals Δt we have again the binomial distribution for n successes in $N = t/\Delta t$ trials

$$W(n) = \frac{N!}{n!(N-n)!} \, p^n \, (1-p)^{N-n}$$

In the limit $\Delta t \to 0$, $W(n) \to \frac{\lambda^n}{n!} e^{\lambda}$ as in problem 1.9 where $\lambda = \frac{\bar{n}}{t}$, the mean number of disintegrations in the interval of time.

(b) $W(n) = \frac{4^n}{n!} e^{-4}$

n	0	1	2	3	4	5	6	7	8
W(n)	.019	.076	.148	.203	.203	.158	.105	.061	.003

1.13

We divide the plate into areas of size b^2. Since b^2 is much less than the area of the plate, the probability of an atom hitting a particular element is much less than one. Clearly $n \ll N$ so we may use the Poisson distribution

$$W(n) = \frac{6^n}{n!} \, e^{-6}$$

n	0	3	6
W(n)	.003	.086	.162

1.14

We use the Gaussian approximation to the binomial distribution.

$$W(n) = \frac{1}{\sqrt{2\pi \frac{400}{4}}} \, e^{- \frac{(215-200)^2}{2(400/4)}} = .013$$

1.15

The probability that a line is in use at any instant is 1/30. We want N lines such that the probability that N+1 or more lines are occupied is less than .01 when there are 2000 trials during the hour.

$$.01 = 1 - \sum_{n=0}^{N} \frac{1}{\sqrt{2\pi} \, \sigma} \, e^{- \frac{(n-\bar{n})^2}{2\sigma^2}}$$

where $\quad \bar{n} = \frac{2000}{30} = 66.67, \quad\quad\quad \sigma = \left[\left(\frac{2000}{30}\right)\left(\frac{29}{30}\right) \right]^{\frac{1}{2}} = 8.02$

The sum may be approximated by an integral

$$.99 = \int_{-\frac{1}{2}}^{N+\frac{1}{2}} \frac{1}{\sqrt{2\pi}\,\sigma} \quad \exp\left[-(n-\bar{n})^2/2\sigma^2\right]\,dn$$

$$.99 = \int_{(-\bar{n}-\frac{1}{2})/\sigma}^{(N-\bar{n}+\frac{1}{2})/\sigma} \frac{1}{\sqrt{2\pi}} \quad e^{-y^2/2}\,dy \quad \text{after a change of integration variable.}$$

The lower limit may be replaced by $-\infty$ with negligible error and the integral found from the tables of error functions.

We find
$$\frac{N-\bar{n}+\frac{1}{2}}{\sigma} = 2.33$$

$$N = 66.67 + (2.33)(8.02) - .5 \approx 85$$

1.16

(a) The probability for N molecules in V is given by the binomial distribution

$$W(N) = \frac{N_o!}{N!(N_o-N)!} \quad \left(\frac{V}{V_o}\right)^N\left(1 - \frac{V}{V_o}\right)^{N-N_o}$$

Thus
$$\bar{N} = N_o p = N_o \frac{V}{V_o}$$

(b)
$$\frac{\overline{(N-\bar{N})^2}}{\bar{N}^2} = \frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{N_o \frac{V}{V_o}\left(1 - \frac{V}{V_o}\right)}{\bar{N}^2} = \frac{1 - \frac{V}{V_o}}{\bar{N}}$$

(c) If $\quad V \ll V_o$,
$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} \approx \frac{1}{\bar{N}}$$

(d) If $V \rightarrow V_o$,
$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} \rightarrow 0$$

1.17

Since $0 \ll \frac{V}{V_o} \ll 1$ and since N_o is large, we may use a Gaussian distribution.

$$P(N)dN = \frac{1}{\left(2\pi \overline{\Delta N^2}\right)^{\frac{1}{2}}} \quad \exp\left[-(N-\bar{N})^2/2\,\overline{\Delta N^2}\right]\,dN$$

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1.18

$$\underline{R} = \sum_i^N \underline{r}_i = \ell \sum_i^N \hat{\underline{S}}_i \qquad\qquad (\hat{\underline{S}}_i\text{'s are unit vectors})$$

$$\overline{\underline{R}\cdot\underline{R}} = \ell^2 \sum_i^N \overline{S_i^2} + \ell^2 \overline{\sum_{i\neq j}^N \sum^N \hat{\underline{S}}_i \cdot \hat{\underline{S}}_j} = N\ell^2 + \ell^2 \overline{\sum_{i\neq j}\sum \cos\theta_{ij}}$$

The second term is 0 because the directions are random. Hence $\overline{R^2} = N\ell^2$.

1.19

The total voltage is $V = \sum_i^N v_i$; hence the mean square is

$$\overline{V^2} = \sum_i^N \overline{v_i^2} + \sum_{i\neq j}^N \sum^N \overline{v}_i\, \overline{v}_j$$

where $\overline{v}_i = vp$ and $\overline{v_i^2} = v^2 p$.

Hence
$$\overline{P} = \overline{V^2}/R = (N^2 V^2/R)\, p^2 [1+(1-p)/Np]$$

1.20

(a) The antennas add in phase so that the total amplitude is $E_t = NE$, and since the intensity is proportional to E_t^2, $I_t = N^2 I$.

(b) To find the mean intensity, we must calculate the mean square amplitude. Since amplitudes may be added vectorially

$$\overline{E_t^2} = \overline{\underline{E}_t \cdot \underline{E}_t} = E^2 \sum_i^N \overline{S_i^2} + E^2 \sum_{i\neq j}\sum \overline{\underline{S}_i \cdot \underline{S}_j}$$

where the $\underline{S}_i$'s are unit vectors. The phases are random so the second term is 0 and

$$\overline{E_t^2} = NE^2 \qquad \text{or} \qquad I_t = NI$$

1.21

$$\overline{A_n^2} = \sum_i^N \overline{a_{n_i}^2} + \sum_{i\neq j}^N \sum^N \overline{a}_{n_i}\, \overline{a}_{n_j}$$

Since $\overline{a}_{n_i} = 0$, the second term on the right is 0 and

$$\left(\overline{A_n^2}\right)^{\frac{1}{2}} = N^{\frac{1}{2}} \left(\overline{a_n^2}\right)^{\frac{1}{2}} = N^{\frac{1}{2}} 10^3 a_s$$

but
$$\left(\overline{A_n^2}\right)^{\frac{1}{2}} = A_S = N a_S$$

Equating these expressions we find $N = 10^6$.

1.22

(a) $\bar{x} = \sum\limits_{i}^{N} \bar{s}_i$, but since $\bar{s}_i = \ell$, $\bar{x} = \sum\limits_{i}^{N} \ell = N\ell$

(b) $\overline{(x-\bar{x})^2} = \sum\limits_{i}^{N} \overline{(s_i-\ell)^2} + \sum\limits_{i}^{N} \sum\limits_{\neq j}^{N} \overline{(s_i-\ell)(s_j-\ell)}$

Since $\overline{(s_i-\ell)} = \ell - \ell = 0$, the second term is 0 and $\overline{(x-\bar{x})^2} = \sum\limits_{i}^{N} \sigma^2 = N\sigma^2$.

1.23

(a) The mean step length is ℓ. $\quad \bar{x} = \sum\limits_{i}^{N} \bar{s}_i = \sum\limits_{i}^{N} \ell = N\ell$

(b) $\overline{(x-\bar{x})^2} = \sum\limits_{i}^{N} \overline{(s_i-\ell)^2} + \sum\limits_{j \neq i}^{N} \sum^{N} \overline{(s_i-\ell)}\,\overline{(s_j-\ell)}$, $\qquad \overline{(s_i-\ell)} = \ell - \ell = 0$

To find the dispersion $\overline{(s_i-\ell)^2}$, we note that the probability that the step length is between s and s + ds in the range ℓ - b to ℓ + b is $\dfrac{ds}{2b}$.

Hence $\qquad \overline{(s_i-\ell)^2} = \int\limits_{\ell-b}^{\ell+b} \dfrac{(s_i-\ell)^2\, ds_i}{2b} = \dfrac{b^2}{3}$

$$\overline{(x-\bar{x})^2} = \sum\limits_{i}^{N} \dfrac{b^2}{3} = \dfrac{Nb^2}{3}$$

1.24

(a) $\qquad\qquad\qquad W(\theta)\, d\theta = \dfrac{d\theta}{2\pi}$

(b) $\qquad\qquad\qquad W(\theta)\, d\theta = \dfrac{2\pi a^2 \sin\theta\, d\theta}{4\pi a^2} = \dfrac{\sin\theta\, d\theta}{2}$

1.25

(a) We find the probability that the proton is in θ and θ + dθ and thus the probability for the resulting field.

From problem 1.24 $\qquad\qquad W(\theta)\, d\theta = \dfrac{\sin\theta\, d\theta}{2}$

Since $b = \dfrac{\mu}{a^3}(3\cos^2\theta - 1)$ we have $\left|\dfrac{db}{d\theta}\right| = \dfrac{6\mu \cos\theta \sin\theta}{a^3}$

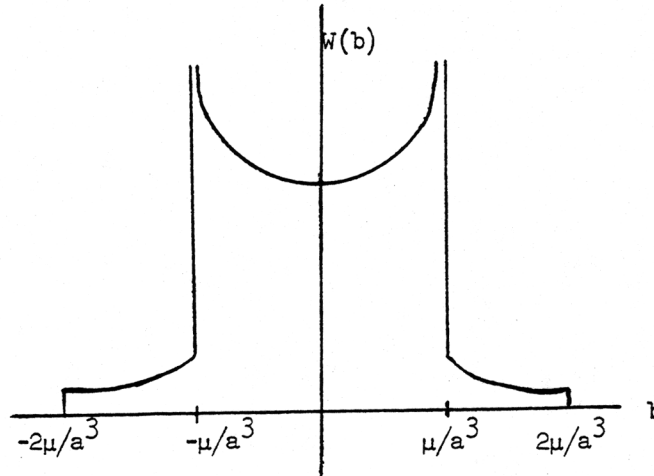and $\qquad\qquad W(b)db = 2W(\theta)d\theta = \dfrac{a^3\sqrt{3}\ db}{6\sqrt{\mu^2 + \mu a^3 b}}$

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(b) If the spin is anti-parallel to the field,

$$W(b)db = \frac{a^3\sqrt{3}\ db}{6\sqrt{\mu^2-\mu\ a^3b}}$$

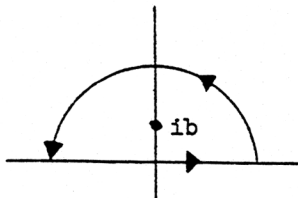Then if either orientation is possible, we add the probabilities and renormalize

$$W(b)db = \begin{cases} \dfrac{a^3\sqrt{3}\ db}{12\sqrt{\mu^2-\mu\ a^3b}} & -\dfrac{2\mu}{a^3} < b < -\dfrac{\mu}{a^3} \\[3ex] \left(\dfrac{a^3\sqrt{3}}{12\sqrt{\mu^2-\mu\ a^3b}} + \dfrac{a^3\sqrt{3}}{12\sqrt{\mu^2+\mu a^3b}}\right)db & -\dfrac{\mu}{a^3} < b < \dfrac{\mu}{a^3} \\[3ex] \dfrac{a^3\sqrt{3}\ db}{12\sqrt{\mu^2+\mu a^3b}} & \dfrac{\mu}{a^3} < b < \dfrac{2\mu}{a^3} \end{cases}$$

1.26

$$Q(k) = \int_{-\infty}^{\infty} ds\ e^{iks}\ W(s) = \frac{b}{\pi} \int_{-\infty}^{\infty} ds\ \frac{e^{iks}}{s^2+b^2}$$

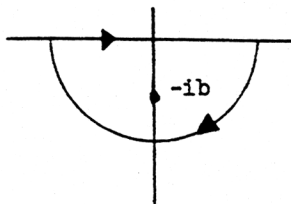Q may be evaluated by contour integration. For $k > 0$, the integral is evaluated on the path

residue $(ib) = \dfrac{e^{-kb}}{2\pi i}$ $Q(k) = e^{-kb}$

For $k < 0$

$-$residue $(-ib) = \dfrac{e^{kb}}{2\pi i}$ $Q(k) = e^{kb}$

8

Thus $Q(k) = e^{-|k|b}$

$$\mathscr{P}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\ e^{-ikx}\ Q^N(k) = \frac{1}{2\pi} \int_{-\infty}^{0} dk\ e^{-ikx}\ e^{Nkb} + \frac{1}{2\pi} \int_{0}^{\infty} dk\ e^{-ikx}\ e^{-Nkb}$$

$$= \frac{1}{\pi} \int_{0}^{\infty} dk\ e^{-Nkb}\ \cos k\ x$$

This integral may be found from tables.

$$\mathscr{P}(x)\ dx = \frac{1}{\pi}\ \frac{Nb\ dx}{x^2 + N^2 b^2}$$

$\mathscr{P}(x)$ does not become Gaussian because the moments $\overline{s^n}$ diverge.
1.27

From equation (1.10.6) and (1.10.8) we see that

$$\mathscr{P}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\ e^{-ikx}\ Q_1(k)\ldots Q_N(k) \tag{1}$$

where $$Q_i(k) = \int_{-\infty}^{\infty} ds\ e^{iks}\ W_i(s)$$

We expand $Q_i(k)$, $$Q_i(k) = 1 + i\ \overline{s}_i k - \frac{1}{2}\ \overline{s_i^2}\ k^2$$

$$\ln Q_i(k) = i\ \overline{s}_i k - \frac{1}{2}\ \overline{(\Delta s_i)^2}\ k^2$$

$$Q_i(k) = \exp[i\ \overline{s}_i k - \frac{1}{2}\ \overline{(\Delta s_i)^2}\ k^2]$$

thus from (1), $$\mathscr{P}(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\ \exp[i(\sum_i^N \overline{s}_i - x)k - \frac{1}{2} \sum_i^N \overline{(\Delta s_i)^2}\ k^2]$$

This integral may be evaluated by the methods of section 1.11. We find

$$\mathscr{P}(x) = \frac{1}{\sqrt{2\pi}\ \sigma}\ \exp[-(x-\mu)^2/2\sigma^2]$$

where $$\mu = \sum_i^N \overline{s}_i \qquad\qquad \sigma = \sum_i^N \overline{(\Delta s_i)^2}$$

1.28

The probability that the total displacement lies in the range $\underline{r}$ to $\underline{r} + d\underline{r}$ after N steps is

$$\mathscr{P}(\underline{r})\ d^3\underline{r} = \int \overset{\infty}{\underset{-\infty}{\ldots}} \int_{(d^3\underline{r})} W(\underline{s}_1)\ W(\underline{s}_2)\ \ldots\ W(\underline{s}_N)\ d^3\underline{s}_1\ \ldots\ d^3\underline{s}_N$$

where the integral is evaluated with the restriction

$$\underline{r} < \sum_{i=1}^{N} \underline{s}_i < \underline{r} + d\underline{r}$$

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We remove the restriction on the limits by introducing a delta function

$$\mathcal{P}(\underline{r}) \, d^3\underline{r} = \int_{-\infty}^{\infty} \cdots \int W(\underline{s}_1) \cdots W(\underline{s}_N) \left[\delta(\underline{r} - \sum_i \underline{s}_i) d^3\underline{r} \right] d^3\underline{s}_1 \cdots d^3\underline{s}_N$$

In three dimensions
$$\delta(\underline{r} - \sum_i \underline{s}_i) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d^3\underline{k} \; e^{i\underline{k}\cdot[\sum_i \underline{s}_i - \underline{r}]}$$

thus
$$\mathcal{P}(r) = \int_{-\infty}^{\infty} \cdots \int W(\underline{s}_1) \cdots W(\underline{s}_N) \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d^3\underline{k} \; e^{i\underline{k}\cdot[\sum_i \underline{s}_i - \underline{r}]} d^3\underline{s}_1 \cdots d^3\underline{s}_N$$

$$\mathcal{P}(r) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d^3\underline{k} \; e^{-i\underline{k}\cdot\underline{r}} \int_{-\infty}^{\infty} d^3\underline{s}_1 \, W(\underline{s}_1) \, e^{i\underline{k}\cdot\underline{s}_1} \cdots \int_{-\infty}^{\infty} d^3\underline{s}_N W(\underline{s}_N) \, e^{i\underline{k}\cdot\underline{s}_N}$$

or
$$\mathcal{P}(r) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d^3\underline{k} \; e^{-i\underline{k}\cdot\underline{r}} \, Q^N(\underline{k}) \qquad \text{where} \quad Q(\underline{k}) = \int_{-\infty}^{\infty} d^3\underline{s} \; e^{i\underline{k}\cdot\underline{s}} \, W(\underline{s})$$

1.29

For displacements of uniform length but of random direction $W(\underline{s}) = \dfrac{\delta(s-\ell)}{4\pi \, s^2}$, in spherical coordinates. $W(\underline{s})$ is a properly normalized probability density since

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} s^2 \sin\theta \; ds \; d\theta \; d\varphi \, \frac{\delta(s-\ell)}{4\pi \, s^2} = 4\pi \int_0^{\infty} \frac{\delta(s-\ell)}{4\pi} = 1$$

We find the Fourier transform $Q(\underline{k})$.

$$Q(\underline{k}) = \iiint d^3\underline{s} \; e^{i\underline{k}\cdot\underline{s}} \, W(\underline{s}) = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} s^2 \sin\theta \; ds \; d\theta \; d\varphi \, \frac{\delta(s-\ell)}{4\pi \, s^2} e^{iks\cos\theta}$$

$$= 2\pi \int_0^{\pi} \frac{\sin\theta \; d\theta}{4\pi} \; e^{ik\ell\cos\theta} = \frac{\sin k\ell}{k\ell}$$

From
$$\mathcal{P}(\underline{r}) = \frac{1}{(2\pi)^3} \iiint d^3\underline{k} \; e^{-i\underline{k}\cdot\underline{r}} \, Q^N(\underline{k})$$

we have, for $N = 3$

$$\mathcal{P}(r) = \frac{1}{(2\pi)^3} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} k^2 \sin\theta \; dk \; d\theta \; d\varphi \; e^{-ikr\cos\theta} \, \frac{\sin^3 k\ell}{(k\ell)^3}$$

The angular integrations are trivial and

$$\mathcal{P}(r) = \frac{1}{2\pi^2 \ell^3 r} \int_0^{\infty} dk \; \frac{\sin^3 k\ell \, \sin kr}{k^2}$$

To evaluate the integral, we use the identities

$$\frac{\sin^3 k\ell \, \sin kr}{k^2} = \frac{1}{k^2} \sin kr \, \sin k\ell \left(\frac{1 - \cos 2 \, k\ell}{2} \right)$$

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$$= \frac{1}{4k^2} \left[\cos k(r-\ell) - \cos k(r+\ell)\right]\left[1-\cos 2k\ell\right]$$

$$= \frac{1}{8k^2} \left[3 \cos k(r-\ell) - 3 \cos k(r+\ell) + \cos k(r+3\ell) - \cos k(r-3\ell)\right]$$

The integral of the first two terms in the last identity is

$$\frac{3}{8} \int_0^\infty \frac{\cos k(r-\ell) - \cos k(r+\ell)}{k^2} \, dk = \frac{3}{4} \int_0^\infty \frac{\sin^2 \frac{k}{2}(r+\ell) - \sin^2 \frac{k}{2}(r-\ell)}{k^2} \, dk$$

On making the substitutions $x = \frac{k}{2}(r+\ell)$ and $y = \frac{k}{2}(r-\ell)$, it follows that

$$\frac{3}{4} \int_0^\infty \frac{|r+\ell|}{2} \frac{\sin^2 x}{x^2} \, dx - \frac{3}{4} \int_0^\infty \frac{|r-\ell|}{2} \frac{\sin^2 y \, dy}{y^2} = \frac{3\pi}{16} (|r+\ell| - |r-\ell|)$$

The third and fourth terms may be evaluated in the same way.

$$\frac{1}{8} \int_0^\infty \frac{\cos k(r+3\ell) - \cos k(r-3\ell)}{k^2} \, dk = \frac{\pi}{16} (|r-3\ell| - |r+3\ell|)$$
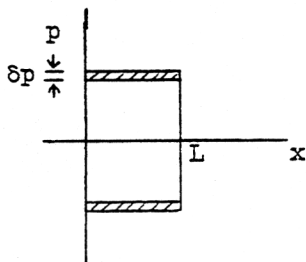
Combining these results, we have

$$\mathcal{P}(r) = \begin{cases} \dfrac{1}{8\pi \ell^3} & 0 < r < \ell \\[2ex] \dfrac{1}{16\pi \ell^3 r} (3\ell-r) & \ell < r < 3\ell \\[2ex] 0 & r > 3\ell \end{cases}$$

CHAPTER 2

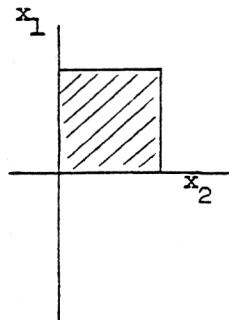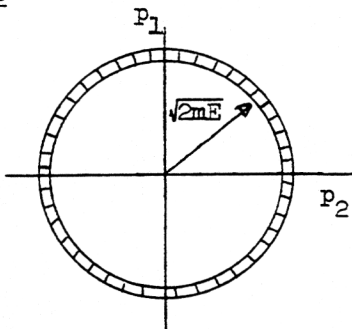### Statistical Description of Systems of Particles

2.1

$$p = \sqrt{2mE} \qquad \delta p = \sqrt{\frac{m}{2E}} \; \delta E$$

Hatched areas are accessible to the particle.

2.2

Since $p_1^2 + p_2^2 = 2mE$, the radius in p space is $\sqrt{2mE}$.

2.3

(a) The probability of displacement x is the probability that φ assumes the required value in the expression $x = A \cos(\omega t + \varphi)$.

$$w(\varphi)d\varphi = \frac{d\varphi}{2\pi} \qquad \text{and} \qquad P(x)dx = 2w(\varphi)\, d\varphi = \frac{d\varphi}{\pi}$$
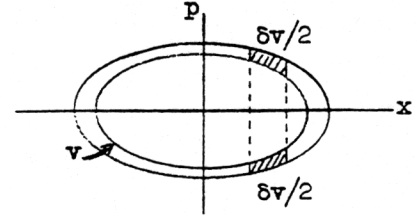
where the factor of 2 is introduced because two values of φ give the same x.

Since

$$\left|\frac{d\varphi}{dx}\right| = \frac{1}{A \sin(\omega t + \varphi)} = \frac{1}{\sqrt{A^2 - x^2}}$$

we have

$$P(x)dx = \frac{dx}{\pi\sqrt{A^2 - x^2}}$$

(b) We take the ratio of the occupied volume, δv, in phase space when the oscillator is in the range x to $x + dx$ and E to $E + \delta E$, to the total accessible volume, v.

The area, A_e, of the ellipse is $\pi p_{max} x_{max}$.

Since

$$E = \frac{p^2}{2m} + \frac{m\,\omega^2 x^2}{2} \qquad\qquad (1)$$

we have

$$A_e = \pi\sqrt{\frac{2E}{m\omega^2}}\sqrt{2mE} = \frac{2\pi E}{\omega}, \quad \text{and} \quad v = \frac{2\pi}{\omega}\,\delta E .$$

Hence

$$P(x)dx = \frac{\delta v}{v} = \frac{2\,\delta p\,\delta x}{\frac{2\pi}{\omega}\,\delta E}$$

For any x, $p\,\dfrac{\delta p}{m} = \delta E$

$$P(x)dx = \frac{m\omega}{\pi}\,\frac{dx}{p} = \frac{m\omega}{\pi}\,\frac{dx}{\sqrt{2mE - m^2\omega^2 x^2}}$$

where we have used (1). From (1) and $x = A \cos(\omega t + \varphi)$, it follows that $E = \frac{1}{2}\omega^2 m A^2$.

Thus

$$P(x)dx = \frac{1}{\pi}\,\frac{dx}{\sqrt{A^2 - x^2}}$$

2.4

(a) The number of ways that N spins can be arranged such that n_1 are parallel and n_2 are anti-parallel to the field is

$$f(n_1) = \frac{N!}{n_1!\, n_2!} \qquad\qquad \text{and} \qquad\qquad \Omega(E) = f(n_1)\frac{\delta E}{2\mu H}$$

Since $\qquad E = -(n_1 - n_2)\mu H = -(2n_1 - N)\mu H,$ $\qquad$ we have $\qquad n_1 = \frac{1}{2}(N - \frac{E}{\mu H})$, $n_2 = \frac{1}{2}(N + \frac{E}{2\mu H})$

Thus

$$\Omega(E) = \frac{N!}{(\frac{N}{2} - \frac{E}{2\mu H})! \; (\frac{N}{2} + \frac{E}{2\mu H})!} \; \frac{\delta E}{2\mu H}$$

(b) Using Stirling's approximation, $\ln n! = n \ln n - n$, we have

$$\ln \frac{N!}{n_1! (N-n_1)!} = -n_1 \ln \frac{n_1}{N} + (n_1 - N) \ln (1 - \frac{n_1}{N})$$

$$\ln \Omega(E) = -\frac{1}{2}(N - \frac{E}{\mu H}) \ln \frac{1}{2}(1 - \frac{E}{N\mu H}) - \frac{1}{2}(N + \frac{E}{\mu H}) \ln \frac{1}{2}(1 + \frac{E}{N\mu H}) + \ln \frac{\delta E}{2\mu H}$$

(c) We expand $\ln f(n_1) = \ln \frac{N!}{n_1! (N-n_1)!}$ about the maximum, $\tilde{n}_1$

$$\ln f(n_1) = \ln f(\tilde{n}_1) + \frac{1}{2} B_2 \eta^2 \qquad (1)$$

where $\qquad \eta = n_1 - \tilde{n}_1 \qquad\qquad B_2 = \left[\frac{d^2 \ln f(n_1)}{dn_1^2} \right]_{\tilde{n}_1}$

From (1) $\qquad\qquad f(n_1) = f(\tilde{n}_1) \, e^{-\frac{1}{2} |B_2| \eta^2} \qquad (2)$

$f(\tilde{n}_1)$ is evaluated by noticing that the integral of $f(n_1)$ over all n_1 must equal the total number of permutations of spin directions, 2^N.

$$\int_{-\infty}^{\infty} f(\tilde{n}_1) \, e^{-\frac{1}{2} |B_2| \eta^2} \, d\eta = 2^N$$

$$f(\tilde{n}_1) = 2^N \sqrt{\frac{|B_2|}{2\pi}}$$

$\tilde{n}_1$ is found from the maximum condition

$$\left. \frac{d \ln f(n_1)}{dn_1} \right|_{\tilde{n}_1} = 0 = -\ln \tilde{n}_1 + \ln (N - \tilde{n}_1), \text{ or } \tilde{n}_1 = \frac{N}{2}$$

and $\qquad |B_2| = \left| \frac{d^2 \ln f(n_1)}{dn_1^2} \right|_{\tilde{n}_1} = \left| -\frac{1}{\tilde{n}_1} - \frac{1}{N - \tilde{n}_1} \right|_{\tilde{n}_1 = N/2} = \frac{4}{N}$

Substituting these expressions into (2), we have

$$f(n_1) = \frac{2^N}{\sqrt{\pi \frac{N}{2}}} \, e^{-\frac{2}{N}(n_1 - \frac{N}{2})^2}$$

Since $\Omega(E) = f(n_1) \dfrac{\delta E}{2\mu H}$, and $n_1 = \dfrac{1}{2}(N - \dfrac{E}{\mu H})$, it follows that

$$\Omega(E) = \frac{2^N}{\sqrt{\pi \frac{N}{2}}} \exp\left[-\frac{2}{N}\left(\frac{E}{2\mu H}\right)^2\right] \frac{\delta E}{2\mu H}$$

2.5

(a) $\qquad\qquad\qquad\qquad\qquad d\!\!\!/\, f = A\,dx + B\,dy$

If $d\!\!\!/\, f$ is an exact differential, $\qquad A = \dfrac{\partial f}{\partial x} \quad B = \dfrac{\partial f}{\partial y}$

Since second derivatives are equal, $\qquad \dfrac{\partial A}{\partial y} = \dfrac{\partial B}{\partial x}$

(b) If $d\!\!\!/\, f$ is exact, $\qquad \displaystyle\int_A^B d\!\!\!/\, f = f(B) - f(A) = 0$ if $A = B$

2.6

(a) not exact $\qquad\qquad\qquad \dfrac{\partial^2 f}{\partial x\,\partial y} \neq \dfrac{\partial^2 f}{\partial y\,\partial x}$

(b) $\displaystyle\int_1^2 dy + \int_1^2 (x^2-2)\,dx = \frac{1}{3}$, $\displaystyle\int_1^2 (x^2-1)\,dx + \int_1^2 2\,dx = \frac{10}{3}$, $\displaystyle\int_1^2 (x^2-x)\,dx + \int_1^2 x\,dx = \frac{7}{3}$

(c) exact

(d) $\qquad\qquad \displaystyle\int_{1,1}^{2,2} d\!\!\!/\, f = \left[x + \frac{y}{x}\right]_{(1,1)}^{(2,2)} = 1 \qquad$ for all paths

2.7

(a) The particle in a state with energy E does work, $d\!\!\!/\, W$, when the length of the box is changed to $L_x + dL_x$. This work is done at the expense of the energy, i.e., $d\!\!\!/\, W = -dE$. Since $d\!\!\!/\, W = F_x dL_x$, it follows that $F_x = -\dfrac{\partial E}{\partial L_x}$.

(b) The energy levels are given by $E = \dfrac{2\pi^2\hbar^2}{m}\left(\dfrac{n_x^2}{L_x^2} + \dfrac{n_y^2}{L_y^2} + \dfrac{n_z^2}{L_z^2}\right)$
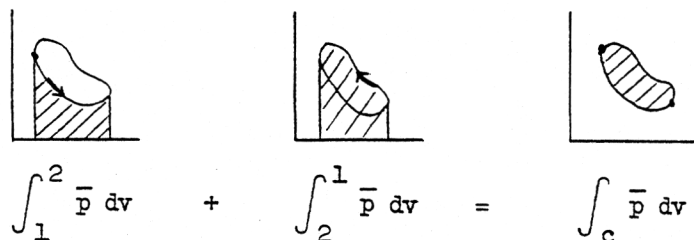
$$p = \frac{F_x}{L_y L_z} = -\frac{1}{L_y L_z}\frac{\partial E}{\partial L_x} = \frac{4\pi^2\hbar^2}{m L_x L_y L_z}\left(\frac{n_x^2}{L_x^2}\right)$$

$$\bar{p} = \frac{4\pi\hbar^2}{mV}\left(\frac{\overline{n_x^2}}{L_x^2}\right) \qquad\qquad \text{where} \quad V = L_x L_y L_z$$

If $L_x = L_y = L_z$, by symmetry $\overline{n_x^2} = \overline{n_y^2} = \overline{n_z^2}$, and using the expression for E we have

$$\bar{p} = \frac{2}{3}\frac{\bar{E}}{V}$$

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2.8

$$\int_1^2 \bar{p} \, dv \quad + \quad \int_2^1 \bar{p} \, dv \quad = \quad \int_c \bar{p} \, dv$$

2.9

From the definition of the Young's modulus, the force is

$$dF = \frac{YA}{L} \, dL$$

$$W = -\int_{F_1}^{F_2} F \frac{L}{YA} \, dF = \frac{L}{2AY} (F_1^2 - F_2^2)$$

2.10

$$W = \int_{V_i}^{V_f} p \, dv = \int_{V_i}^{V_f} \frac{K}{V^\gamma} \, dV$$

$$= \frac{K}{1-\gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) = \frac{P_f V_f - P_i V_i}{1-\gamma}$$

2.11

$\bar{p} = \alpha V^{-5/3}$, α may be found by evaluating this expression at a point on the curve. In units of 10^6 dynes/m^2 and 10^3 cm^3, $\alpha = 32$. For the adiabatic process,

$$\Delta E = E_B - E_A = -\int_1^8 32 V^{-5/3} \, dV = -36 = -3600 \text{ joules}$$

Since energy is a state function, this is the energy change for all paths.

(a)

$$W = 32 \int_1^8 dV = 22,400 \text{ joules}$$

$$Q = \Delta E + W = -3600 + 22,400 = 11,800 \text{ joules}$$

(b)

$$p = 32 - \frac{31}{7} (V-1)$$

$$W = \int_1^8 \left[32 - \frac{31}{7} (V-1) \right] = 11,550 \text{ joules}$$

$$Q = 11,550 - 3600 = 7,950 \text{ joules}$$

(c)

$$W = \int_1^8 (1) \, dV = 700 \text{ joules}$$

$$Q = 700 - 3600 = -2900 \text{ joules}$$

Statistical Thermodynamics

3.1

(a) In equilibrium, the densities on both sides of the box are the same. Thus, in the larger volume, the mean number of Ne molecules is 750 and the mean number of He molecules is 75.

(b)
$$P = \left(\frac{3}{4}\right)^{1000} \left(\frac{1}{4}\right)^{100} = 10^{-185}$$

3.2

From problem 2.4 (b)

(a)
$$\ln \Omega(E) = -\frac{1}{2}\left(N - \frac{E}{\mu H}\right) \ln \frac{1}{2}\left(1 - \frac{E}{N\mu H}\right) - \frac{1}{2}\left(N + \frac{E}{\mu H}\right) \ln \frac{1}{2}\left(1 + \frac{E}{N\mu H}\right)$$

where we have neglected the small term $\ln \frac{\delta E}{2\mu H}$.

$$\beta = \frac{\partial}{\partial E} \ln \Omega(E) = \frac{1}{2\mu H} \ln \frac{\frac{1}{2}\left(1 - \frac{E}{N\mu H}\right)}{1 - \frac{1}{2}\left(1 - \frac{E}{N\mu H}\right)}$$

Consequently
$$E = -N\mu H \tanh \frac{\mu H}{kT}$$

(b)
$$T < 0 \quad \text{if} \quad E > 0$$

(c) $M = \mu(n_1 - n_2) = \mu(2n_1 - N)$ where n_1 is the number of spins alligned parallel to H.

Since $n_1 = \frac{1}{2}\left(N - \frac{E}{\mu H}\right)$ from problem 2.4 (a), $\quad M = \mu\left(N - \frac{E}{\mu H} - N\right) = -\frac{E}{H}$

$$M = N\mu \tanh \frac{\mu H}{kT}$$

3.3

(a) for system A, we have from 2.4 (c) $\quad \ln \Omega(E) = -\frac{E^2}{2\mu^2 H^2 N} + \frac{\ln 2^N}{\sqrt{\frac{\pi N}{2}}} \quad$ (1)

where we have neglected the term $\ln \frac{\delta E}{2\mu H}$

$$\beta = \frac{\partial}{\partial E} \ln \Omega(E) = -\frac{E}{\mu^2 H^2 N} \, , \, \beta' = -\frac{E'}{\mu'^2 H^2 N'}$$

In equilibrium, $\qquad \beta = \beta' \qquad\qquad$ Hence $\qquad \frac{\tilde{E}}{\mu^2 N} = \frac{\tilde{E}'}{\mu'^2 N'}$

(b) Since energy is conserved, $\qquad \tilde{E} + \tilde{E}' = bN\mu H + b'N'\mu H$

Substituting from (a) we find $\qquad \tilde{E} = \frac{\mu^2 N(bN\mu H + b'N'\mu'H)}{\mu^2 N + \mu'^2 N'} \qquad\qquad$ (2)

(c) $\qquad Q = \tilde{E} - bN\mu H = \frac{NN'H(b'\mu'\mu^2 - b\mu'^2\mu)}{\mu^2 N + \mu'^2 N'} \qquad$ from (2)

(d) $\quad P(E) \propto \Omega(E)\, \Omega'(E_o - E)$ where E_o is the total energy, $E_o = bN\mu H + b'N'\mu'H$.

From (1) $\qquad P(E) \propto \exp\left[-\dfrac{E^2}{2\mu^2 H^2 N}\right]\ \exp\left[-\dfrac{(E_o-E)^2}{2\mu'^2 H^2 N'}\right]$

This expression may be rewritten in terms of the most probable energy $\tilde{E}$, equation (2).

$$P(E)dE = C\exp\left[-\frac{(E-\tilde{E})^2}{2\sigma^2}\right]dE$$

where $\qquad \sigma^2 = \dfrac{\mu^2\mu'^2 H^2 NN'}{\mu^2 N + \mu'^2 N'}$

The constant C is determined by the normalization requirement

$$\int_{-\infty}^{\infty} C\exp\left[-\frac{(E-\tilde{E})^2}{2\sigma^2}\right]dE = 1$$

Thus $\qquad P(E)dE = \dfrac{1}{\sqrt{2\pi}\,\sigma}\ \exp\left[-\dfrac{(E-\tilde{E})^2}{2\sigma^2}\right]dE$, where σ is given above.

(e) $\qquad \overline{(\Delta^{*}E)^2} = \sigma^2 = \dfrac{\mu^2\mu'^2 H^2 NN'}{\mu^2 N + \mu'^2 N'} \qquad\qquad$ (3)

(f) $\qquad$ From equation (3), $\qquad \Delta^{*}E \approx \mu H\sqrt{N} \qquad\qquad N' \gg N$

$$\tilde{E} = \frac{\mu\, N(b\mu HN + b'\mu'N'H)}{\mu^2 N + \mu'^2 N'} \approx b'\,\frac{N\mu^2 H}{\mu'} \qquad\qquad N' \gg N$$

hence $\qquad \left|\dfrac{\Delta^{*}E}{\tilde{E}}\right| = \dfrac{\mu'}{\mu\, b'\sqrt{N}}$

3.4

The entropy change of the heat reservoir is $\Delta S' = -\dfrac{Q}{T'}$ and for the entropy change of the entire system, $\Delta S + \Delta S' = \Delta S - \dfrac{Q}{T'} \geqq 0.$, by the second law.

Hence $\qquad\qquad\qquad\qquad \Delta S \geqq \dfrac{Q}{T'}$

3.5

(a) In section 2.5 it is shown that $\Omega(E) \propto V^N \chi(E)$, where V is the volume and $\chi(E)$ is independent of volume. Then for two non-interacting species with total energy E_o

$$\Omega(E) = C\,\Omega_1(E)\,\Omega_2(E_o - E) = CV^{N_1+N_2}\,\chi_1(E)\,\chi_2(E)$$

(b) $\qquad\qquad \ln\Omega(E) = (N_1+N_2)\ln V + \ln C + \ln\chi_1(E)\,\chi_2(E)$

$$\bar{p} = \frac{1}{\beta}\,\frac{\partial}{\partial V}\ln\Omega(E) = \frac{1}{\beta}\,\frac{(N_1+N_2)}{V}\ ,\quad \text{or}\quad \bar{p}V = (N_1+N_2)kT$$

2 atmospheres.

CHAPTER 4

Macroscopic Parameters and their Measurement

4.1

(a)
$$\Delta S_W = mc \int_{273}^{373} \frac{dT}{T} = 4180 \ln \frac{373}{273} = 1310 \text{ joules/}^\circ K$$

Since
$$Q_{res} = -Q_W$$

$$\Delta S_{res} = -\frac{Q_W}{T} = -\frac{mc}{T}(373-273) = -1120 \text{ joules/}^\circ K$$

$$\Delta S_{tot} = \Delta S_W + \Delta S_{res} = 190 \text{ joules/}^\circ K$$

(b) The heat given off by either reservoir is $Q = mc(50) = 2.09 \times 10^5$ joules. Since the entropy change of the water is the same as in (a) we have

$$\Delta S = 1310 - \frac{2.09 \times 10^5}{323} - \frac{2.09 \times 10^5}{373} = 102 \text{ joules/}^\circ K$$

(c) There will be no entropy change if the system is brought to its final temperature by inter-action with a succession of heat reservoirs differing infinitesimally in temperature.

4.2

(a) The final temperature is found by relating the heats, Q, exchanged in the system. The heat required for melting the ice is $m_i \ell$ where m_i is the mass of the ice. Since for the other compo-nents of the system, $Q = mc\Delta T$, where m is mass and c is the specific heat, we have

$$m_i \ell + Q_{(melted\ ice)} + Q_{(original\ water)} + Q_{(calorimeter)} = 0$$

$$m_i \ell + m_i c_W(T_f-273) + m_W c_W(T_f-293) + m_c c_c(T_f-293) = 0$$

$$(30)(333) + (30)(4.18)(T_f-273)+(200)(4.18)(T_f-293)+(750)(.418)(T_f-293) = 0$$

$$T_f = 283^\circ K$$

(b) The change in entropy when the ice melts is $\frac{m_i \ell}{T}$. For the other components

$$\Delta S = mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln \frac{T_f}{T_i}$$

Hence
$$\Delta S = \frac{m_i \ell}{273} + m_W c \ln \frac{283}{293} + m_i c \ln \frac{283}{273} + m_c c_c \ln \frac{283}{293} = 1.6 \text{ joules/}^\circ K$$

(c) The work required is the amount of heat it would take to raise the water to this temperature.

$$W = m_W c_W (T_f - T_i) + m_c c_c (T_f - T_i)$$

$$= \left[(750)(.418) + (230)(4.18) \right] (293-283) = 12{,}750 \text{ joules}$$

4.3

$$\bar{d} Q = c \, dT + \bar{p} \, dV \qquad \text{by the first law}$$

$$= c \, dT + \frac{RT}{V} \, dV \qquad \text{Since } pV = RT$$

$$\Delta S = \int_i^f \frac{\bar{d} Q}{T} = \int_{T_i}^{T_f} c \frac{dT}{T} + \int_{V_i}^{V_f} \frac{R \, dV}{V}$$

$$= c \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i} \qquad \text{independent of process}$$

4.4

The spins become randomly oriented in the limit of high temperatures. Since each spin has 2 available states, for N spins we have

$$S(T \rightarrow \infty) = k \ln \Omega = k \ln 2^N = Nk \ln 2 \qquad (1)$$

But since

$$S(T) - S(0) = \int_0^T \frac{C(T)}{T} \, dT$$

we have

$$S(T \rightarrow \infty) = \int_{\frac{1}{2}T_1}^{T_1} c_1 (\frac{2T}{T_1} - 1) \frac{dT}{T} = c_1 (1 - \ln 2) \qquad (2)$$

where we have set $S(0) = 0$ by the third law. From (1) and (2) $Nk \ln 2 = c_1 (1 - \ln 2)$

$$c_1 = \frac{Nk \ln 2}{1 - \ln 2} = 2.27 \, Nk$$

4.5

The entropy at temperature T is found by evaluating $S(T) - S(0) = \int_0^T \frac{C(T)}{T} \, dT$. Labeling the undiluted and diluted systems by u and d, we have

$$S_u(T_1) - S_u(0) = \int_{\frac{1}{2}T_1}^{T_1} c_1 (2 \frac{T}{T_1} - 1) \frac{dT}{T} = c_1 (1 - \ln 2)$$

$$S_d(T_1) - S_d(0) = \int_{\frac{1}{2}T_1}^{T_2} c_2 \frac{T}{T_2} \frac{dT}{T} = c_2$$

$S_d(0) = S_u(0)$ by the third law. Since there are only $\frac{7}{10}$ as many magnetic atoms in the diluted case as in the other, we must have $S_d(T_1) = .7 \, S_U(T_1)$. Hence

$$\frac{c_2}{c_1} = .7 \, (1 - \ln 2) = .214$$

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CHAPTER 5

Simple Applications of Macroscopic Thermodynamics

5.1

(a) pV^γ = constant for an adiabatic quasistatic process. Substituting $pV = \nu RT$ we have

$$\frac{\nu R\, T_i V_i^{\ \gamma}}{V_i} = \frac{\nu\, RT_f V_f^{\ \gamma}}{V_f} \quad \text{or} \quad T_f = T_i \left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

(b) The entropy change of an ideal gas in a process taking it from T_1, V_i to T_f, V_f was found in problem 4.3

$$\Delta S = \nu c_V \ln \frac{T_f}{T_i} + \nu R \ln \frac{V_f}{V_i}$$

$\Delta S = 0$ for an adiabatic quasistatic process. Hence

$$0 = \ln \frac{T_f}{T_i} \left(\frac{V_f}{V_i}\right)^{R/c_V}$$

Since $R/c_V = c_p - c_V/c_V = \gamma - 1$, and since $\ln 1 = 0$, it follows that

$$T_f = T_i \left(\frac{V_f}{V_i}\right)^{1-\gamma}$$

5.2

(a) $W = \displaystyle\int p\, dV$ = area enclosed by curve = 314 joules

(b) Since the energy of an ideal gas is only a function of the temperature and since $pV = RT$,

$$\Delta E = c_V\, \Delta T = \frac{3}{2} R \left(\frac{P_c V_c}{R} - \frac{P_A V_A}{R}\right)$$

$$= \frac{3}{2}\,(6-2) \times 10^9 \text{ ergs} = 600 \text{ joules}$$

(c) $Q = \Delta E + W$ where ΔE is calculated in (b) since the energy change is independent of path. Again the work is the area under the curve.

$$Q = 600 + \left[400 + \frac{100\pi}{2}\right] = 1157 \text{ joules}$$

5.3

(a)
$$c_V = \frac{\partial E}{\partial T} = \frac{5}{2} R$$

(b)
$$W = \int p\, dV = \text{area under curve} = 1300 \text{ joules}$$

(c) To find the heat, Q, we first find the energy change in going from A to C. This, of course, is independent of the path.

$$\Delta E = c_V \Delta T = \frac{5}{2} R(T_C - T_A) = \frac{5}{2}(P_c V_c - P_A V_A) = 1500 \text{ joules}$$

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Then since $Q = \Delta E + W$

$$Q = 1500 + 1300 = 2800 \text{ joules}$$

(d) From problem 4.3

$$\Delta S = c_V \ln \frac{T_c}{T_A} + R \ln \frac{V_c}{V_A}$$

$$= \frac{5}{2} R \ln \frac{12 \times 10^2/R}{6 \times 10^2/R} + R \ln \frac{3 \times 10^3}{10^3} = 2.84 \, R = 23.6 \text{ joules}/{}^\circ K$$

5.4

(a) The total system, i.e., water and gases, does not exchange energy with the environment, so its energy remains the same after the expansion. Since the water cannot do work, its energy change is given by the heat it absorbs, $\Delta E = Q = C_W \Delta T$, where C_W is the heat capacity. The energy of the two ideal gases is, of course, dependent only on temperature, $\Delta E = C \Delta T$, where C is the heat capacity.

$$\Delta E_{(water)} + \Delta E_{(He)} + \Delta E_{(A)} = 0$$

$$C_W(T_f - T_i) + C_{He}(T_f - T_i) + C_A(T_f - T_i) = 0$$

Thus $T_f = T_i$, no temperature change.

(b) Let ℓ be the distance from the left and ν the number of moles.

$$\frac{\nu_{He}}{\nu_A} = \frac{P_{He} V_{He}}{P_A V_A} = \frac{(5)(30)}{(1)(50)} = 3$$

Hence, in equilibrium $\ell = 3(80 - \ell)$, $\ell = 60$ cm.

(c) Since there is no temperature change, the entropy change is $\nu R \ln \frac{V_f}{V_i}$.

$$\Delta S = \Delta S_A + \Delta S_{He} = \frac{R}{3} \ln \frac{20}{50} + R \ln \frac{60}{30} = 3.24 \text{ joules}/{}^\circ K.$$

5.5

(a) The temperature decreases. The gas does work at the expense of its internal energy.

(b) The entropy of the gas increases since the process is irreversible.

(c) The system is isolated, $Q = 0$, and from the first law

$$\Delta E = -W = -\frac{mg}{A}(V_f - V_o)$$

The internal energy of the gas is only a function of temperature, $\Delta E = \nu c_V(T_f - T_o)$

Thus

$$\nu c_V(T_f - T_o) = -\frac{mg}{A}(V_f - V_o) \qquad (1)$$

In equilibrium $p = \frac{mg}{A}$ and since $pV_f = \nu R T_f$, we have

$$V_f = \frac{\nu A R T_f}{mg}$$

Substitution in (1) yields
$$T_f = \frac{1}{1 + (R/c_V)} \left[T_o + \frac{mg\, V_o}{\nu\, c_V A} \right]$$

5.6

The equation of motion is
$$m\ddot{x} = pA - mg - p_o A \qquad (1)$$

Since the process is approximately adiabatic

$$pV^\gamma = \text{constant} = \left(p_o + \frac{mg}{A}\right) V_o^{\,\gamma}$$

and
$$m\ddot{x} = \left(p_o + \frac{mg}{A}\right) \frac{A V_o^{\,\gamma}}{(Ax)^\gamma} - mg - p_o A \qquad (2)$$

The displacements from the equilibrium position, $\frac{V_o}{A}$, are small so we can introduce the coordinate change $x = \frac{V_o}{A} + \eta$ and expand about $\frac{V_o}{A}$.

$$\frac{1}{x^\gamma} = \frac{1}{\left(\frac{V_o}{A} + \eta\right)^\gamma} = \left(\frac{A}{V_o}\right)^\gamma \left(1 - \frac{\gamma A \eta}{V_o} + \dots\right)$$

We keep only the first and second terms and substitute into (2).

$$m\ddot{\eta} = -\left(p_o + \frac{mg}{A}\right) \frac{A^2 \gamma}{V_o} \; \eta$$

This is the equation for harmonic motion and the frequency may be determined by inspection.
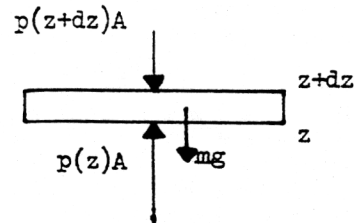
Hence

$$\nu = \frac{1}{2\pi} \left[\left(p_o + \frac{mg}{A}\right) \frac{A^2 \gamma}{V_o m} \right]^{\frac{1}{2}}$$

$$\gamma = \frac{4\pi^2 \nu^2 m V_o}{p_o A^2 + mg\, A}$$

5.7

The volume element of atmosphere shown must be in equilibrium under the forces (pressure) $\times$ (area) and gravity. Then if n is the number of particles per unit volume, m the mass per particle, and g the acceleration of gravity,

$$p(z+dz)A - p(z)A = -n(A\,dz)mg$$

$$\frac{dp}{dz}\, dz = -\frac{n\mu g}{N_A}\, dz, \quad \text{where} \quad \frac{\mu}{N_A} = m$$

Since $p = nkT$,
$$\frac{dp}{p} = -\frac{\mu g}{RT} dz \qquad (1)$$

(b) $pV^\gamma = $ constant. Substituting $V = \frac{\nu RT}{p}$, we obtain

$$T^\gamma \, p^{1-\gamma} = \text{constant}$$

Thus
$$\gamma T^{\gamma-1} \, p^{1-\gamma} \, dT + (1-\gamma) \, T^\gamma \, p^{-\gamma} \, dp = 0$$

$$\frac{dp}{p} = \frac{\gamma}{\gamma-1} \frac{dT}{T} \qquad (2)$$

(c) From (1) and (2)

$$\frac{dT}{dz} = \frac{(1-\gamma)}{\gamma R} \mu g \qquad (3)$$

For N_2, $\mu = 28$ and letting $\gamma = 1.4$, $\frac{dT}{dz} = -9.4$ degrees/kilometer.

(d) Integrating (1) with constant T we have
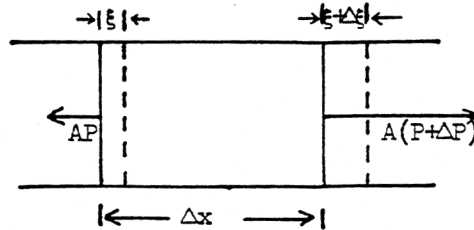
$$p = p_0 \exp\left[-\mu g z/RT\right]$$

(e) From (3) $T = T_0 - \frac{(\gamma-1)}{\gamma R} \mu g z$

Thus
$$\int_{p_0}^{p} \frac{dp'}{p'} = \int_0^z \frac{-\mu g \, dz'}{R\left(T_0 - \frac{(\gamma-1)}{\gamma} \frac{\mu g z'}{R}\right)}$$

$$p = p_0 \left(1 - \frac{(\gamma-1)}{\gamma R T_0} \mu g z\right)^{\gamma/\gamma-1}$$

5.8

Consider the element shown. Δx is its initial width. The wave disturbance causes the left face to move a distance ξ and the right a distance $\xi + \Delta\xi$. Let P_0 and ρ be the equilibrium pressure and density, and $p = P - P_0$ is the departure from the equilibrium pressure.

$$\kappa_S = -\frac{1}{V} \frac{\Delta V}{P-P_0} = -\frac{1}{A\Delta x} \frac{A\Delta\xi}{p}$$

or
$$p = -\frac{1}{\kappa_S} \frac{\partial \xi}{\partial x}$$

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where we have neglected the pressure difference Δp across the slab. The displacement is found from the equation of motion.

$$m \frac{\partial^2 \xi}{\partial t^2} = PA - (P+\Delta P)\, A = -\Delta PA$$

Since

$$\Delta P \approx \frac{\partial P}{\partial x} \Delta x \quad \text{and} \quad m = \rho \, A\Delta x$$

we have

$$\frac{\partial P}{\partial x} = \frac{\partial p}{\partial x} = -\rho \frac{\partial^2 \xi}{\partial t^2}$$

Then

$$\left(\frac{\partial}{\partial t}\right)^2 \frac{\partial \xi}{\partial x} = -\kappa_S \frac{\partial^2 p}{\partial t^2}$$

$$\left(\frac{\partial}{\partial x}\right) \frac{\partial^2 \xi}{\partial t^2} = -\frac{1}{\rho} \frac{\partial^2 p}{\partial x^2}$$

but since the order of differentiation is immaterial,

$$\frac{\partial^2 p}{\partial t^2} = \frac{1}{\kappa_S \rho} \frac{\partial^2 p}{\partial x^2}$$

5.9

(a) For an adiabatic process $pV^\gamma = $ const.

Hence $\dfrac{\partial V}{\partial p} = -\dfrac{V}{\gamma p}$ and $\kappa_S = -\dfrac{1}{V}\dfrac{\partial V}{\partial p} = \dfrac{1}{\gamma p}$.

(b)
$$u = \left(\rho \, \kappa_S\right)^{-\frac{1}{2}} = \left(\frac{\rho}{\gamma p}\right)^{-\frac{1}{2}}$$

Substituting $p = \dfrac{\nu RT}{V}$ and $\rho = \dfrac{\nu \mu}{V}$, we find

$$u = \left(\frac{\gamma RT}{\mu}\right)^{\frac{1}{2}}$$

(c)
$$u \propto T^{\frac{1}{2}}, \text{ independent of pressure}$$

(d)
$$u = 354 \text{ meters/ sec.}$$

5.10

Substituting the given values into the equation

$$c_p - c_V = \frac{VT^2 \alpha^2}{\kappa}$$

we find

$$c_V = 24.6 \text{ joules mole}^{-1}\text{deg}^{-1}, \qquad \gamma = 1.14$$

5.11

When the solid, of dimensions xyz, expands an increment dV, we have

$$V+dV = (x+dx)(y+dy)(z+dz)$$

To first order

$$V+dV = V + yz\,dx + xz\,dy + xy\,dz$$

$$\alpha = \frac{1}{V}\frac{dV}{dT} = \frac{1}{x}\frac{dx}{dT} + \frac{1}{y}\frac{dy}{dT} + \frac{1}{z}\frac{dz}{dT}$$

Therefore

$$\alpha = 3\alpha_L$$

5.12

For the adiabatic, quasistatic process

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp = 0$$

Using $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$ and the Maxwell relation $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$, we have

$$\left(\frac{\partial p}{\partial T}\right)_S = \frac{C_p}{\alpha V T} \qquad \text{where} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Thus

$$\Delta T = \frac{\alpha T}{\rho c_p}\,\Delta p \qquad \text{where} \quad c_p = \frac{C_p}{\rho V}$$

5.13

From the first law $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T\left(\frac{\partial}{\partial p}\right)_T \left(\frac{\partial s}{\partial T}\right)_p = T\left(\frac{\partial}{\partial T}\right)_p \left(\frac{\partial s}{\partial p}\right)_T$$

Substituting the Maxwell relation $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ and the definition $\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ we have

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial}{\partial T}\right)_p \alpha v = \alpha^2 vT - vT\frac{d\alpha}{dT}$$

5.14

(a)
$$TdS = dE - FdL \qquad\qquad (1)$$

(b) From (1) we may read off the Maxwell relation

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial F}{\partial T}\right)_L \qquad\qquad (2)$$

Since
$$F = aT^2(L-L_o) \qquad\qquad (3)$$

$$\left(\frac{\partial S}{\partial L}\right)_T = -2aT\,(L-L_o)$$

(c)
$$S(L_o,T) - S(L_o,T_o) = \int_{T_o}^{T}\frac{C_L}{T'}\,dT' = \int_{T_o}^{T}\frac{bT'}{T'}\,dT' = b(T-T_o)$$

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$$S(L,T) - S(L_o,T) = \int_{L_o}^{L} \left(\frac{\partial S}{\partial L}\right)_T dL = \int_{L_o}^{L} -2aT(L'-L_o)dL' = -aT(L-L_o)^2$$

Hence

$$S(L,T) = S(L_o,T_o) + b(T-T_o) - aT(L-L_o)^2$$

(d) In the quasistatic adiabatic process $\Delta S = 0$

$$S(T_o,L_o) + b(T_f-T_o) - aT_i(L_f-L_o)^2 = S(T_o,L_o) + b(T_i-T_o) - aT_f(L_f-L_o)^2$$

Hence

$$T_f = T_i \frac{b-a(L_i-L_o)^2}{b-a(L_f-L_o)^2}$$

Thus if $L_f > L_i$ we have $T_f > T_i$, i.e. the temperature increases.

(e) From the first law

$$C_L = T\left(\frac{\partial S}{\partial T}\right)_L$$

$$\left(\frac{\partial C_L}{\partial L}\right)_T = T\left(\frac{\partial}{\partial L}\right)_L \left(\frac{\partial S}{\partial T}\right)_L = T\left(\frac{\partial}{\partial T}\right)_L \left(\frac{\partial S}{\partial L}\right)_T$$

Substituting (2) and (3) we find

$$\left(\frac{\partial C_L}{\partial L}\right)_T = -2aT\ (L-L_o)$$

Hence

$$C_L(L,T) = C(L_o,T) + \int_{L_o}^{L} \left(\frac{\partial C_L}{\partial L}\right)_T dL = bT - aT(L-L_o)$$

(f)

$$S(L,T_o) - S(L_o,T_o) = \int_{L_o}^{L} \left(\frac{\partial S}{\partial L}\right)_T dL' = \int_{L_o}^{L} -2a\,T_o(L'-L_o)\ dL' = -aT_o(L-L_o)^2$$

$$S(L,T) - S(L,T_o) = \int_{T_o}^{T} \frac{C_L\,dT'}{T'} = \int_{T_o}^{T} \frac{bT' - aT'(L-L_o)^2}{T'}\ dT'$$

$$= b(T-T_o) - a(L-L_o)^2\ (T-T_o)$$

Thus

$$S(L,T) = S(T_o,L_o) + b(T-T_o) - aT(L-L_o)^2$$

5.15

(a)

$$đQ = TdS = dE - 2\sigma\ell\,dx \qquad\qquad (1)$$

(b) From (1)

$$dS = \frac{dE}{T} - \frac{2\sigma\ell}{T}\,dx$$

Hence

$$\left(\frac{\partial S}{\partial x}\right)_T dx + \left(\frac{\partial S}{\partial T}\right)_x dT = \frac{1}{T}\left(\frac{\partial E}{\partial x}\right)_T dx + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_x dT - \frac{2\sigma\ell}{T}\,dx$$

Equating coefficients, we have

$$\left(\frac{\partial E}{\partial x}\right)_T = T\left(\frac{\partial S}{\partial x}\right)_T + 2\sigma\ell$$

From (1), we can read off the Maxwell relation

$$\left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial(-2\sigma\ell)}{\partial T}\right)_x = -2\ell\,\frac{d\sigma}{dT}$$

Since $\sigma = \sigma_0 - \alpha T$,

$$\left(\frac{\partial S}{\partial x}\right)_T = 2\ell\alpha$$

$$\left(\frac{\partial E}{\partial x}\right)_T = 2\ell\alpha T + 2\ell\sigma_0 - 2\ell\alpha T = 2\ell\sigma_0$$

If the film is stretched at constant temperature

$$E(x) - E(o) = 2\ell\sigma_0\, x$$

(c)

$$W\,(0 \to x) = -\int F\,dx = -\int_0^x 2\sigma\ell\,dx' = -2\sigma\ell x$$

5.16

By the first law

$$dS = \frac{dE}{T} + \frac{zf\mathcal{Y}\,dv}{T} \qquad\qquad (1)$$

Hence

$$\left(\frac{\partial S}{\partial v}\right)_T dv + \left(\frac{\partial S}{\partial T}\right)_v dT = \frac{1}{T}\left(\frac{\partial E}{\partial v}\right)_T dv + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_v dT + \frac{zf\mathcal{Y}}{T}\,dv$$

Equating coefficients, we have

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial S}{\partial v}\right)_T - zf\mathcal{Y}$$

From (1), we may read off the Maxwell relation

$$\left(\frac{\partial S}{\partial v}\right)_T = zf\left(\frac{\partial \mathcal{Y}}{\partial T}\right)_v$$

Thus

$$\left(\frac{\partial E}{\partial v}\right)_T = zfT\left(\frac{\partial \mathcal{Y}}{\partial T}\right)_v - zf\mathcal{Y}$$

If one mole is produced

$$\Delta E = zfT\left(\frac{\partial \mathcal{Y}}{\partial T}\right)_v - zf\mathcal{Y}$$

5.17

By equation (5.8.12)

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Substituting $p = n\,kT\,[1 + B_2(T)\,n]$ we find

$$\left(\frac{\partial E}{\partial V}\right)_T = p + n^2 kT\,\frac{dB_2}{dT} - p = n^2 kT\,\frac{dB_2}{dT} > 0$$

5.18

(a)
$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

Since $\quad \left(\frac{\partial E}{\partial T}\right)_V = C_V$ and $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad$ from (5.8.12)

we have
$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{T\left(\frac{\partial p}{\partial T}\right)_V - p}{C_V}$$

(b) From the first law, $dE = TdS - pdV$. Hence
$$0 = T\left(\frac{\partial S}{\partial V}\right)_E - p \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}$$

(c) For a van der Waals gas
$$p = \frac{\nu RT}{V-\nu b} - \frac{\nu^2 a}{V^2}$$

Thus
$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{\nu^2 a}{C_V V^2}$$

$$T_2 - T_1 = \int_{V_1}^{V_2}\left(\frac{\partial T}{\partial V}\right)_E dV = \frac{a\nu^2}{C_V}\int_{V_1}^{V_2}\frac{dV}{V^2} = -\frac{a\nu^2}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

5.19

(a) From $\left(p + \frac{a}{v^2}\right)(v-b) = RT$ $\qquad\qquad\qquad\qquad$ (1)

we have
$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0$$

Solving, we find $a = \frac{9}{8} RT_c v_c$, $b = \frac{v_c}{3}$.

(b) Substituting a and b in (1) yields $p_c = \frac{3}{8}\frac{RT_c}{v_c}$.

(c)
$$\left(p' + \frac{3}{v'^2}\right)\left(v' - \frac{1}{3}\right) = \frac{8}{3} T'$$

5.20

To find the inversion curve, we must have
$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}\left(\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_p - 1\right) = 0$$

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or
$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v}{T}$$

From the van der Waals equation

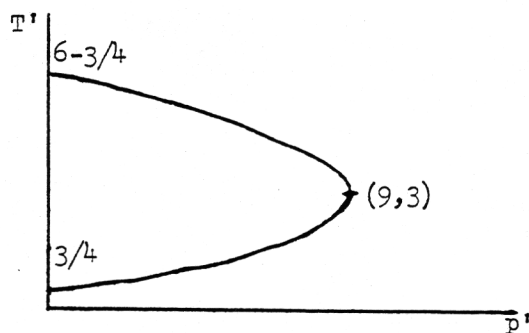$$dp = \frac{R\,dT}{v-b} + \left(-\frac{RT}{(v-b)^2} - \frac{2a}{v^3}\right)dv$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v-b}{T - \frac{2a}{Rv}\left(\frac{v-b}{v}\right)^2} = \frac{v}{T}$$

thus
$$\frac{2a}{RT}\left(\frac{v-b}{v}\right)^2 = b$$

On eliminating v and putting the equation in terms of the dimensionless variables of problem 5.19, it follows that

$$p' = 9 - 12\left(\sqrt{T'} - \sqrt{3}\right)^2$$

5.21

(a)
$$\mu = \frac{v}{C_p}\left[\frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p - 1\right] \tag{1}$$

We have

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial \vartheta}\right)_p \frac{d\vartheta}{dT} = \alpha'\frac{d\vartheta}{dT}, \qquad C_p = T\left(\frac{\partial S}{\partial \vartheta}\right)_p \frac{d\vartheta}{dT} = C_p'\frac{d\vartheta}{dT}$$

$$\mu = \left(\frac{\partial \vartheta}{\partial p}\right)_H \frac{dT}{d\vartheta} = \mu'\frac{dT}{d\vartheta}$$

Substituting these expressions into (1) we find

$$\mu' = \frac{v}{C_p'}\left(\alpha'T\frac{d\vartheta}{dT} - 1\right) \tag{2}$$
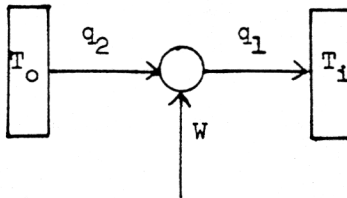
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(b) From (2)

$$\int_{T_o}^{T} \frac{dT}{T} = \int_{\vartheta_o}^{\vartheta} \frac{\alpha' d\vartheta'}{1 + \frac{\mu' C_p'}{V}}$$

$$T = T_o \exp\left[\int_{\vartheta_o}^{\vartheta} \frac{\alpha' d\vartheta}{1 + \frac{\mu' C_p'}{V}} \right]$$

5.22

The system may be represented by the diagram

(a) By the second law

$$\Delta S = \frac{q_1}{T} - \frac{q_2}{T} \geq 0$$

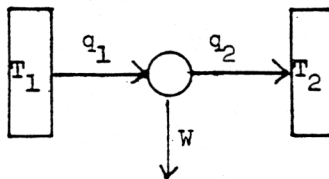For maximum heat, the equality holds and since $q_2 = q_1 - W$, it follows that

$$\frac{q_1}{W} = \frac{T_i}{T_i - T_o}$$

(b)

$$\frac{q_1}{W} = 11.9$$

5.23

We have the system

(a)

$$W = q_1 - q_2 = C(T_1 - T_f) + C(T_2 - T_f) = C(T_1 + T_2 - 2T_f) \qquad (1)$$

(b) By the second law, $\Delta S \geq 0$

Thus

$$\int_{T_1}^{T_f} \frac{CdT}{T} + \int_{T_2}^{T_f} \frac{CdT}{T} = C \ln \frac{T_f^2}{T_1 T_2} \geq 0$$

It follows that

$$T_f \geq \sqrt{T_1 T_2}$$

(c) The maximum amount of work will be obtained when $T_f = \sqrt{T_1 T_2}$.

From (1)

$$W = C(T_1 + T_2 - 2T_f) = C(\sqrt{T_1} - \sqrt{T_2})^2$$

30

5.24

To freeze an additional mass m of water at T_o, heat mL must be removed from the ice-water mixture resulting in an entropy change $\Delta S_1 = -\frac{mL}{T_o}$. The heat rejected to the body of heat capacity C increases its temperature to T_f with an entropy change $\Delta S_2 = C \int_{T_o}^{T_f} \frac{dT}{T} = C \ln \frac{T_f}{T_o}$. By the second law $\Delta S_1 + \Delta S_2 = -\frac{mL}{T_o} + C \ln \frac{T_f}{T_o} \geqq 0$. For minimum temperature increase and thus minimum heat rejection the equality holds and it follows that

$$T_f = T_o \, e^{mL/T_o C}$$

The heat rejected is $Q = C(T_f - T_o) = CT_o \left(e^{mL/T_o C} - 1 \right)$

5.25

The probability that the system occupies a state with energy E is proportional to the number of states at that energy, $\Omega(E)$. By the general definition of entropy, $S = k \ln \Omega(E)$, we have for the probability

$$P \propto \Omega(E) = e^{S/k} \qquad (1)$$

To raise the weight a height x, an amount of energy, mgx, in the form of heat, Q, must be given off by the water. The temperature change is found from

$$Q = C\Delta T = -mgx$$

$$\Delta T = -mgx/C$$

where C is the heat capacity of water. For a mole of liquid and x = 1 cm, ΔT is on the order of $10^{-4} \, ^\circ K$. Hence we may approximate the water as a heat reservoir and find for the entropy when the weight is at height x

$$S = S_o - \frac{Q}{T_o} = S_o - \frac{mgx}{T_o}$$

where S_o is the entropy at height x = 0. Thus (1) becomes

$$P(x) = A e^{-mgx/kT_o}$$

Here we have absorbed the term $e^{S_o/k}$ into the constant A which is found to be kT_o/mg by the usual normalization condition. Then the probability that the weight is raised to a height L or more is

$$\mathscr{P} = \int_L^\infty P(x)dx = \int_L^\infty \frac{kT_o}{mg} e^{-mgx/kT_o} \, dx = e^{-mgL/kT_o}$$

Substituting L = 1 cm and the given values yields

$$\mathscr{P} = e^{-10^{18}}$$

5.26

In the processes $a \to b$ and $c \to d$ no heat is absorbed, so by the first law $W = -\Delta E$, and since $\Delta E = C\Delta T$, where C is the heat capacity, we have

$$W_{a \to b} = -(E_b - E_a) = -\nu C_V (T_b - T_a)$$

$$W_{c \to d} = -(E_d - E_c) = -\nu C_V (T_d - T_c)$$

However, in an adiabatic expansion $TV^{\gamma-1} = $ const.

Hence

$$W_{a \to b} = -\nu C_V T_b \left(1 - \frac{T_a}{T_b}\right) = -\nu C_V T_b \left(1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\right)$$

$$W_{c \to d} = -\nu C_V T_c \left(\frac{T_d}{T_c} - 1\right) = \nu C_V T_c \left(1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\right)$$

The volume is constant in process $b \to c$ so no work is performed.

Thus

$$Q_1 = (E_c - E_b) = \nu C_V (T_c - T_b)$$

$$\eta = \frac{W_{a \to b} + W_{c \to d}}{Q_1} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

CHAPTER 6

Basic Methods and Results of Statistical Mechanics

6.1

(a) The probability that the system is in a state with energy E is proportional to the Boltzman factor $e^{-E/kT}$. Hence the ratio of the probability of being in the first excited state to the probability of being in the ground state is

$$\frac{e^{-3\hbar\omega/2kT}}{e^{-\hbar\omega/2kT}} = e^{-\hbar\omega/kT}$$

(b) By the definition of mean value

$$\bar{E} = \frac{\frac{1}{2}\hbar\omega e^{-\hbar\omega/kT} + \frac{3}{2}\hbar\omega e^{-3\hbar\omega/2kT}}{e^{-\hbar\omega/2kT} + e^{-3\hbar\omega/2kT}} = \frac{\hbar\omega}{2}\frac{1 + 3e^{-\hbar\omega/kT}}{1 + e^{-\hbar\omega/kT}}$$

6.2

The mean energy per particle is

$$\bar{e} = \frac{\mu H e^{-\mu H/kT} - \mu H e^{\mu H/kT}}{e^{-\mu H/kT} + e^{\mu H/kT}} = -\mu H \tanh\frac{\mu H}{kT}$$

Hence for N particles, $$E = -N\mu H \tanh\frac{\mu H}{kT}$$

6.3

(a) The probability that a spin is parallel to the field is

$$P = \frac{e^{\mu H/kT}}{e^{-\mu H/kT} + e^{\mu H/kT}} = \frac{1}{1 + e^{-2\mu H/kT}}$$

which yields
$$T = \frac{2\mu H}{k \ln[P/1-P]} \tag{1}$$

For $P = .75$ and $H = 30,000$ gauss, $T = 3.66\,^{\circ}K$

(b) From (1), with $\mu = 1.41 \times 10^{-23}$ ergs/gauss, $T = 5.57 \times 10^{-3}\,^{\circ}K$

6.4

The power absorbed is proportional to the difference in the number of nuclei in the two levels. This is,

$$n_+ - n_- = \frac{N\,e^{\mu H/kT}}{e^{\mu H/kT} + e^{-\mu H/kT}} - \frac{N\,e^{-\mu H/kT}}{e^{\mu H/kT} + e^{-\mu H/kT}}$$

where N is the total number of nuclei. Since $\mu H \ll kT$, we may expand the exponentials and keep only the first two terms.
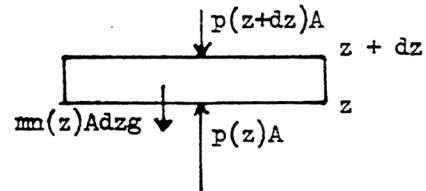
Hence,
$$n_+ - n_- \approx N\,\frac{(1 + \frac{\mu H}{kT} - 1 + \frac{\mu H}{kT})}{1 + \frac{\mu H}{kT} + 1 - \frac{\mu H}{kT}} = \frac{N\mu H}{kT}$$

Thus the absorbed power is proportional to T^{-1}.

6.5

The volume element of atmosphere shown must be in equilibrium under the forces of the pressure and gravity. Then if m is the mass per particle, A the area, and g the acceleration of gravity, we have

$$p(z+dz)\,A - p(z)A = \frac{dp}{dz}\,dz\,A = -\,mn(z)\,A\,dzg$$

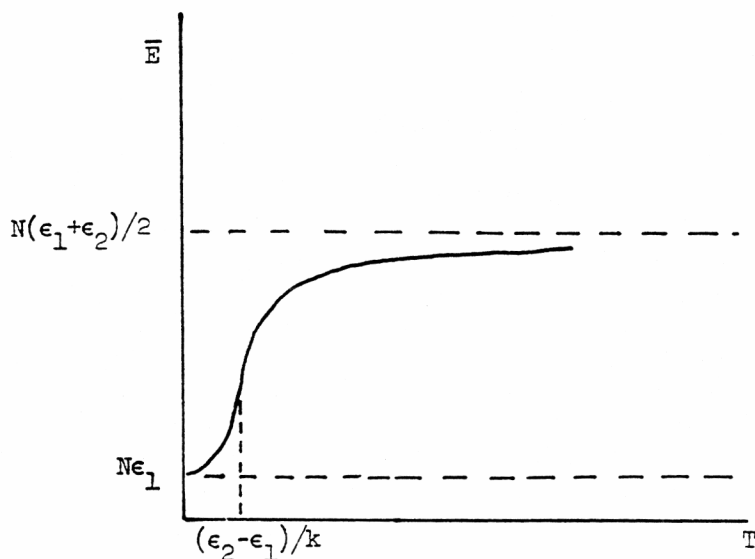Substituting the equation of state, $p = nkT$ leads to

$$\frac{dn(z)}{dz} = -\frac{mg}{kT}\,n(z)$$
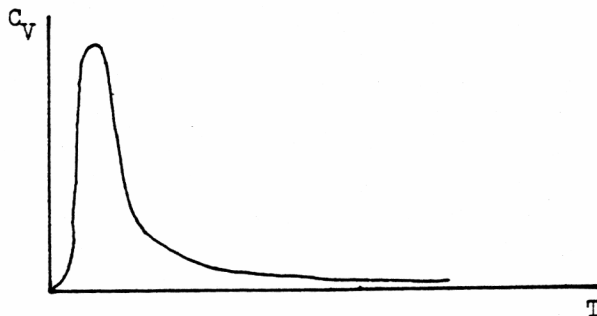
Thus
$$n(z) = n(0)e^{-mgz/kT}$$

6.6

(a)

As T approaches 0 the system tends to the low energy state, while in the limit of high temperatures all states become equally probable. The energy goes from the low to the high temperature limit when $\epsilon_2 - \epsilon_1 \approx kT$.

(b) The specific heat is, $C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V$, i.e., the slope of $\overline{E}$.

(c)

$$\overline{E} = N\left[\frac{\epsilon_1 e^{-\epsilon_1/kT} + \epsilon_2 e^{-\epsilon_2/kT}}{e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT}}\right] = N\left[\frac{\epsilon_1 + \epsilon_2 e^{-(\epsilon_2-\epsilon_1)/kT}}{1 + e^{-(\epsilon_2-\epsilon_1)/kT}}\right]$$

$$T \rightarrow 0, \quad \overline{E} \rightarrow N\epsilon_1, \quad \text{and} \quad T \rightarrow \infty, \quad \overline{E} \rightarrow N\left(\frac{\epsilon_1+\epsilon_2}{2}\right)$$

To find the temperature at which $\overline{E}$ changes from the low to the high temperature limit, we evaluate T where

$$\overline{E} = N\epsilon_1 + \frac{N}{2}\left[\frac{\epsilon_1+\epsilon_2}{2} - \epsilon_1\right] = N\left[\frac{\epsilon_1 + \epsilon_2 e^{-(\epsilon_2-\epsilon_1)/kT}}{1 + e^{-(\epsilon_2-\epsilon_1)/kT}}\right]$$

which yields

$$\frac{\epsilon_2-\epsilon_1}{kT} = \ln 3 \approx 1 \quad \text{or} \quad (\epsilon_2-\epsilon_1) \approx kT$$

The heat capacity is

$$C_V = \frac{\partial \overline{E}}{\partial T} = \frac{N(\epsilon_2 - \epsilon_1)^2 \, e^{-(\epsilon_2 - \epsilon_1)/kT}}{kT^2 \left[1 + e^{-(\epsilon_2 - \epsilon_1)/kT}\right]^2}$$

and $C_V \to 0$ as $T \to 0$, $T \to \infty$.

6.7

(a) The mean energy   per mole is

$$\overline{E} = N_A \, \frac{0 e^{-0/kT} + 2\epsilon e^{-\epsilon/kT}}{1 + 2e^{-\epsilon/kT}} = \frac{2 \, N_A \, \epsilon e^{-\epsilon/kT}}{1 + 2e^{-\epsilon/kT}} \qquad (1)$$

where N_A is Avogadro's number.

(b) We find the molar entropy from the partition function Z. Clearly, $Z = \zeta^{N_A}$ where $\zeta = \sum_i e^{-\epsilon_i/kT}$, the sum being over states of a single nucleus.

Thus
$$\zeta = 1 + e^{-\epsilon/kT} + e^{-\epsilon/kT}$$

and
$$S = k (\ln Z + \beta\overline{E}) = N_A k \ln (1 + 2e^{-\epsilon/kT}) + \frac{N_A \, \epsilon e^{-\epsilon/kT}}{T(1+2e^{-\epsilon/kT})} \qquad (2)$$

(c) As $T \to 0$, the nucleii go to the ground state, and by the general definition of entropy

$$S = N_A k \ln \Omega = N_A k \ln 1 = 0$$

as $T \to \infty$, all states become equally probable, $\Omega \to 3$ and

$$S = N_A k \ln 3$$

It is easily verified that expression (2) approaches these limits.

(d) From (1) we have

$$c = \frac{\partial \overline{E}}{\partial T} = \frac{2N_A \, \epsilon^2 e^{-\epsilon/kT}}{kT^2 (1+2e^{-\epsilon/kT})^2}$$

For large T, $e^{-\epsilon/kT} \approx 1$ and $c \propto T^{-2}$.

6.8

The polarization, $\underline{P}$, is defined as $N \, e\underline{\ell}$ where
N is the number of negative ions per unit volume,
e is the electronic charge, and $\underline{\ell}$ is the vector
from the negative to the positive ion. Then the

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mean x component of $\underline{P}$ is

$$P_x = |\underline{P}| \; \overline{\cos \theta} = Ne \, |\underline{\ell}| \, \frac{\overline{x}}{|\underline{\ell}|} = Ne \, \overline{x}$$

where x and θ are shown in the diagram. The positive ion can have energy $+\frac{e\epsilon a}{2}$ or $-\frac{e\epsilon a}{2}$, and since there are two lattice sites for each energy we have

$$P_x = Ne \; \frac{\left(\frac{a}{2}\right) e^{\frac{e\ell a}{2}\beta} + \left(-\frac{a}{2}\right) e^{-\frac{e\ell a}{2}\beta}}{e^{\frac{e\ell a}{2}\beta} + e^{-\frac{e\ell a}{2}\beta}} = \frac{Nea}{2} \tanh \frac{e\ell a}{2kT}$$

6.9

(a) The electric field is found from Gauss's Theorem

$$\int_\sigma \underline{E} \cdot \hat{\underline{n}} \, d\sigma = 4\pi q$$

where q is the enclosed charge and $\hat{\underline{n}}$ is the vector normal to the surface, σ.

By symmetry,
$$E\sigma = E \, 2\pi r \, L = 4\pi q$$

$$\underline{E}(\underline{r}) = \frac{2q}{rL} \, \hat{\underline{r}}$$

The electric potential is given by

$$U(r) = -\int_{r_o}^{r} \underline{E} \cdot d\underline{\ell} = -\frac{2q}{L} \ln \frac{r}{r_o}$$

Since $U(r) = -V$ at $r = R_o$, we can evaluate q.

Thus
$$\underline{E}(\underline{r}) = \frac{V}{r} \ln \frac{R}{r_o} \, \hat{\underline{r}} \; , \qquad U(\underline{r}) = -\frac{V}{\ln \frac{R}{r_o}} \ln \frac{r}{r_o}$$

(b) The energy of an electron at position $\underline{r}$ is $qU(\underline{r}) = -eU(r)$ where e is the electronic charge. Since the probability of being at $\underline{r}$ is proportional to the Boltzman factor, we have for the density

$$\rho(\underline{r}) = \rho(0) \exp\left[-\frac{eV\beta}{\ln(R_o/r_o)} \ln(r/r_o)\right] = \rho(0) \left(\frac{r}{r_o}\right)^{-eV/kT \, \ln(R/r_o)}$$

6.10

(a) The centrifugal force $m\omega^2 r$ yields the potential energy $-\frac{m\omega^2 r^2}{2}$. Since the probability that a molecule is at r is proportional to the Boltzmann factor, the density is

$$\rho(r) = \rho(0) \exp[m\omega^2 r^2/2kT] \qquad (1)$$

(b) Substituting $\mu = N_A m$, the molecular weight, into (1) and evaluating this expression at r_1 and r_2 we have

$$\mu = \frac{2N_A kT}{\omega^2(r_1^2 - r_2^2)} \ln \frac{\rho(r_1)}{\rho(r_2)}$$

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The mean separation, $\bar{x}$, is found from the probability that the separation is between x and x+dx,

$$P(x)dx \propto e^{-\frac{U(x)}{kT}} dx$$

Where

$$U(x) = U_o \left[\left(\frac{a}{x}\right)^{12} - 2\left(\frac{a}{x}\right)^6 \right]$$

It is easily verified that the minimum of the potential is at x = a. Since departures from this position are small, we may expand U(x) about a to obtain

$$U(x) \approx -U_o + \frac{36\, U_o}{a^2} (x-a)^2 - \frac{252\, U_o}{a^3} (x-a)^3$$

where we have kept only the first three terms. It follows that

$$P(x)dx = C \exp\left[-\frac{36\, U_o\, (x-a)^2}{a^2 kT} + \frac{252\, U_o (x-a)^3}{a^3 kT} \right] dx$$

We have absorbed the irrelevent constant term, $e^{-U_o/kT}$, into the normalization constant C. This constant is evaluated from the usual requirement

$$\int_\infty^\infty P(x)dx = C \int_0^\infty \exp\left[-\frac{36\, U_o\, (x-a)^2}{a^2\, kT} \right] \exp\left[\frac{252\, U_o (x-a)^3}{a^3 kT} \right] dx = 1$$

The predominent factor in the integrand is $\exp\left[-36\, U_o\, (x-a)^2/a^2 kT\right]$ so the second factor may be expanded in a Taylor's series as in Appendix A.6. Furthermore, the region of integration can be extended to $-\infty$ since the exponential is negligably small except near a.

Thus

$$1 = C \int_{-\infty}^\infty \exp\left[-\frac{36\, U_o (x-a)^2}{a^2 kT} \right] \left(1 + \frac{252\, U_o\, (x-a)^3}{a^3\, kT}\right) dx \qquad (1)$$

where we neglect all but the first two terms. The first integral is evaluated in Appendix A.4 while the second is 0 since the integrand is an odd function.

Then

$$C = \frac{6}{a} \left(\frac{U_o}{\pi\, kT}\right)^{\frac{1}{2}}$$

By definition, $\bar{x} = \int_{-\infty}^\infty x\, P(x)\, dx$, and to the same approximation as in (1) we have

$$\bar{x} = \int_{-\infty}^\infty x\, \frac{6}{a} \left(\frac{U_o}{\pi kT}\right)^{\frac{1}{2}} \exp\left[-\frac{36\, U_o}{a^2\, kT} (x-a)^2 \right] \left(1 + \frac{252\, U_o (x-a)^3}{a^3 kT}\right) dx$$

The first term in the integrand is a Gaussian times x and the integral is just a. The second may be evaluated by making the substitution $\xi = x-a$

$$\bar{x} = a + \frac{6}{a}\left(\frac{U_o}{\pi kT}\right)^{\frac{1}{2}} \frac{252\, U_o}{a^3 kT} \left[\int_{-\infty}^{\infty} \xi^4 \exp\left[-\left(\frac{36\, U_o}{kT\, a^2}\right)\xi^2\right] d\xi + \int_{-\infty}^{\infty} a\xi^3 \exp\left[-\left(\frac{36\, U_o}{kT}\right)\xi^2\right] d\xi\right]$$

Noting that the second integral is 0 since the integrand is an odd function, and evaluating the first by Appendix A.4, we find

$$\bar{x} = a\left(1 + \frac{.15\, kT}{U_o}\right)$$

Thus $\qquad\qquad\qquad \alpha = \frac{1}{\bar{x}} \frac{d\bar{x}}{dT} = \frac{.15\, ak}{aU_o + (.15)akT} \approx \frac{.15k}{U_o} \qquad$ since $U_o \gg kT$

6.12

(a) Let the dimensions of the box be x, y, z. Then the volume and area are

$$V = xyz \qquad\qquad\qquad\qquad A = xy + 2yz + 2xz \qquad\qquad (1)$$

Eliminating x, we have

$$V = yz\, \frac{A - 2yz}{y + 2z}$$

From the conditions for an extremum, $\frac{\partial V}{\partial y} = \frac{\partial V}{\partial z} = 0$, it follows that

$$(A-2yz)(y+2z) - 2yz(y+2z) - y(A-2yz) = 0$$
$$(A-2yz)(y+2z) - 2yz(y+2z) - 2z(A-2yz) = 0 \qquad\qquad (2)$$

Subtracting these equations yields $y = 2z$. Then substitution in (2) gives $y = \dfrac{A^{\frac{1}{2}}}{\sqrt{3}}$, $z = \dfrac{A^{\frac{1}{2}}}{2\sqrt{3}}$, and from (1) we find $x = \dfrac{A^{\frac{1}{2}}}{\sqrt{3}}$.

(b) From equation (1), we have

$$dV = yz\, dx + xz\, dy + xy\, dz \qquad\qquad (3)$$

The equation of constraint is

$$g(x,y,z) = xy + 2yz + 2xz - A = 0 \qquad\qquad (4)$$

and $\qquad\qquad \lambda dg = \lambda(y+2z)\, dx + \lambda(x+2z)\, dy + \lambda(2x + 2y)\, dz = 0 \qquad\qquad (5)$

Adding (3) and (4) and noting that the differentials are now independent, we have

$$yz + \lambda(y+2z) = 0$$
$$xz + \lambda(x+2z) = 0 \qquad\qquad (6)$$
$$xy + \lambda(2x+2y) = 0$$

We multiply the first equation by x, the second by y, and the third by z, and add.

$$3xyz + \lambda(2xy + 4xz + 4yz) = 0$$

Substituting (4) yields

$$\lambda = -\frac{3xyz}{2A}$$

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and substituting λ into equations (6) gives

$$1 - \frac{3x}{2A}(y + 2z) = 0$$

$$1 - \frac{3y}{2A}(x + 2z) = 0$$

$$1 - \frac{3z}{2A}(2x + 2y) = 0$$

The first two equations show that $x = y$ and the third yields $x = \frac{A}{6x}$. Then substitution in the first and second equations gives $x = \frac{A^{1/2}}{\sqrt{3}}$, $y = \frac{A^{1/2}}{\sqrt{3}}$, $z = \frac{A^{1/2}}{2\sqrt{3}}$

6.13

$$S_1 + S_2 = -k \sum_r P_r^{(1)} \ln P_r^{(1)} - k \sum_s P_s^{(2)} \ln P_s^{(2)}$$

But since $\sum_r P_r^{(1)} = \sum_s P_s^{(2)} = 1$, we may write

$$S_1 + S_2 = -k \sum_r \sum_s P_r^{(1)} P_s^{(2)} \ln P_r^{(1)} - k \sum_s \sum_r P_s^{(2)} P_r^{(1)} \ln P_s^{(2)}$$

$$= -k \sum_r \sum_s P_r^{(1)} P_s^{(2)} \left[\ln P_r^{(1)} + \ln P_s^{(2)} \right]$$

$$= -k \sum_r \sum_s P_r^{(1)} P_s^{(2)} \ln P_r^{(1)} P_s^{(2)}$$

$$= -k \sum_r \sum_s P_{rs} \ln P_{rs} \qquad \text{since } P_r^{(1)} P_s^{(2)} = P_{rs}$$

6.14

From the definition, we have

$$S_1 + S_2 = -k \sum_r P_r^{(1)} \ln P_r^{(1)} - k \sum_s P_s^{(1)} \ln P_s^{(1)} \qquad (1)$$

Substituting $P_r^{(1)} = \sum_s P_{rs}$ and $P_s^{(2)} = \sum_r P_{rs}$ in (1) we have

$$S_1 + S_2 = -k \sum_r \sum_s P_{rs} \ln P_r^{(1)} - k \sum_r \sum_s P_{rs} \ln P_s^{(2)}$$

$$= -k \sum_r \sum_s P_{rs} \ln P_r^{(1)} P_s^{(2)} \qquad (2)$$

For the total system, the entropy is

$$S = -k \sum_r \sum_s P_{rs} \ln P_{rs} \qquad (3)$$

Then from (2) and (3)

$$S - (S_1 + S_2) = -k \sum_r \sum_s P_{rs} \ln P_{rs} + k \sum_r \sum_s P_{rs} \ln P_r^{(1)} P_s^{(2)}$$

$$= -k \sum_r \sum_s P_{rs} \ln \frac{P_{rs}}{P_r^{(1)} P_s^{(2)}} \qquad (4)$$

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(b) Since $-\ln x \geq -x + 1$ or $\ln x \leq x-1$, we have

$$\frac{\ln P_r^{(1)}P_s^{(2)}}{P_{rs}} \leq \frac{P_r^{(1)}P_s^{(2)}}{P_{rs}} - 1$$

From (4),
$$S-(S_1+S_2) = k \sum_r \sum_s P_{rs} \ln \frac{P_r^{(1)}P_s^{(2)}}{P_{rs}} \leq k \sum_r \sum_s P_{rs} \left(\frac{P_r^{(1)}P_s^{(2)}}{P_{rs}} - 1 \right)$$

But since $\sum_r \sum_s P_r^{(1)}P_s^{(2)} = 1$, it follows that

$$S-(S_1+S_2) \leq k \sum_r \sum_s P_r^{(1)}P_s^{(2)} - 1 = 0$$

Thus $S \leq S_1 + S_2$.

6.15

(a) Since $S = -k \sum_r P_r \ln P_r$ and $S_o = -k \sum_r P_r^{(0)} \ln P_r^{(0)}$, we have

$$S-S_o = k \sum_r \left[- P_r \ln P_r + P_r \ln P_r^{(0)} - P_r \ln P_r^{(0)} + P_r^{(0)} \ln P_r^{(0)} \right] \quad (1)$$

where we have added and subtracted the term $k \sum_r P_r \ln P_r^{(0)}$. We show that the sum of the last two terms in (1) is zero.

Since
$$P_r^{(0)} = e^{-\beta E_r}/Z$$

$$\ln P_r^{(0)} = -\beta E_r - \ln Z$$

Then using $\sum_r P_r = 1$, we have

$$-\sum_r P_r \ln P_r^{(0)} = \beta \sum_r P_r E_r + \sum_r P_r \ln Z = \beta \overline{E} + \ln Z$$

Similarly
$$\sum_r P_r^{(0)} \ln P_r^{(0)} = -\beta \sum_r P_r^{(0)} E_r - \sum_r P_r^{(0)} \ln Z = -\beta \overline{E} - \ln Z$$

Adding, we obtain

$$-\sum_r P_r \ln P_r^{(0)} + \sum_r P_r^{(0)} \ln P_r^{(0)} = 0$$

Thus (1) becomes

$$S-S_o = k \sum_r \left[-P_r \ln P_r + P_r \ln P_r^{(0)} \right] = k \sum_r P_r \ln \frac{P_r^{(0)}}{P_r} \quad (2)$$

(b) Since $\ln \frac{P_r^{(0)}}{P_r} \leq \frac{P_r^{(0)}}{P_r} - 1$, equation (2) yields

$$S-S_o \leq k \sum_r P_r \left[\frac{P_r^{(0)}}{P_r} - 1 \right] = k \sum_r \left[P_r^{(0)} - P_r \right] = 0$$

Consequently $S_o \geq S$.

Simple Applications of Statistical Mechanics

7.1

(a) We label the positions and momenta such that $\underline{r}_{ij}$ and $\underline{p}_{ij}$ refer to the jth molecule of type i. There are N_i molecules of species i. Then the classical partition function for the mixture of ideal gases is

$$Z' = \int \exp\left[-\frac{\beta}{2m_1}(\underline{p}_{11}^2 + \ldots + \underline{p}_{1N_1}^2) \ldots - \frac{\beta}{2m_k}(\underline{p}_{k1}^2 + \ldots + \underline{p}_{kN_k}^2)\right] \frac{d^3\underline{r}_{11} \ldots d^3\underline{r}_{kN_k} d^3\underline{p}_{11} \ldots d^3\underline{p}_{kN_k}}{h_o^{3N_1} \ldots h_o^{3N_k}}$$

The integrations over $\underline{r}$ yield the volume, V, while the $\underline{p}$ integrals are identical. Since there are $N_1 + N_2 + \ldots N_k$ integrations, we have

$$Z' = V^{(N_1 + \ldots + N_k)}\left[\int e^{-\frac{\beta p^2}{2m}} \frac{d^3\underline{p}}{h_o^3}\right]^{(N_1 + \ldots + N_k)}$$

The term in brackets is independent of volume, consequently

$$\ln Z' = (N_1 + \ldots + N_k) \ln V + \ln \text{(constant)}$$

and

$$\overline{p} = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z' = (N_1 + \ldots + N_k)\frac{1}{\beta V}$$

$$\overline{p}V = (N_1 + \ldots + N_k)kT = (\nu_1 + \ldots + \nu_k) RT \tag{1}$$

(b) For the ith gas, $p_i V = \nu_i RT$, hence by (1)

$$\overline{p} = \sum_i \overline{p}_i$$

7.2

(a) By the equipartition theorem the average value of the kinetic energy of a particle is $\overline{\epsilon} = \frac{3}{2} kT$.

(b) The average potential energy is

$$\overline{u} = \frac{\int_o^L mgz\, e^{-\beta mgz}\, dz}{\int_o^L e^{-\beta mgz}\, dz}$$

Then

$$\overline{u} = -\frac{\partial}{\partial\beta} \ln \int_0^L e^{-mgz\beta}\, dz = -\frac{\partial}{\partial\beta} \ln \frac{e^{-mgL\beta} - 1}{-mg\beta}$$

On carrying out the differentiation, we find

$$\overline{u} = kT + \frac{mgL}{1 - e^{mgL/kT}}$$

7.3

(a) Before the partition is removed, we have on the left, $pV = \nu RT$. After removal the pressure is

$$p_f = \frac{2\nu\,RT}{(1+b)V} = \frac{2p}{1+b}$$

(b) The initial and final entropies of the system for different gases are

$$S_i = \nu R\left[\ln\frac{V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_1\right] + \nu R\left[\ln\frac{bV}{N_A\nu} + \frac{3}{2}\ln T + \sigma_2\right]$$

$$S_f = \nu R\left[\ln\frac{(1+b)V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_1\right] + \nu R\left[\ln\frac{(1+b)V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_2\right]$$

Here one adds the entropies of the gases in the left and right compartments for S_i while S_f is the entropy of two different gases in volume $(1+b)V$.

Then
$$\Delta S = S_f - S_i = \nu R\left[2\ln\frac{V(1+b)}{N_A\nu} - \ln\frac{V}{N_A\nu} - \ln\frac{bV}{N_A\nu}\right] = \nu R\ln\frac{(1+b)^2}{b}$$

(c) In the case of identical gases, S_i is again the sum of the entropies of the left and right compartments. S_f is the entropy of 2ν moles in a volume $(1+b)V$.

$$S_i = \nu R\left[\ln\frac{V}{N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right] + \nu R\left[\ln\frac{bV}{N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right]$$

$$S_f = 2\nu R\left[\ln\frac{(1+b)V}{2N_A\nu} + \frac{3}{2}\ln T + \sigma_0\right]$$

Thus
$$\Delta S = \nu R\left[\ln\frac{(1+b)V}{2N_A\nu} - \ln\frac{V}{N_A\nu} - \ln\frac{bV}{N_A\nu}\right] = \nu R\ln\frac{(1+b)^2}{4b}$$

7.4

(a) The system is isolated so its total energy is constant, and since the energy of an ideal gas depends only on temperature, we have

$$\Delta E_1 + \Delta E_2 = C_V(T_f - T_1) + C_V(T_f - T_2) = 0$$

or
$$T_f = \frac{T_1 + T_2}{2}$$

The total volume is found from the equation of state

$$V = \frac{\nu_1 RT_1}{p_1} + \frac{\nu_2 RT_2}{p_2}$$

Thus the final pressure is
$$p_f = \frac{(\nu_1+\nu_2)\,RT_f}{V} = \frac{(\nu_1+\nu_2)}{2}\left(\frac{T_1 + T_2}{(\nu_1 T_1/p_1)+(\nu_2 T_2/p_2)}\right)$$

(b) Using $\frac{V}{N} = \frac{kT}{p}$, we have for the initial and final entropies of different gases

$$S_i = \nu_1 R \left[\ln \frac{kT_1}{p_1} + \frac{3}{2} \ln T_1 + \sigma_1 \right] + \nu_2 R \left[\ln \frac{kT_2}{p_2} + \ln T_2 + \sigma_2 \right]$$

$$S_f = \nu_1 R \left[\ln \frac{k}{\nu_1} \left(\frac{\nu_1 T_1}{p_1} + \frac{\nu_2 T_2}{p_2} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2} + \sigma_1 \right] + \nu_2 R \left[\ln \frac{k}{\nu_2} \left(\frac{\nu_1 T_1}{p_1} + \frac{\nu_2 T_2}{p_2} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2} + \sigma_2 \right]$$

Thus $\Delta S = S_f - S_i = \nu_1 R \left[\ln \left(1 + \frac{\nu_2 T_2 p_1}{\nu_1 T_1 p_2} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2 T_1} \right] + \nu_2 R \left[\ln \left(1 + \frac{\nu_1 T_1 p_2}{\nu_2 T_2 p_1} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2 T_2} \right]$

(c) For identical gases

$$S_i = \nu_1 R \left[\ln \frac{kT_1}{p_1} + \frac{3}{2} \ln T_1 + \sigma_o \right] + \nu_2 R \left[\ln \frac{kT_2}{p_2} + \frac{3}{2} \ln T_2 + \sigma_o \right]$$

$$S_f = (\nu_1 + \nu_2) R \left[\ln \frac{k}{(\nu_1 + \nu_2)} \left(\frac{\nu_1 T_1}{p_1} + \frac{\nu_2 T_2}{p_2} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2} + \sigma_o \right]$$

$$\Delta S = \nu_1 R \left[\ln \frac{1}{(\nu_1 + \nu_2)} \left(\nu_1 + \frac{\nu_2 T_2 p_1}{T_1 p_2} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2 T_1} \right] + \nu_2 R \left[\ln \frac{1}{(\nu_1 + \nu_2)} \left(\nu_2 + \frac{\nu_1 T_1 p_2}{T_2 p_1} \right) + \frac{3}{2} \ln \frac{T_1 + T_2}{2 T_2} \right]$$

7.5

We take the zero of potential energy so that if a segment is oriented parallel to the vertical it contributes energy Wa and if antiparallel it contributes -Wa to the total energy of the rubber band (Thus if the rubber band were fully extended, the total energy would be -NWa). Since the segments are non-interacting,

$$\bar{\ell} = N \frac{a e^{-Wa\beta} - a e^{Wa\beta}}{e^{-Wa\beta} + e^{Wa\beta}} = Na \tanh \frac{Wa}{kT}$$

7.6

Since the total energy is additive,

$$E_i = \epsilon_i(p_i) + U(q_1 \ldots q_n) = \frac{p^2}{2m} + U(q_1 \ldots q_n)$$

where U is the energy of interaction, the equipartition theorem still applies and

$$\bar{\epsilon} = \frac{3}{2} kT$$

7.7

If the gas is ideal, its mean energy per particle is

$$\bar{\epsilon} = \frac{\overline{p_x^2}}{2m} + \frac{\overline{p_y^2}}{2m} = kT$$

and the mean energy per mole becomes $\bar{E} = N_A kT$

Thus $$C = \frac{\partial \bar{E}}{\partial T} = N_A k = R$$

7.8

For classical harmonic motion the mean energy is

$$\overline{E} = \frac{\overline{p^2}}{2m} + \frac{1}{2} m\omega^2 \overline{x^2}$$

By equipartition, each of these terms contributes $\frac{1}{2} kT$.

Hence

$$\rho \propto \overline{x^2} \propto T$$

7.9
(a)
The mean elongation is found by equating the gravitational and restoring forces

$$\alpha \overline{x} = Mg, \quad \text{thus} \quad \overline{x} = \frac{Mg}{\alpha}$$

(b) By the equipartition theorem

$$\frac{1}{2} \alpha \overline{(x-\overline{x})^2} = \frac{1}{2} kT$$

or

$$\overline{(x-\overline{x})^2} = \frac{kT}{\alpha}$$

(c)

$$\left[\overline{(x-\overline{x})^2} \right]^{\frac{1}{2}} = \overline{x}$$

$$\left(\frac{kT}{\alpha} \right)^{\frac{1}{2}} = \frac{Mg}{\alpha} \quad \text{or} \quad M = \sqrt{\frac{kT \, \alpha}{g^2}}$$

7.10

(a) Let the restoring force be $-\alpha x$. Then the mean energy of N particles is

$$\overline{E} = N \left(\frac{1}{2} m\overline{\dot{x}^2} + \frac{1}{2} \alpha \overline{x^2} \right)$$

By equipartition

$$\overline{E} = N \left(\frac{1}{2} kT + \frac{1}{2} kT \right) = N \, kT$$

Thus

$$c = \frac{\partial \overline{E}}{\partial T} = Nk$$

(b) If the restoring force is $-\alpha x^3$, the mean energy per particle is

$$\overline{\epsilon} = \frac{1}{2} m\overline{\dot{x}^2} + \frac{1}{4} \alpha \overline{x^4}$$

The kinetic energy term contributes $\frac{1}{2} kT$ by equipartition. The mean of the potential energy is found from

$$\overline{\frac{\alpha x^4}{4}} = \frac{\int_{-\infty}^{\infty} \exp\left[-\frac{\beta \alpha x^4}{4} \right] \frac{\alpha x^4}{4} \, dx}{\int_{-\infty}^{\infty} \exp\left[-\frac{\beta \alpha x^4}{4} \right] dx}$$

$$\overline{\frac{\alpha x^4}{4}} = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\beta(\alpha x^4/4)} dx = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\alpha y^4/4} \beta^{-1/4} dy$$

where we have made the substitution, $y = \beta^{1/4} x$.

Thus
$$\overline{\frac{\alpha x^4}{4}} = -\frac{\partial}{\partial \beta} \left(-\frac{1}{4} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-\alpha y^4/4} dy \right) = \frac{1}{4\beta} = \frac{1}{4} kT$$

Hence
$$\overline{\epsilon} = \frac{1}{2} m \overline{\dot{x}^2} + \frac{1}{4} \overline{\alpha x^4} = \frac{1}{2} kT + \frac{1}{4} kT = \frac{3}{4} kT$$

Then the total energy is $\overline{E} = N\overline{\epsilon}$ and

$$C = \frac{\partial \overline{E}}{\partial T} = \frac{3}{4} Nk$$

7.11

Since the probability of excitation is proportional to $e^{-\frac{n\hbar\omega}{kT}}$ where n is an integer, it is

clear that the two parallel components are negligibly excited at 300° where $\hbar\omega_\parallel \gg 300\,k$.

The perpendicular component is excited since $\hbar\omega_\perp \ll 300\,k$; and since 300° is in the classical

region, the equipartition theorem holds and we have for the mean energy per mole

$$\overline{E} = N_A \left(\frac{1}{2} m\overline{\dot{x}^2} + \frac{1}{2} m\omega_\perp^2 \overline{x^2} \right) = N_A kT$$

Thus
$$C = \frac{\partial \overline{E}}{\partial T} = N_A k = R$$

7.12

(a) Consider a cube of side a. The force necessary to decrease the length of a side by Δa is

$\kappa_o \Delta a$ and therefore the pressure is $\Delta p = \kappa_o \Delta a/a^2$. The change in volume is $\Delta V = -a^2 \Delta a$.

Hence
$$\kappa = -\frac{1}{V}\left(\frac{\Delta V}{\Delta p}\right) = -\frac{1}{a^3}\left(-\frac{a^2 \Delta a}{\kappa_o \Delta a/a^2}\right) = \frac{a}{\kappa_o} \qquad (1)$$

(b) The Einstein temperature is $\theta_E = \hbar\omega/k$. Since $\omega = \sqrt{\kappa_o/m}$ where m is mass, we have from (1)

$$\theta_E = \frac{\hbar}{k}\sqrt{\frac{\kappa_o}{m}} = \frac{\hbar}{k}\sqrt{\frac{a}{m\kappa}} \qquad (2)$$

The length a is found by considering that the volume per atom is $\mu/\rho N_A$ where μ is the atomic

weight, ρ the density, and N_A is Avogadro's number.

Thus
$$a = \left(\frac{\mu}{\rho N_A}\right)^{1/3} = \left(\frac{63.5}{(8.9)(6\times10^{23})}\right)^{1/3} = 2.3 \times 10^{-8} \text{ cm}$$

Substitution of $m = \mu/N_A$ and the given values yields

$$\theta_E \approx 150^\circ K$$

7.13

We have $\bar{M}_Z = N_o g \mu_o J B_J(\eta)$. By equation 7.8.14, $B_J(\eta)$ for $J = \frac{1}{2}$ becomes

$$B_{\frac{1}{2}}(\eta) = 2\left(\coth \eta - \frac{1}{2}\coth \frac{\eta}{2}\right) = 2\,\frac{\cosh \eta}{\sinh \eta} - \frac{\cosh(\eta/2)}{\sinh(\eta/2)}$$

$$= 2\,\frac{\cosh^2(\eta/2) + \sinh^2(\eta/2)}{2\sinh(\eta/2)\cosh(\eta/2)} - \frac{\cosh(\eta/2)}{\sinh(\eta/2)}$$

$$= \frac{\sinh^2(\eta/2)}{\sinh(\eta/2)\cosh(\eta/2)} = \frac{\sinh(\eta/2)}{\cosh(\eta/2)} = \tanh(\eta/2)$$

Thus
$$M_Z = \frac{N_o g \mu_o}{2}\tanh\frac{g\mu_o H}{2kT}$$

7.14

The energy of the magnetic moment in the field H is

$$E = -\underline{\mu}\cdot\underline{H} = -\mu H \cos\theta$$

where θ is the angle between the magnetic moment and the direction of the field or z-axis. Then the probability that the magnetic moment lies in the range θ to $\theta + d\theta$ is proportional to the Boltzmann factor and the solid angle $2\pi \sin\theta\, d\theta$.

Thus
$$P(\theta)d\theta \propto e^{\beta\mu H \cos\theta}\sin\theta\, d\theta$$

and
$$\bar{M}_Z = N_o\bar{\mu}_Z = \frac{N_o\displaystyle\int_o^\pi e^{\beta\mu H\cos\theta}\sin\theta\, d\theta(\mu\cos\theta)}{\displaystyle\int_o^\pi e^{\beta\mu H\cos\theta}\sin\theta\, d\theta}$$

or
$$\bar{M}_Z = \frac{N_o}{H}\frac{\partial}{\partial\beta}\ln\int_o^\pi e^{\beta\mu H\cos\theta}\sin\theta\, d\theta = \frac{N_o}{H}\frac{\partial}{\partial\beta}\ln\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{\beta\mu H}$$

$$= \frac{N_o}{H}\frac{\partial}{\partial\beta}\ln\frac{2\sinh\beta\mu H}{\beta\mu H} = \frac{N_o}{H\beta\sinh\beta\mu H}\left[\mu H\beta\cosh\beta\mu H - \sinh\beta\mu H\right]$$

$$\bar{M}_Z = N_o\mu\left[\coth\beta\mu H - \frac{1}{\beta\mu H}\right]$$

7.15

We have
$$\bar{M}_Z = N_o g \mu_o J B_J(\eta) \qquad (1)$$

$\quad\quad\quad B_J(\eta) = \frac{1}{J}\left[(J + \frac{1}{2})\ \text{coth}\ (J + \frac{1}{2})\eta - \frac{1}{2}\ \text{coth}\ \frac{1}{2}\ \eta \right]$

If $\eta \ll 1$ and $J \gg 1$ in such a way that $J\eta \gg 1$, $B_J(\eta)$ becomes

$$B_J(\eta) = \frac{1}{J}\ \left[J\ \text{coth}\ J\eta - \frac{1}{2}\ (\frac{2}{\eta}) \right]\ = \text{coth}\ J\eta - \frac{1}{J\eta}$$

where we have used

$$\text{coth}\ x = \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{(1 + x + ...) + (1 - x + ...)}{(1 + x + ...) - (1 - x + ...)} \approx \frac{1}{x}\ \text{for small x}$$

Let $\mu H\beta = J\eta = Jg\mu_o H\beta$ where $\mu = g\mu_o J$ is by (7.8.2) the classical magnetic moment. Then (1)

becomes $\quad\quad\quad\quad\quad \bar{M}_Z = N_o\mu\ \left[\text{coth}\ \beta\mu H - \frac{1}{\beta\mu H} \right]$

7.16

(a) The energy of a magnetic moment in a field is $E = -\underline{\mu} \cdot \underline{H}$. For spin $\frac{1}{2}$ atoms

$$\frac{n_+(Z_2)}{n_+(Z_1)}\ = \frac{e^{\mu H_2\beta}}{e^{\mu H_1\beta}} = \exp\left[\frac{\mu}{kT}\ (H_2 - H_1) \right]$$

(b) $\quad\quad\quad\quad\quad \frac{n(Z_2)}{n(Z_1)} = \frac{e^{\mu H_2\beta} + e^{-\mu H_2\beta}}{e^{\mu H_1\beta} + e^{-\mu H_1\beta}}$

$n(Z_2)/n(Z_1) > 1$ since $H_2 > H_1$.

(c) If $\mu H \ll kT$ we have

$$\frac{n_+(Z_2)}{n_-(Z_1)} \approx\ 1 + \frac{\mu}{kT}\ (H_2 - H_1)$$

and $\quad\quad \frac{n(Z_2)}{n(Z_1)} \approx \frac{(1 + \mu H_2\beta + \frac{1}{2}\mu^2 H_2^2\beta^2) + (1 - \mu H_2\beta + \frac{1}{2}\mu^2 H_2^2\beta^2)}{(1 + \mu H_1\beta + \frac{1}{2}\mu^2 H_1^2\beta^2) + (1 - \mu H_1\beta + \frac{1}{2}\mu^2 H_1^2\beta^2)}$

$$\approx \frac{2 + \mu^2 H_2^2\beta^2}{2 + \mu^2 H_1^2\beta^2}\ \approx\ \left[1 + \frac{1}{2}\ (\frac{\mu H_2}{kT})^2 \right] \left[1 - \frac{1}{2}\ (\frac{\mu H_1}{kT})^2 \right]$$

$$\frac{n(Z_2)}{n(Z_1)}\ \approx\ 1 + \frac{1}{2}\ (\frac{\mu}{kT})^2\ (H_2^2 - H_1^2)$$

7.17

To find the fraction, ξ, of molecules with x component of velocity between $-\tilde{v}$ and $\tilde{v}$, we must

integrate the distribution between these limits, i.e.,

$$\xi = \frac{1}{n} \int_{-\widetilde{v}}^{\widetilde{v}} g(v_x) dv_x = \int_{-\sqrt{\frac{2kT}{m}}}^{\sqrt{\frac{2kT}{m}}} \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-(mv_x^2/2kT)} dv_x$$

Making the change of variable, $y = \sqrt{\frac{m}{kT}} \, v_x$, we have,

$$\xi = \frac{1}{\sqrt{2\pi}} \int_{-\sqrt{2}}^{\sqrt{2}} e^{-(y^2/2)} dy = \frac{2}{\sqrt{2\pi}} \int_0^2 e^{-(y^2/2)} = 2 \, \text{erf} \, \sqrt{2}$$

Then from tables $\xi = .843$.

7.18

In problem 5.9 we found that the velocity of sound is

$$u = \left(\frac{\gamma RT}{\mu}\right)^{\frac{1}{2}}$$

where $\gamma = C_p/C_v$ and μ is the atomic weight. Since $\mu = N_A m$, we have

$$u = \left(\frac{\gamma RT}{N_A m}\right)^{\frac{1}{2}} = \left(\frac{\gamma kT}{m}\right)^{\frac{1}{2}}$$

The most probable speed is $\widetilde{v} = (2kT/m)^{\frac{1}{2}}$. Thus

$$u = \left(\frac{\gamma}{2}\right)^{\frac{1}{2}} \widetilde{v}$$

For helium, $\gamma = 1.66$ so that $u = .91 \, \widetilde{v}$, and the fraction of molecules with speeds less than u is

$$\xi = \frac{1}{n} \int_0^{.91\widetilde{v}} F(v) dv = 4\pi \int_0^{.91(2kT/m)^{\frac{1}{2}}} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv$$

Making the change of variable $y = (m/kT)^{\frac{1}{2}} v$, we have

$$\xi = \frac{4\pi}{(2\pi)^{\frac{3}{2}}} \int_0^{.91\sqrt{2}} y^2 e^{-y^2/2} dy$$

This integral may be evaluated by noticing that integration by parts of $\int_0^a e^{-y^2/2} dy$ yields

$$\int_0^a e^{-y^2/2} dy = ye^{-y^2/2} \Big|_0^a + \int_0^a y^2 e^{-y^2/2} dy$$

Since the integral on the right is the required one, we have,

$$\xi = 4\pi^{-\frac{1}{2}}(2)^{-\frac{3}{2}} \int_0^{.91\sqrt{2}} y^2 e^{-y^2/2} dy = 4\pi^{-\frac{1}{2}}(2)^{-\frac{3}{2}} \int_0^{.91\sqrt{2}} e^{-y^2/2} dy - .91\sqrt{2} \exp\left[-(.91 \, 2)^2/2\right]$$

The integral on the right may be evaluated from tables of error functions. Thus we find $\xi = .37$·

7.19

(a) $\qquad \overline{v}_x = 0$ by symmetry

(b) $\qquad \overline{v_x^2} = \dfrac{kT}{m}$ by equipartition

(c) $\qquad \overline{(v^2 v_x)} = (\overline{v_x^3} + \overline{v_y^2}\,\overline{v}_x + \overline{v_z^2}\,\overline{v}_x) = 0$

(d) $\qquad \overline{(v_x^3 v_y)} = \overline{v_x^3}\,\overline{v}_y = 0$

(e) $\overline{(v_x + bv_y)^2} = \overline{v_x^2} + 2b\,\overline{v}_x\,\overline{v}_y + b^2\overline{v_y^2}$

$\qquad\qquad\qquad = (1+b^2)\,\dfrac{kT}{m}$

(f) $\qquad \overline{v_x^2 v_y^2} = \left(\dfrac{kT}{m}\right)^2$

7.20

(a) $\qquad \overline{(1/v)} = \dfrac{1}{n}\displaystyle\int_0^\infty \dfrac{F(v)}{v}\,dv = \int_0^\infty 4\pi \left(\dfrac{m}{2\pi\,kT}\right)^{3/2} v e^{-\frac{mv^2}{2kT}}\,dv$

By appendix A.4 we find $\overline{(1/v)} = \left(\dfrac{2m}{\pi kT}\right)^{\frac{1}{2}}$, and since $\overline{v} = \left(\dfrac{8}{\pi}\dfrac{kT}{m}\right)^{\frac{1}{2}}$,

$$\dfrac{\overline{(1/v)}}{(1/\overline{v})} = \dfrac{4}{\pi} = 1.27$$

(b) Since the energy is $\epsilon = \frac{1}{2}mv^2$, we have $v^2 = 2\epsilon/m$ and $dv = d\epsilon/\sqrt{2m\epsilon}$. On substituting these relations into the speed distribution $F(v)\,dv$, it follows that

$$F(\epsilon)\,d\epsilon = 2\pi m\,(\pi kT)^{-\frac{3}{2}}\,\epsilon^{\frac{1}{2}}\,e^{-\frac{\epsilon}{kT}}\,d\epsilon$$

7.21

The most probable energy is given by the condition $\dfrac{dF(\epsilon)}{d\epsilon} = 0$ or from problem 7.20b

$$\dfrac{1}{2}\epsilon^{-\frac{1}{2}}\,e^{-\frac{\epsilon}{kT}} - \dfrac{\epsilon^{\frac{1}{2}}}{kT}\,e^{-\frac{\epsilon}{kT}} = 0$$

Thus $\qquad\qquad\qquad\qquad \tilde{\epsilon} = \dfrac{1}{2}kT$

The most probable speed is $\qquad \tilde{v} = (2kT/m)^{\frac{1}{2}}$

Hence $\qquad\qquad\qquad\qquad \dfrac{1}{2}m\tilde{v}^2 = kT$

7.22

(a) $\qquad \overline{\nu} = \nu_0\left(1 + \dfrac{\overline{v_x}}{c}\right) = \nu_0 \qquad\qquad$ since $\overline{v}_x = 0$

(b) The rms frequency shift is given by

$$(\Delta\nu)_{rms} = \left[\overline{(\nu-\overline{\nu})^2}\right]^{\frac{1}{2}} = \left[\overline{\nu^2} - \overline{\nu}^2\right]^{\frac{1}{2}}$$

But $\qquad\qquad\qquad \overline{\nu^2} = \nu_0^2\left(1 + \dfrac{2\overline{v}_x}{c} + \dfrac{\overline{v_x^2}}{c^2}\right)$

Since $\overline{v}_x = 0$ and $\overline{v_x^2} = kT/m$ by equipartition, we have

$$\overline{\nu^2} = \nu_0^2\left(1 + \dfrac{kT}{mc^2}\right)$$

Thus
$$(\Delta\nu)_{rms} = \left[\nu_o^2 + \frac{kT}{mc^2}\,\nu_o^2 - \nu_o^2\right]^{\frac{1}{2}} = \frac{\nu_o}{c}\left(\frac{kT}{m}\right)^{\frac{1}{2}}$$

(c) The intensity distribution is proportional to the distribution of the x component of velocity. Since $v_x = \frac{c}{\nu_o}(\nu-\nu_o)$, we have

$$I(\nu)d\nu = I_o \exp\left[-\frac{mc^2(\nu-\nu_o)^2}{2kT\,\nu_o^2}\right]d\nu$$

where I_o is the intensity at $\nu=\nu_o$.

7.23

(a) The number of molecules which leave the source slit per second is

$$\Phi_o A = \frac{1}{4}\,n\bar{v}A = \frac{\bar{p}_s A}{\sqrt{2\pi\,mkT}} = 1.1\times10^{18}\ \text{molecules/sec}$$

where A is the area of the slit.

(b) Approximating the slit as a point source, we have by (7.11.7), the number of molecules with speed in the range between v and $v + dv$ which emerge into solid angle $d\Omega$ is

$$A\Phi(v)\,d^3\underset{\sim}{v} = A[f(v)v\cos\theta][v^2\,dv\,d\Omega]$$

$\cos\theta \approx 1$ for molecules arriving at the detector slit; hence the total number which reach the detector is

$$A\int_{\Omega_d}d\Omega\int_0^\infty n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}v^3\,e^{-\frac{\beta mv^2}{2}}\,dv = \frac{A\,\Omega_d\,\bar{p}_s}{\pi\sqrt{2\pi mkT}} \tag{1}$$

where we have used the results of appendix A.4 and $\bar{p}_s = nkT$. Letting $L = 1m$ be the distance between source and detector, the solid angle Ω_d is approximately A/L^2. Substitution of the given values into (1) then gives 1.7×10^{11} molecules/sec arriving at the detector slit.

(c) In the steady state, the number of molecules entering the detection chamber per second is equal to the number being emitted. From (1) we find

$$\frac{A^2\underline{p}_s}{\pi L^2\sqrt{2\pi mkT}} = \Phi_d A = \frac{A\,\bar{p}_d}{\sqrt{2\pi\,mkT}}$$

or

$$\bar{p}_d = \bar{p}_s\,\frac{A}{\pi L^2} = 2.4\times10^{-8}\ \text{mm of Hg.}$$

7.24

The rate of change of the number of particles in the container is given by

$$\frac{dN}{dt} = -\varphi A = -\frac{1}{4}\,n\bar{v}A$$

Since the pressure is proportional to the number of particles, we have

$$\frac{dp}{dt} = - \frac{\bar{v}A}{4V} \, p$$

or

$$p(t) = p(0) \exp\left[- \frac{\bar{v}A}{4V} \, t\right]$$

where $p(0)$ is the original pressure. Hence the time required for the pressure to decrease to $p(t)/p(0) = 1/e$ is

$$t = \frac{4V}{\bar{v}A}$$

7.25

As in problem 7.24, we have

$$\frac{dp}{dt} = - \frac{\bar{v}A}{4V} \, p$$

or

$$t = - \frac{4V}{\bar{v}A} \ln \frac{p(t)}{p(0)}$$

where $p(0)$ is the original pressure. The mean speed, $\bar{v}$, is for nitrogen at 300°K,

$$\bar{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}} = .475 \times 10^5 \text{ cm/sec}$$

Thus

$$t = - \frac{4(4\pi/3)(10^3)}{(.475 \times 10^5)(1)} \ln \frac{10^{-6}}{10^{-1}} = 4.07 \text{ sec}$$

7.26

(a) Since the rate of effusion is $\varphi = p/(2\pi m \, kT)^{\frac{1}{2}}$, and the concentration is proportional to the pressure, it follows that

$$\frac{c_2{'}}{c_1{'}} = \frac{c_2}{c_1} \sqrt{\frac{m_2}{m_1}}$$

(b) For the uranium separation, we have

$$c'_{235}/c'_{238} = c_{235}/c_{238} \left(\frac{238 + 6(19)}{235 + 6(19)}\right)^{\frac{1}{2}} = (c_{235}/c_{238})(1.003)$$

7.27

The rate of change of the number of particles inside the container is

$$\frac{dN}{dt} = - \frac{1}{4} n\bar{v}A = - \frac{NA}{4V} \sqrt{\frac{8}{\pi} \frac{kT}{m}} = - \frac{\lambda N}{\sqrt{m}}$$

thus defining λ. Since pressure is proportional to the number of particles, we find after integrating

$$p/p_0 = \exp\left[- \frac{\lambda t}{\sqrt{m}}\right] \qquad (1)$$

For Helium gas $p/p_0 = 1/2$ at $t = 1$ hour. Substituting we have

$$\lambda = \sqrt{m_{He}} \ln 2 \qquad (2)$$

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where m_{He} is the mass of the helium molecule. From (1) and (2) it follows that the ratio of the Ne and He concentrations in terms of the initial concentrations is

$$n_{Ne}/n_{He} = (n_{Ne}/n_{He})_0 \exp\left[-\lambda \left(1/\sqrt{m_{Ne}} - 1/\sqrt{m_{He}}\right) t\right]$$

$$= (n_{Ne}/n_{He})_0 \exp\left[-\ln 2 \left(\sqrt{m_{He}/m_{Ne}} - 1\right) t\right]$$

Since $(n_{Ne}/n_{He})_0 = 1$, we have at $t = 1$ hour,

$$n_{Ne}/n_{He} = 2^{\left(1-\sqrt{m_{He}/m_{Ne}}\right)} = 2^{\left(1-\sqrt{\mu_{He}/\mu_{Ne}}\right)}$$

7.28

(a) The rate of change of the number of particles in the left side of the box is

$$\frac{dN_1(t)}{dt} = (\text{no. entering/sec}) - (\text{no. escaping/sec})$$

Since the rate of effusion is $\frac{1}{4} n\bar{v}A$, we have

$$\frac{dN_1(t)}{dt} = \frac{A\bar{v}}{4V/2}\left[N_2(t) - N_1(t)\right] = \frac{A\bar{v}}{2V}\left[N - 2N_1(t)\right]$$

where N is the total number of particles. From the equation of state,

$$N_1(t) = p_1(t)\frac{V}{2kT} \quad \text{and} \quad N = \frac{p_1(0) + p_2(0)}{2}\frac{V}{kT} \qquad (1)$$

Thus

$$\frac{dp_1(t)}{dt} = \frac{A\bar{v}}{2V}\left(\left[p_1(0) + p_2(0)\right] - 2p_1(t)\right)$$

Integrating, we find

$$p_1(t) = \left(\frac{p_1(0) + p_2(0)}{2}\right) + \left(\frac{p_1(0) - p_2(0)}{2}\right)e^{-\frac{A\bar{v}}{V}t}$$

(b) The initial entropy is

$$S_i = N_1(0)k\left(\ln\frac{V}{2N_1(0)} + \frac{3}{2}\ln T + \sigma_0\right) + N_2(0)k\left(\ln\frac{V}{2N_2(0)} + \frac{3}{2}\ln T + \sigma_0\right)$$

In final equilibrium, $N_1 = N_2 = \frac{N}{2}$

$$S_f = Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right)$$

Then $\Delta S = S_f - S_i$ and using (1), we find

$$\Delta S = \frac{p_1(0) + p_2(0)}{2}\frac{V}{T}\ln\left[\frac{2kT}{p_1(0) + p_2(0)}\right] - \frac{p_1(0)}{2}\frac{V}{T}\ln\left[\frac{kT}{p_1(0)}\right] - \frac{p_2(0)}{2}\frac{V}{T}\ln\left[\frac{kT}{p_2(0)}\right]$$

$$= \frac{V}{2T}\left(p_1(0)\ln\frac{2p_1(0)}{p_1(0) + p_2(0)} + p_2(0)\ln\frac{2p_2(0)}{p_1(0) + p_2(0)}\right)$$

7.29

(a)   Inside the container $\overline{v}_z = 0$ by symmetry.

(b)   The velocity distribution, $\Phi(\underline{v})$, of the molecules which have effused into the vacuum is

$$\Phi(\underline{v}) \; d^3\underline{v} = f(\underline{v}) \; v_z \; d^3\underline{v}$$

where $f(\underline{v})$ is the Maxwell distribution.

Thus
$$\overline{v}_z = \frac{\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{0}^{\infty} dv_z \; \Phi(v) \; v_z}{\int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{0}^{\infty} dv_z \; \Phi(v)} = \frac{\int_{0}^{\infty} dv_z \; e^{-\frac{mv_z^2}{2kT}} \; v_z^2}{\int_{0}^{\infty} dv_z \; e^{-\frac{mv_z^2}{2kT}} \; v_z}$$

The second equality follows because the integrations over v_x and v_y are identical in the numerator and denominator and therefore cancel. The integrals over v_z are tabulated in appendix A.4.

$$\overline{v}_z = \frac{\frac{\sqrt{\pi}}{4}\left(\frac{2kT}{m}\right)^{\frac{3}{2}}}{\frac{1}{2}\left(\frac{2kT}{m}\right)} = \sqrt{\frac{\pi}{2} \; \frac{kT}{m}}$$

7.30

(a)   In time dt, molecules with velocity component v_z which are in a cylinder of height $v_z \, dt$ with base at the aperture can escape from the container. Molecules of higher speed can escape from a larger cylinder than can molecules of lower speed, and a proportionally larger share of the fast molecules effuse. Thus the mean kinetic energy of particles in the beam is greater than in the container.

(b)
$$\overline{\epsilon}_o = \overline{\frac{1}{2}mv^2} = \frac{\int d^3\underline{v} \; \frac{1}{2} mv^2 \; \Phi(\underline{v})}{\int d^3\underline{v} \; \Phi(\underline{v})}$$

Since $\Phi(\underline{v}) = f(\underline{v}) \, v \cos\theta$ and $d^3\underline{v} = v^2 dv \sin\theta \, d\theta \, d\varphi$, we have

$$\overline{\epsilon}_o = \frac{\int_{0}^{\infty}\int_{0}^{\pi/2}\int_{0}^{\pi} (v^2 \, dv \sin\theta \, d\theta \, d\varphi)(\frac{1}{2} mv^2) \; e^{-\frac{mv^2}{2kT}} \; v \cos\theta}{\int_{0}^{\infty}\int_{0}^{\pi/2}\int_{0}^{\pi} (v^2 \, dv \sin\theta \, d\theta \, d\varphi) \; e^{-\frac{mv^2}{2kT}} \; v \cos\theta}$$

$$= \frac{\frac{1}{2} m \int_{0}^{\infty} v^5 \; e^{-\frac{mv^2}{2kT}} \; dv}{\int_{0}^{\infty} v^3 \; e^{-\frac{mv^2}{2kT}} \; dv} = 2kT$$

where the integrals over v are evaluated by appendix A.4. Since the mean kinetic energy in the

the enclosure is $\overline{\epsilon_i} = \frac{3}{2} kT$, it follows that $\overline{\epsilon_o} = \frac{4}{3} \overline{\epsilon_i}$.

7.31

When a molecule is scattered, it commutes momentum $\Delta p_z = 2mv_z$ to the disk. The force is $\Delta p_z / dt$. To find the total force, we must multiply $\Delta p_z / dt$ by the number of molecules with velocity in the range $\{\underset{\sim}{v}, dv\}$ which strike the disk in time dt and then integrate over all velocities. Clearly only molecules in the cone of half-angle $\theta_o = \sin^{-1} R/L$ will strike the disk.

$$F = \int d^3\underset{\sim}{v} \left[A\Phi \, (\underset{\sim}{v}) \, dt \right] \frac{\Delta p_z}{dt}$$

$$= \int_o^\infty \int_o^{\theta_o} \int_o^{2\pi} (v^2 dv \sin\theta \, d\theta \, d\varphi)(A \, f(v) \, v \cos\theta \, dt)(\frac{2m \, v \cos\theta}{dt})$$

$$= \left| (2mA)(2\pi)(- \frac{1}{3} \cos^3\theta) \right|_o^{\theta_o} \int_o^\infty v^4 \, f(v) dv$$

The integral can be expressed in terms of the mean square speed inside the container, i.e.,

$$\int_o^\infty v^4 f(v) dv = \frac{n\overline{v^2}}{4\pi}$$

Thus
$$F = \frac{1}{3} nm \, \overline{v^2} \, A \, (- \frac{1}{3} \cos^3\theta)_o^{\theta_o} = \frac{1}{3} nm \, \overline{v^2} \, A \left[1 - \cos^3 (\sin^{-1} \frac{R}{L}) \right]$$

But by equipartition we have
$$\frac{1}{3} n \, m\overline{v^2} = nkT = \overline{p}$$

Hence
$$F = \overline{p}A \left[1 - \cos^3 (\sin^{-1} \frac{R}{L}) \right]$$

CHAPTER 8

Equilibrium between Phases and Chemical Species

8.1

By equation (8.3.8), we have the proportionality

$$\mathcal{P}(v,T) \, dV \, dT \propto \exp \left[-G_o \, (V,T)/kT_o \right] dV \, dT$$

where V and T are the volume and temperature of the portion of substance of mass M, and T_o is the temperature of the surrounding medium. Expanding the Gibbs Free Energy $G_o(V,T)$ about the minimum at $V = \widetilde{V}$, and $T = \widetilde{T}$ yields

$$G_o(V,T) = G_o(\widetilde{V},\widetilde{T}) + (\frac{\partial G_o}{\partial T})_V (T-\widetilde{T}) + (\frac{\partial G_o}{\partial V})_T (V-\widetilde{V}) + \frac{1}{2} (\frac{\partial^2 G_o}{\partial T^2})_V (T-\widetilde{T})^2$$

$$+ \frac{1}{2} (\frac{\partial^2 G_o}{\partial V^2})_T (V-\widetilde{V})^2 + (\frac{\partial^2 G_o}{\partial V \partial T}) (V-\widetilde{V})(T-\widetilde{T}) + \dots \qquad (1)$$

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where the derivatives are evaluated at $T = \tilde{T}$ and $V = \tilde{V}$. Since we are expanding about a **minimum**, the first derivatives in (1) are 0. By (8.4.7)

$$\left(\frac{\partial G_o}{\partial T}\right)_V = \left(1 - \frac{T_o}{T}\right)\left(\frac{\partial E}{\partial T}\right)_V \tag{2}$$

Since this is 0 at $T = \tilde{T}$, we have $\tilde{T} = T_o$. $(\partial E/\partial T)_V$ is the heat capacity, C_V.

Thus

$$\left(\frac{\partial^2 G_o}{\partial T^2}\right)_V = \frac{T_o}{T^2} C_V + \left(1 - \frac{T_o}{T}\right)\left(\frac{\partial C_V}{\partial T}\right)_V$$

and at $T = T_o = \tilde{T}$,

$$\left(\frac{\partial^2 G_o}{\partial T^2}\right)_V = \frac{C_V}{T_o}$$

From (2) we also find the mixed derivative

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial G_o}{\partial T}\right)_V = \left(1 - \frac{T_o}{T}\right)\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \qquad \text{at } T = T_o$$

By the equation preceding (8.4.13)

$$\left(\frac{\partial G_o}{\partial V}\right)_T = (T - T_o)\left(\frac{\partial S}{\partial V}\right)_T - \bar{p} + p_o$$

$$\left(\frac{\partial^2 G_o}{\partial V^2}\right)_T = (T - T_o)\left(\frac{\partial^2 S}{\partial V^2}\right)_T - \left(\frac{\partial \bar{p}}{\partial V}\right)_T = -\left(\frac{\partial \bar{p}}{\partial V}\right)_T \quad \text{at } T = T_o, V = \tilde{V}$$

By definition, $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, thus $\left(\frac{\partial^2 G_o}{\partial V^2}\right)_T = \frac{1}{\tilde{V}\kappa}$. Substitution of these results into (1) yields

$$G_o(V,T) = G_o(\tilde{V}, T_o) + \frac{C_V}{2T_o}(T - T_o)^2 + \frac{1}{2\tilde{V}\kappa}(V - \tilde{V})^2$$

and since $\tilde{V} = M/\rho_o$ and $C_V = Mc_V$ where c_V is the specific heat per gram, it follows that

$$\mathcal{P}(V,T)dV\, dT \propto \exp\left[-\frac{Mc_V}{2kT_o^2}(T - T_o)^2 - \frac{\rho_o}{2M\kappa\, kT_o}(V - M/\rho_o)^2\right] dV\, dT$$

where we have absorbed the constant term $G_o(\tilde{V}, T_o)$ into the normalization factor. Performing the usual normalization, we find

$$\mathcal{P}(V,T)\, dV\, dT = \frac{1}{2\pi}\left(\frac{c_V\rho_o}{k^2 T_o^3 \kappa}\right)^{\frac{1}{2}} \exp\left[-\frac{Mc_V}{2kT_o^2}(T - T_o)^2 - \frac{\rho_o}{2M\kappa\, kT_o}(V - M/\rho_o)^2\right] dV\, dT$$

8.2

(a) For the solid, $\ln p = 23.03 - 3754/T$ and for the liquid $\ln p = 19.49 - 3063/T$. At the triple point, the pressures of the solid and liquid are equal.

$$23.03 - 3754/T = 19.49 - 3063/T$$

hence $\qquad\qquad\qquad\qquad\qquad$ $T = 691/3.54 = 195^{\circ}K$

(b) Since $\ln p = -\dfrac{\ell}{RT} + \text{constant}$ where ℓ is the latent heat, we have

$$\ell_{sublimation} = 3754\ R = 31{,}220\ \text{joules/mole}$$

$$\ell_{vaporization} = 3063\ R = 25{,}480\ \text{joules/mole}$$

(c) $\ell_{fusion} = \ell_{sublimation} - \ell_{vaporization}$

$$= 31{,}220 - 25{,}480 = 5740\ \text{joules/mole}.$$

8.3

The latent heat of sublimation is equal to the sum of the latent heats of melting and vaporization, i.e., $\ell_s = \ell_m + \ell_v$. Since $\ell = T\Delta V\,(dp/dT)$, the Clausius-Clapeyron equation, where v is the volume per mole, it follows that

$$\left(\frac{dp}{dT}\right)_s = \frac{1}{T_0(v_{gas} - v_{sol})}\left[T_0\,(v_{liq} - v_{sol})\left(\frac{dp}{dT}\right)_m + T_0(v_{gas} - v_{liq})\left(\frac{dp}{dT}\right)_v\right]$$

or $\qquad$ $\left(\dfrac{dp}{dT}\right)_s = \left(\dfrac{RT_0}{p_0} - \dfrac{\mu}{\rho_s}\right)^{-1}\left[\left(\dfrac{\mu}{\rho_\ell} - \dfrac{\mu}{\rho_s}\right)\left(\dfrac{dp}{dT}\right)_m + \left(\dfrac{RT_0}{p_0} - \dfrac{\mu}{\rho_\ell}\right)\left(\dfrac{dp}{dT}\right)_v\right]$

8.4

Since $\dfrac{dp}{dT} = \dfrac{\Delta S}{\Delta V}$ and $\Delta S \to 0$ as $T \to 0$ by the third law, it follows that $\dfrac{dp}{dT} \to 0$ as $T \to 0$.

8.5

(a) Q/L moles/sec evaporate and are swept out by the pump. Then by the equation of state

$$\frac{Q}{L} = \frac{p_m\,\mathscr{V}}{RT_r} \qquad \text{or} \qquad p_m = \frac{QRT_r}{L\mathscr{V}}$$

(b) We find the temperature at the pressure p_m from the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{T(v_{gas} - v_{liquid})} \approx \frac{L}{T\,v_{gas}}$$

where we have neglected v_{liquid} since the volume per mole of the gas is much greater than that of the liquid. Then using $v_{gas} = RT/p$ we find

$$\int_{p_0}^{p_m}\frac{dp}{p} = \frac{L}{R}\int_{T_0}^{T_m}\frac{dT}{T^2}$$

$$\ln\frac{p_m}{p_0} = \frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T_m}\right)$$

Hence $\qquad\qquad\qquad$ $T_m = T_0\left(1 - \frac{T_0 R}{L}\ln\frac{p_m}{p_0}\right)^{-1}$

8.6

The intensity, I, is given by

$$I = \frac{1}{4} n\bar{v} = \frac{p}{\sqrt{2\pi \, m \, kT}}$$

Differentiating with respect to T and dividing by I, we have

$$\frac{1}{I}\frac{dI}{dT} = \frac{1}{p}\frac{dp}{dT} - \frac{1}{2T} \tag{1}$$

Since p is the vapor pressure, the Clausius-Clapeyron equation yields dp/dT.

$$\frac{dp}{dT} = \frac{L}{T(v_{gas} - v_{liquid})} \approx \frac{L}{T\,v_{gas}}$$

Substituting into (1) and using $v_{gas} = RT/p$ gives

$$\frac{1}{I}\frac{dI}{dT} = \frac{L}{RT^2} - \frac{1}{2T}$$

8.7

Differentiating the molar latent heat yields

$$\frac{d\ell}{dT} = \left(\frac{\partial \ell}{\partial p}\right)_T \frac{dp}{dT} + \left(\frac{\partial \ell}{\partial T}\right)_p \tag{1}$$

Now $\ell = T(s_2 - s_1)$ where $(s_2 - s_1)$ is the molar entropy difference between the phases.

Thus
$$\left(\frac{\partial \ell}{\partial p}\right)_T = T\left[\left(\frac{\partial s_2}{\partial p}\right)_T - \left(\frac{\partial s_1}{\partial p}\right)_T\right]$$

But $(\partial s/\partial p)_T = -(\partial v/\partial T)_p$, a Maxwell relation, and since the coefficient of expansion is $\alpha = -1/v\,(\partial v/\partial T)_p$, it follows that

$$\left(\frac{\partial \ell}{\partial p}\right)_T = -T\left[\alpha_2 v_2 - \alpha_1 v_1\right] \tag{2}$$

Differentiating at constant p gives

$$\left(\frac{\partial \ell}{\partial T}\right)_p = (s_2 - s_1) + T\left[\left(\frac{\partial s_2}{\partial T}\right)_p - \left(\frac{\partial s_1}{\partial p}\right)_T\right]$$

$T(\partial s/\partial T)_p$ is the specific heat at constant pressure. Thus

$$\left(\frac{\partial \ell}{\partial T}\right)_p = \frac{\ell}{T} + (c_{p_2} - c_{p_1}) \tag{3}$$

Substituting (2) and (3) into (1) yields

$$\frac{d\ell}{dT} = -T(\alpha_2 v_2 - \alpha_1 v_1)\frac{dp}{dT} + \frac{\ell}{T} + (c_{p_2} - c_{p_1})$$

Since
$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)}$$

$$\frac{d\ell}{dT} = (c_{p_2} - c_{p_1}) + \frac{\ell}{T} - \frac{(\alpha_2 v_2 - \alpha_1 v_1)\ell}{v_2 - v_1}$$

8.8

The bar moves because the higher pressure underneath it lowers the melting point. The water is then forced up along the sides to the top of the bar and refreezes under the lower pressure. To melt a mass dm of ice, heat ℓdm must be conducted through the bar. The heat passing through it per unit time is

$$\mathcal{H} = -\kappa \ (bc) \ \frac{\Delta T}{a}$$

where ΔT is the temperature drop across the bar and κ is the thermal conductivity. Letting x be the position in the vertical direction, we have $dm = \rho_i (bc \ dx)$, and equating the rate at which heat is conducted to the rate it is absorbed in the melting process we have

$$-\kappa \ (bc) \ \frac{\Delta T}{a} = \ell \ \rho_i \ (bc \ \frac{dx}{dt}) \tag{1}$$

ΔT is given by the Clausius-Clapeyron equation

$$\frac{dp}{dt} \approx \frac{\Delta p}{\Delta T} = \frac{\ell}{T(v_{water} - v_{ice})}$$

where v is the volume per gram or $1/\rho$. Then since $\Delta p = 2 \ mg/bc$,

$$\Delta T = \frac{mg \ T}{\ell \ bc} \ (\frac{1}{\rho_w} - \frac{1}{\rho_i})$$

Substitution in (1) yields

$$\frac{dx}{dt} = \frac{2 \ mg \ \kappa T}{abc \ \ell^2 \ \rho_i} \ (\frac{1}{\rho_i} - \frac{1}{\rho_w})$$

8.9

From the Clausius-Clapeyron relation, $dp/dT = L/T\Delta v$ we find

$$\int \frac{dT}{T} = \int \frac{\Delta V}{L} \ dp$$

We know $L(\varphi)$ and $\Delta V(\varphi)$, and we can find $dp/d\varphi$ from the curve of vapor pressure vs. emf.

Thus

$$\int_{273.16}^{T} \frac{dT'}{T'} = \int_{0}^{\varphi} \frac{\Delta V(\varphi')}{L(\varphi')} \ (\frac{dp}{d\varphi}) \ d\varphi'$$

where $273.16^{\circ}K$ is the temperature of the reference junction of the thermocouple.

Then

$$T = 273.16 \ \exp\left[\int_{0}^{\varphi} \frac{\Delta V(\varphi')}{L(\varphi')} \ (\frac{dp}{d\varphi'}) \ d\varphi'\right]$$

8.10

We divide the substance into small volume elements. The total entropy is just the sum of the entropies of each of these, or

$$S = \sum_i S_i \ (E_i, N_i)$$

where E_i and N_i denote the energy and number of particles in the ith volume. If we consider

an interchange of energy between the ith and j^{th} volumes, we have since the entropy is stationary

$$dS = 0 = \frac{\partial S_i}{\partial E_i} \, dE_i + \frac{\partial S_j}{\partial E_j} \, dE_j$$

but since $dE_i = -dE_j$, we have

$$\frac{\partial S_i}{\partial E_i} = \frac{\partial S_j}{\partial E_j} \qquad \text{or} \qquad T_i = T_j$$

Similarly, if we interchange particles

$$dS = 0 = \frac{\partial S_i}{\partial N_i} \, dN_i + \frac{\partial S_j}{\partial N_j} \, dN_j$$

implies $\qquad \dfrac{\partial S_i}{\partial N_i} = \dfrac{\partial S_j}{\partial N_j} \qquad\qquad$ or $\qquad\qquad \mu_i = \mu_j$

8.11

(a) The chemical potential can be found from the free energy by $\mu = \frac{\partial F}{\partial N}$. We consider a small volume element at height z over which the potential energy may be considered constant. It is clear that the addition of a constant term to the energy does not change the entropy of the substance in the small volume element. Explicitly, the partition function will be the free particle function times the factor $e^{-\beta mgz}$.

Thus $\qquad S = \left[k \, \ln \left(Z_{free} \, e^{-\beta mgz} \right) + \beta \left(\overline{E}_{free} + mgz \right) \right] = k \left[\ln Z_{free} + \beta \overline{E}_{free} \right]$

Hence the free energy is, letting N be the number of particles in ΔV

$$F = E - TS$$
$$= \frac{3}{2} NkT + Nmgz - NkT \left[\ln \frac{\Delta V}{N} + \frac{3}{2} \ln T + \sigma_0 \right]$$

and $\qquad \mu = \dfrac{\partial F}{\partial N} = \dfrac{5}{2} kT + mgz - kT \left[\ln \dfrac{kT}{p} + \dfrac{3}{2} \ln T + \sigma_0 \right]$

where we have put $\Delta V/N = kT/p$.

(b) Since μ is independent of z,

$$\frac{d\mu}{dz} = mg + \frac{kT}{p} \frac{dp}{dz} = 0 \qquad\qquad \text{or} \qquad\qquad \frac{dp}{p} = -\frac{mg}{kT} \, dz$$

Integration yields

$$p(z) = p(0) \, e^{-\frac{mgz}{kT}}$$
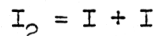
8.12

The relative concentration remains the same. The dissociation is described by

$$\frac{n_{CO} \, n_{H_2O}}{n_{CO_2} \, n_{H_2}} = K_n(T)$$

Generally, when the number of particles is conserved, equilibrium is independent of v

8.13

The intensity of the I atoms in the beam is proportional to their concentration n_I in the oven. Since dissociation proceeds according to

$$I_2 = I + I$$

We have

$$n_I^{-2} n_{I_2} = K_n(T)$$

which gives

$$p_I^{-2} p_{I_2} = \frac{K_n(T)}{kT} \equiv K_p(T) \tag{1}$$

by the equation of state. The total pressure is $p = p_I + p_{I_2}$ which yields on substitution into (1)

$$p - p_I = K_p \, p_I^2$$

or

$$p_I = (-1 + \sqrt{1 + 4K_p p}\,)/2K_p$$

Thus, if the total pressure is doubled, the ratio of final to initial intensities is

$$\frac{\phi_f}{\phi_i} = \frac{(p_I)_f}{(p_I)_i} = \frac{-1 + \sqrt{1 + 8K_p p}}{-1 + \sqrt{1 + 4K_p p}}$$

Since K_p is small we may expand the square roots to obtain

$$\frac{\phi_f}{\phi_i} \approx \frac{-1 + 1 + 4K_p p}{-1 + 1 + 2K_p p} = 2$$

8.14

For chemical equilibrium we have

$$n_1^{b_1} n_2^{b_2} \ldots n_m^{b_m} = K_n(T)$$

where n is the number of molecules per unit volume. Since $n_i = p_i/kT$ it follows that

$$p_1^{b_1} p_2^{b_2} \ldots p_m^{b_m} = (kT)^{b_1 + b_2 + \ldots + b_m} K_n(T) = K_p(T)$$

8.15

By the first law $d\!\!\!\!/\, Q = dE + p\, dV$. Letting $d(pV) = V\, dp + p\, dV$ we have

$$d\!\!\!\!/\, Q = dE + d(pV) - V\, dp$$

$$= d(E + pV) - V dp$$

$$= dH - V\, dp$$

where the last follows from the definition of enthalpy, $H = E + pV$. Then if p is constant

$$d\!\!\!\!/\, Q = dH$$

i.e., in a constant pressure process, the heat absorbed is equal to the change in enthalpy. In a chemical reaction, $Q = \Delta H = \sum_i b_i h_i$ since enthalpy is an extensive quantity.

8.16

By the equation preceding (8.10.25)

$$\sum_i b_i \ln \zeta_i' = \sum_i b_i \ln n_i \tag{1}$$

Substitution of $n_i = p_i/kT$ into (1) yields

$$\sum_i b_i \ln p_i = \sum_i (b_i \ln \zeta_i' + b_i \ln kT)$$

or

$$p_1^{b_1} p_2^{b} \cdots p_m^{b_m} = K_p(T)$$

where

$$\ln K_p(T) = \sum_i (b_i \ln \zeta_i' + b_i \ln kT)$$

Thus

$$\frac{d}{dT} \ln K_p(T) = \sum_i (b_i \frac{d}{dT} \ln \zeta_i' + \frac{b_i}{T})$$

By (8.10.30) $\frac{d}{dT} \ln \zeta_i' = \frac{\epsilon_i}{kT}$ where ϵ_i is the mean energy per molecule. Then multiplying $\frac{b_i}{T}$ by $1 = \frac{\overline{p_i V_i}}{N_i kT}$ we have

$$\frac{d}{dT} \ln K_p(T) = \sum_i \frac{b_i}{kT^2} (\overline{\epsilon_i} + \frac{\overline{p_i V_i}}{N_i}) = \sum_i \frac{b_i h_i'}{kT^2}$$

where h_i' is the enthalpy per molecule. Multiplying and dividing by Avogadro's number gives

$$\frac{d}{dT} \ln K_p(T) = \sum_i \frac{b_i h_i}{RT^2} = \frac{\Delta H}{RT^2}$$

where h_i is the enthalpy per mole.

8.17

We let ξ be the fraction of H_2O molecules which are dissociated. Since the pressure is proportional to the number of molecules, we have

$$\xi = \frac{p_{H_2}}{p_{H_2O} + p_{H_2}} = \frac{2p_{O_2}}{p_{H_2O} + p_{H_2}} \tag{1}$$

The total pressure is the sum of the partial pressures.

$$p = p_{H_2} + p_{O_2} + p_{H_2O} \tag{2}$$

Substituting (1) and (2) into

$$K_p(T) = \frac{p_{H_2}^2 \, p_{O_2}}{p_{H_2O}^2}$$

we find

$$K_p(T) = \frac{p\xi^3}{(1-\xi)^2 (2+\xi)} \tag{3}$$

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8.18

In problem 8.16 it was shown that

$$\Delta H = RT^2 \frac{d}{dT} \ln K_p(T)$$

Using $K_p(T)$ from problem 8.17 would give ΔH for the dissociation of 2 moles of H_2O since the reaction is $2H_2O \rightarrow 2H_2 + O_2$. Hence for the dissociation of 1 mole

$$\Delta H = \frac{RT^2}{2} \frac{d}{dT} \ln K_p(T)$$

where $K_p(T)$ is given by equation (3) in 8.17. Since $\xi \ll 1$, we have

$$K_p(T) = \frac{p\xi^3}{(1-\xi)^2 (2+\xi)} \approx \frac{p\xi^3}{2}$$

Hence
$$\Delta H = \frac{RT^2}{2} \frac{d}{dT} \ln \frac{p\xi^3}{2} = \frac{3}{2} RT^2 \frac{d}{dT} \ln \xi$$

$\frac{d}{dT} \ln \xi$ is found by plotting $\ln \xi$ vs. temperature using the given values and measuring the slope of this curve at 1700°. We find $\frac{d}{dT} \ln \xi = .0064$. Thus at $1700^{\circ}K$

$$\Delta H = \frac{3}{2} (1.99)(1700)^2(.0064) = 56,000 \text{ cal/mole}$$

8.19

(a) The partition function is $Z = \frac{\zeta^N}{N!}$ where ζ is the partition function for a single molecule. For a liquid we assume a constant interaction potential $-\eta$ and that the molecule is free to move in a volume N_{v_o}.

Thus
$$\zeta = \frac{1}{h_o^3} \int' d^3\underline{p}\ d^3\underline{r}\ e^{-(\beta\underline{p}^2/2m)+\beta\eta}$$

where the integration is over $N_\ell v_o$ and all $\underline{p}$.

$$\zeta = N_\ell v_o\ e^{\beta\eta}\ \frac{1}{h_o^3} \int d^3\underline{p}\ e^{-\beta\underline{p}^2/2m} = N_\ell\ e^{\beta\eta}\ v_o \zeta'$$

thus defining ζ'.

Hence
$$Z_\ell = \frac{\zeta^{N_\ell}}{N_\ell!} = \frac{1}{N_\ell!} \left[N_\ell\ e^{\beta\eta}\ v_o\ \zeta' \right]^{N_\ell} \tag{1}$$

(b) For an ideal gas, the partition function is

$$Z_g = \frac{1}{N_g!} \left[V_g \zeta' \right]^{N_g}$$

The Helmholz free energy is

$$F_g = -kT \ln Z_g = -kT \left(\ln \left[V_g \zeta' \right]^{N_g} - \ln N_g! \right)$$

$$= -kT \left(N_g \ln V_g\ \zeta' - N_g \ln N_g + N_g \right)$$

where we have used Sterling's approximation $\ln N_g! \approx N_g \ln N_g - N_g$

Then
$$\mu_g = \frac{\partial F_g}{\partial N_g} = -kT \left(\ln V_g \, \zeta' - \ln N_g \right)$$

(c) For the liquid, we have by (1)

$$F_\ell = -kT \left(\ln \left[N_\ell \, e^{\beta \eta} \, v_o \zeta' \right]^{N_\ell} - \ln N_\ell! \right)$$

$$= -kT \left(N_\ell \ln v_o \zeta' + N_\ell \, \beta \eta + N_\ell \right)$$

Therefore
$$\mu_\ell = \frac{\partial F_\ell}{\partial N_\ell} = -kT \left(\ln v_o \, \zeta' + \beta \eta + 1 \right)$$

(d) When the liquid is in equilibrium with the vapor, the chemical potentials are equal or $\mu_g = \mu_\ell$

$$-kT(\ln V_g \zeta' - \ln N_g) = -kT \left(\ln v_o \zeta' + \beta \eta + 1 \right)$$

Thus
$$\frac{V_g}{N_g} = v_o \, e^{\beta \eta + 1}$$

but since $p/kT = N_g/V_g$ we have

$$\frac{p}{kT} = \frac{e^{-\beta \eta}}{e v_o} \qquad\qquad (2)$$

(e) We calculate the molar entropy difference from the Clausius-Clapeyron relation.

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} \approx \frac{\Delta s}{v_g}$$

where in the second equality we have assumed that the molar volume of the liquid is much less than that of the gas. Since $pv_g = RT$ we have

$$\frac{1}{p} \frac{dp}{dT} = \frac{\Delta s}{RT}$$

Then using (2) in this relation we find

$$\Delta s = R \left(1 + \frac{\eta}{kT} \right)$$

The molar heat of evaporation is

$$L = T\Delta s = RT \left(1 + \frac{\eta}{kT} \right) \qquad\qquad (3)$$

$$\approx \frac{R\eta}{kT} = N_A \eta \quad \text{if} \quad \eta \gg kT$$

(f) From (3) $\quad \frac{L}{RT} = 1 + \frac{\eta}{kT}$.

Taking the logarithm of (2), we find

$$1 + \frac{\eta}{kT} = \ln \frac{kT}{p v_o} = \ln \frac{v_g}{v_o}$$

where v_g is the volume per molecule of the vapor.

Hence

$$\frac{L}{RT_b} = \ln \frac{v_g}{v_o} \qquad (4)$$

when v_g and v_o are evaluated at T_b.

(b) In (4) we can take v to be the volume per mole instead of the volume per molecule since we have the ratio v_g/v_o. To estimate the order of magnitude of L/RT_b we let $v_g \approx 22.4$ liters/mole and $v_o \approx \frac{4}{3} \pi r_o^3 N_A \approx \frac{4}{3} \pi (.5 \times 10^{-8})^3 (6 \times 10^{23}) \approx 10^{-3}$ liters/mole.

Thus

$$\frac{L}{RT_b} \approx \ln \frac{20}{10^{-3}} \approx 10$$

(h) We find L/T_b from eq. (4).

	v_o	v_g	L/T_b calculated	L/T_b experimental
water	.018 liters/mole	31 liters/mole	.83 cal/gm°K	1.45 cal/gm°K
nitrogen	.035	6.4	.37	.64
benzene	.087	29	.16	.27

These results are remarkably good in view of the very simple theory considered here.

CHAPTER 9

Quantum Statistics of Ideal Gases

9.1

configuration			no. of states		
O	ϵ	3ϵ	MB	BE	FD
xx			1	1	--
	xx		1	1	--
		xx	1	1	--
x	x		2	1	1
x		x	2	1	1
	x	x	2	1	1

(a) $Z_{MB} = 1 + e^{-2\epsilon\beta} + e^{-6\epsilon\beta} + 2e^{-\epsilon\beta} + 2e^{-3\epsilon\beta} + 2e^{-4\epsilon\beta}$

(b) $Z_{BE} = 1 + e^{-2\epsilon\beta} + e^{-6\epsilon\beta} + e^{-\epsilon\beta} + e^{-3\epsilon\beta} + e^{-4\epsilon\beta}$

(c) $Z_{FD} = e^{-\epsilon\beta} + e^{-3\epsilon\beta} + e^{-4\epsilon\beta}$

9.2

(a) For an FD gas, we have

$$\ln Z = \alpha N + \sum_r \ln (1 + e^{-\alpha - \beta E_r}) \quad \text{and} \quad \bar{n}_r = \frac{1}{e^{\alpha + \beta \epsilon_r} + 1}$$

Hence $$S = k [\ln Z + \beta \bar{E}] = k \left[\alpha N + \sum_r \ln (1 + e^{-\alpha - \beta E_r}) + \beta \bar{E} \right]$$

but since $N = \sum\limits_r \bar{n}_r$ and $\bar{E} = \sum\limits_r \bar{n}_r \epsilon_r$, we find

$$S = k\left[\sum_r \bar{n}_r(\alpha + \beta\epsilon_r) + \sum_r \ln(1 + e^{-\alpha-\beta\epsilon_r})\right] \tag{1}$$

From $\bar{n}_r = \dfrac{1}{e^{\alpha+\beta\epsilon_r} + 1}$ it follows that

$$\alpha + \beta\epsilon_r = \ln(1-\bar{n}_r) - \ln\bar{n}_r \tag{2}$$

$$e^{-\alpha-\beta\epsilon_r} = \frac{\bar{n}_r}{1-\bar{n}_r} \tag{3}$$

Substituting (2) and (3) in (1) we find

$$S = k\left[\sum_r \bar{n}_r\left(\ln(1-\bar{n}_r) - \ln\bar{n}_r\right) + \sum_r \ln\left(1 + \frac{\bar{n}_r}{1-\bar{n}_r}\right)\right]$$

$$= -k\sum_r \left[\bar{n}_r \ln\bar{n}_r + (1-\bar{n}_r)\ln(1-\bar{n}_r)\right] \tag{4}$$

(b) For the BE case

$$\ln Z = \alpha N - \sum_r \ln(1 - e^{-\alpha-\beta\epsilon_r}) \quad \text{and} \quad \bar{n}_r = \frac{1}{e^{\alpha+\beta\epsilon_r} - 1}$$

The calculation of S proceeds in exactly the same way as in (a). We quote the result.

$$S = -k\sum_r \bar{n}_r \ln\bar{n}_r - (1+\bar{n}_r)\ln(1+\bar{n}_r) \tag{5}$$

(c) From (4) and (5) we see that in the classical limit where $\bar{n}_r \ll 1$

$$S \to -k\sum_r \bar{n}_r \ln\bar{n}_r$$

for both FD and BE statistics.

9.3

The partition function in $\zeta^N/N!$ where

$$\zeta = \sum_{\kappa_x \kappa_y \kappa_z} \exp\left[-\frac{\beta\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2)\right] \tag{1}$$

The sum is over all positive $\kappa_x \kappa_y \kappa_z$ when we use the standing wave solution, equation (9.9.22). The density of state is now greater than in the traveling wave case, and by (9.9.25)

$$\rho_\kappa \, d^3\kappa = \frac{V}{\pi^3} d^3\kappa$$

If we assume that successive terms in ζ differ little from each other, we can approximate (1) with integrals.

Thus
$$\sum_{\kappa_x=0}^{\infty} e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \approx \int_0^{\infty} e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \left(\frac{L_x}{\pi}\, d\kappa_x\right)$$

$$= \frac{L_x}{2\pi\hbar}\left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}} \quad \text{by (A.3.6)}$$

Hence
$$\zeta = \frac{V}{h^3}(2\pi\, m\, kT)^{\frac{3}{2}}$$

which is identical to (9.10.7).

9.4

(a) The chemical potential can be found from the Helmholtz free energy, $F = -kT \ln Z$.

$$F = -kT \ln \frac{\zeta^N}{N!} \approx -kT\,[N \ln \zeta - N \ln N + N]$$

where we have used Sterling's approximation, $\ln N! \approx N \ln N - N$ and $\zeta = \frac{V}{h^3}(2\pi\, m\, kT)^{\frac{3}{2}}$.

Then
$$\mu = \frac{\partial F}{\partial N} = -kT \ln \frac{\zeta}{N} \tag{1}$$

(b) The partition function for a single molecule of a 2 dimensional gas with binding energy $-\epsilon_o$
is
$$\zeta' = \sum_{\kappa_x \kappa_y} \exp\left[-\frac{\beta\hbar^2}{2m}(\kappa_x^2+\kappa_y^2)+\beta\epsilon_o\right] \approx e^{\beta\epsilon_o}\iint_{-\infty}^{\infty} \exp\left[-\frac{\beta\hbar^2}{2m}(\kappa_x^2+\kappa_y^2)\right]\frac{A}{(2\pi)^2}\,d\kappa_x d\kappa_y$$

where A is the area. Thus $\zeta' = e^{\beta\epsilon_o}\zeta^{\frac{2}{3}}$ where we put $A = V^{\frac{2}{3}}$.

Hence
$$\mu' = -kT \ln \frac{\zeta'}{N'} = -kT \ln \frac{e^{\beta\epsilon_o}\zeta^{\frac{2}{3}}}{N'} \tag{2}$$

(c) In equilibrium $\mu = \mu'$ and by (1) and (2)
$$\frac{\zeta}{N} = \frac{e^{\beta\epsilon_o}\zeta^{\frac{2}{3}}}{N'}$$

or
$$\frac{V}{N}\frac{(2\pi\, m\, kT)^{\frac{3}{2}}}{h^3} = e^{\beta\epsilon_o}\frac{A}{N'}\frac{(2\pi\, m\, kT)}{h^2}$$

Letting $n' = N'/A$ and since $\bar{p}/kT = N/V$, we find

$$n' = \bar{p}h\,(2\pi m\, k^3 T^3)^{-1/2}\, e^{\epsilon_o/kT}$$

9.5

(a) By equation (9.9.14) if $L = L_x = L_y = L_z = V^{\frac{1}{3}}$ we have

$$\epsilon_r(V) = \frac{2\pi^2 \hbar^2 V^{-\frac{2}{3}}}{m}(n_x^2 + n_y^2 + n_z^2) \qquad (1)$$

(b)
$$p_r = -\left(\frac{\partial \epsilon_r}{\partial V}\right) = \frac{2\pi^2 \hbar^2}{m}\left(\frac{2}{3}V^{-\frac{5}{3}}\right)(n_x^2 + n_y^2 + n_z^2)$$

$$= \frac{2}{3}\frac{\epsilon_r}{V} \qquad (2)$$

(c) The mean pressure is $\bar{p} = \sum_r \bar{n}_r\, p_r$ where $\bar{n}_r$ is the mean number of particles in state r.

Thus
$$\bar{p} = \frac{2}{3V} \sum_r \bar{n}_r\, \epsilon_r = \frac{2}{3}\frac{\bar{E}}{V}$$

(d) The expression for $\bar{p}$ is valid for a system in which the energy of a quantum state is given by (1). For photons,

$$\epsilon_r = c\hbar\kappa = \hbar c\left(2\pi V^{-\frac{1}{3}}(n_x^2 + n_y^2 + n_z^2)\right)^{\frac{1}{2}}$$

Hence
$$p_r = -\left(\frac{\partial \epsilon_r}{\partial V}\right) = \frac{1}{3}\frac{\epsilon_r}{V} \quad\text{and}\quad \bar{p} = \frac{1}{3}\frac{\bar{E}}{V}$$

(e) The mean force on the wall is found by multiplying the change of momentum per collision, $2mv$, by the number of particles which collide with the wall per unit time, $\frac{1}{6}\,n\bar{v}A$. Hence the pressure is

$$\bar{p} = \frac{1}{A}(2m\bar{v})(\tfrac{1}{6}n\bar{v}A) = \frac{1}{3}nm\bar{v}^2$$

Letting $\bar{v}^2 \approx \overline{v^2}$ we have

$$\bar{p} = \frac{1}{3}nm\overline{v^2} = \frac{2}{3}\frac{N}{V}(\tfrac{1}{2}m\overline{v^2}) = \frac{2}{3}\frac{\bar{E}}{V} \qquad (3)$$

since $N(\tfrac{1}{2}m\overline{v^2}) = \bar{E}$.   Equation (3) is the exact result as shown in section 7.14.

9.6

(a) The dispersion is $\overline{(\Delta p)^2} = \overline{p^2} - \bar{p}^2$. By problem 9.5, $\bar{p}^2 = \frac{4}{9}\frac{\bar{E}^2}{V^2}$, and it remains to find $\overline{p^2}$.

$$\overline{p^2} = \sum_r \bar{n}_r\, p_r^2 = \frac{4}{9V^2}\sum_r \bar{n}_r\,\epsilon_r^2 \quad\text{by (2) in 9.5}$$

$$= \frac{4}{9}\frac{\overline{E^2}}{V^2}$$

Hence
$$\overline{(\Delta p)^2} = \frac{4}{9V^2}(\overline{E^2} - \bar{E}^2) = \frac{4}{9V^2}\overline{(\Delta E)^2}$$

(b) Since $\bar{E} = -\frac{\partial}{\partial\beta}\ln Z$ and $\overline{(\Delta E)^2} = \frac{\partial^2}{\partial\beta^2}\ln Z$, it follows that

$$\overline{(\Delta p)^2} = \frac{4}{9V^2} \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{4}{9V^2} \frac{\partial \overline{E}}{\partial \beta}$$

but by (2) in 9.5, $\overline{E} = \frac{3}{2} V \overline{p}$.

Thus
$$\overline{(\Delta p)^2} = -\frac{2}{3V} \frac{\partial \overline{p}}{\partial \beta} = \frac{2kT^2}{3V} \frac{\partial \overline{p}}{\partial T}$$

(c) Substituting $\overline{p} = \frac{N}{V} kT$, we find
$$\overline{(\Delta p)^2} / \overline{p}^2 = \frac{2kT^2}{3V} (\frac{N}{V} kT)^{-2} \frac{\partial}{\partial T} (\frac{N}{V} kT) = \frac{2}{3N}$$

*9.7

The probability that a state of energy ϵ is occupied is proportional to the Boltzmann factor $e^{-\epsilon/kT_o}$. Since the vibrational levels have a spacing large compared to kT_o, we see that $e^{-\epsilon/kT_o}$ is small and we may neglect this contribution to the specific heat. On the other hand, the spacing between rotational levels is small so that these states are appreciably excited. For a dumbbell molecule the rotational energy should be

$$\epsilon_r = \frac{1}{2} A_1 \omega_1^2 + \frac{1}{2} A_2 \omega_2^2$$

where A is the moment of inertia and ω the angular frequency. We have neglected rotation about the axis of the molecule because the moment of inertia is small.   At room temperature, we may use the equipartion theorem yielding $\overline{\epsilon}_r = kT_o$. Adding the energy of the translational motion gives for the total energy
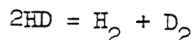
$$\overline{\epsilon} = \overline{\epsilon}_t + \overline{\epsilon}_r = \frac{3}{2} kT_o + kT_o = \frac{5}{2} kT_o$$

Thus the molar specific heat is

$$c = N_A \frac{\partial \overline{\epsilon}}{\partial T_o} = \frac{5}{2} N_A k = \frac{5}{2} R$$

9.8

The reaction proceeds according to
$$2HD = H_2 + D_2$$

and the law of mass action becomes

$$\frac{n_{H_2} n_{D_2}}{n_{HD}^2} = K_n = \frac{\zeta_{H_2} \zeta_{D_2}}{\zeta_{HD}^2} \qquad (1)$$

From the results of section 9.12, we can immediately write down the quantities ζ. In the notation of that section,

$$\zeta_{H_2} = \frac{V}{h^3} [2\pi(2m)\,kT]^{\frac{3}{2}}\, e^{\beta\epsilon'_{H_2}}\, \frac{2A_{H_2}\,kT}{2\hbar^2}\, e^{-\frac{1}{2}\beta\hbar\omega_{H_2}}$$

$$\zeta_{D_2} = \frac{V}{h^3} [2\pi(2M)\,kT]^{\frac{3}{2}}\, e^{\beta\epsilon'_{D_2}}\, \frac{2A_{D_2}\,kT}{2\hbar^2}\, e^{-\frac{1}{2}\beta\hbar\omega_{D_2}}$$

$$\zeta_{HD} = \frac{V}{h^3} [2\pi(m+M)kT]^{\frac{3}{2}}\, e^{\beta\epsilon'_{HD}}\, \frac{2A_{HD}\,kT}{\hbar^2}\, e^{-\frac{1}{2}\beta\hbar\omega_{HD}}$$

where we have assumed that molecules are predominantly in the lowest vibrational state and have treated the rotational degrees of freedom classically.

The electronic ground state energies ϵ' are approximately equal for the three species since this quantity is altered only slightly by the addition of a neutral particle to the neucleus (to form D). Thus

$$\epsilon'_{HD} \approx \epsilon'_{H_2} \approx \epsilon'_{D_2} \tag{2}$$

Similarly, the moments of inertia are of the form

$$A = \frac{1}{2}\mu^* R_o^2 = \frac{1}{2}\frac{m_1 m_2}{m_1+m_2} R_o^2$$

where R_o, the equilibrium distance between nuclei, depends primarily on electromagnetic forces. It is then approximately the same for the three species, and we have

$$A_{H_2}\, A_{D_2}\, A_{HD}^{-2} = \left(\frac{m}{2}\right)\left(\frac{M}{2}\right)\left(\frac{mM}{m+M}\right)^{-2} = \frac{1}{4}\frac{(m+M)^2}{mM} \tag{3}$$

Finally, the frequency for two masses coupled by a spring of constant κ is

$\omega = \left(\frac{\kappa(m_1+m_2)}{m_1 m_2}\right)^{\frac{1}{2}}$. Again, κ must be the same for the three molecules, and

$$\omega_{HD} = \left(\frac{\kappa(m+M)}{mM}\right)^{\frac{1}{2}} = \omega_o$$

$$\omega_{D_2} = \left(\frac{2\kappa}{M}\right)^{\frac{1}{2}} = \left(\frac{2m}{m+M}\right)^{\frac{1}{2}}\omega_o \tag{4}$$

$$\omega_{H_2} = \left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} = \left(\frac{2M}{m+M}\right)^{\frac{1}{2}}\omega_o$$

Substituting the ζ's into (1) and using the results (2), (3), and (4) yields

$$K_n = \frac{1}{2}\frac{(mM)^{\frac{1}{2}}}{(m+M)} \exp\left[\frac{\hbar\omega_o}{kT}\left(1 - \frac{m^{\frac{1}{2}}+M^{\frac{1}{2}}}{[2(m+M)]^{\frac{1}{2}}}\right)\right]$$

Since $n_{H_2} = n_{D_2}$, we have

$$\left(\frac{N - n_{HD}}{2}\right)^2 = K_n \; n_{HD}^2$$

or

$$\frac{n_{HD}}{N} = \frac{1}{1 + 2\sqrt{K_n}} \approx \frac{1}{2\sqrt{K_n}}$$

$$\approx \left[\frac{(m+M)^2}{mM}\right] \exp\left[-\frac{\hbar\omega}{2kT}\left(1 - \frac{m^{\frac{1}{2}} + M^{\frac{1}{2}}}{[2(m+M)]^{\frac{1}{2}}}\right)\right]$$

9.9

In a thermally isolated quasistatic process, there is no entropy change. Hence by the first law,

$$T \, dS = 0 = d\bar{E} + \bar{p} \, dV$$

Substituting $\bar{E} = V\bar{u}$ and $\bar{p} = \frac{1}{3}\bar{u}$ where $\bar{u}(T)$ is the energy density, we have

$$0 = \bar{u} \, dV + V \, d\bar{u} + \frac{1}{3}\bar{u} \, dV$$

Thus $-\int_V^{8V} \frac{4}{3} \frac{dV'}{V'} = \int \frac{d\bar{u}}{\bar{u}} = \int_{T_i}^{T_f} 4 \frac{dT'}{T'}$ since $\bar{u} \propto T^4$. Integrating, we find $-\frac{4}{3}\ln 8 = 4 \ln \frac{T_f}{T_i}$

or

$$T_f = \frac{T_i}{2}$$

9.10

(a) By the fundamental thermodynamic relation

$$T \, dS = d\bar{E} + \bar{p} \, dV$$

Then substituting $\bar{E} = V\bar{u}$ and $\bar{p} = \frac{1}{3}\bar{u}$, we have

$$T \, dS = \bar{u} \, dV + V \, d\bar{u} + \frac{1}{3}\bar{u} \, dV = \frac{4}{3}\bar{u} \, dV + V \, d\bar{u}$$

But since $\bar{u}$ is only a function of T, $d\bar{u} = \frac{d\bar{u}}{dT} dT$, and it follows that

$$dS = \frac{4}{3}\frac{\bar{u}}{T} \, dV + \frac{V}{T}\frac{d\bar{u}}{dT} \, dT \qquad (1)$$

We also have $\qquad dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \qquad (2)$

Equating coefficients in (1) and (2) yields

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4}{3}\frac{\bar{u}}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{d\bar{u}}{dT} \qquad (3)$$

(b) Since $(\partial^2 S/\partial V \, \partial T) = (\partial^2 S/\partial T \, \partial V)$, it follows from (3) that

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$$\frac{d\bar{u}}{dT} = \frac{4\bar{u}}{T} \quad \text{or} \quad 4 \int \frac{dT}{T} = \int \frac{d\bar{u}}{\bar{u}}$$

Thus $\ln T^4 = \ln \bar{u} + C$ where C is the constant of integration. Finally $\bar{u} \propto T^4$.

9.11

The energy of the black body radiation in the dielectric is

$$\bar{E} = V\bar{u} = V \frac{\pi^2}{15} \frac{(kT)^4}{(c'\hbar)^3}$$

where c' is the velocity of light in the material. c' is related to the velocity of light in vacuum by $c' = c/n_o$, n_o being the index of refraction.

Thus

$$\bar{E} = V \frac{\pi^2}{15} \frac{(kT)^4}{(c\hbar)^3} n_o^3 = \frac{4\sigma n_o^3 V T^4}{c}$$

Here σ is the Stefan Boltzmann constant, $\sigma = \pi^2 k^4 / 60 \, c^2 \hbar^3$.

Hence

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{16 \, \sigma n_o^3 V T^3}{c} \tag{1}$$

Substituting v, the volume per mole, for V in (1) gives the heat capacity per mole, c_V'. The classical lattice heat capacity per mole is $c_V = 3R$. The ratio of these two quantities is

$$\frac{c_V'}{c_V} = \frac{16 \, \sigma n_o^3 v T^3}{3Rc}$$

For an order of magnitude calculation, we can let $v = 10 \text{ cm}^3/\text{mole}$ and $n_o = 1.5$. At $300^\circ K$, we find $c_V'/c_V \approx 10^{-13}$.

9.12

(a) The total rate of electromagnetic radiation or power is

$$P = \mathcal{P}(4\pi r^2) = 4\pi r^2 \sigma T^4$$

$$= (4\pi)(10^2)(5.7 \times 10^{-5})(10^6)^4 = 7.2 \times 10^{22} \text{ ergs/sec}$$

$$= 7.2 \times 10^{15} \text{ watts}$$

(b) Since the total energy/sec crossing the area of a sphere of radius r' = 1km must be the same as that crossing the sphere of radius r = 10 cm, we have

$$\mathcal{P}'(4\pi r'^2) = \mathcal{P}(4\pi r^2)$$

or

$$\mathcal{P}' = \mathcal{P}\left(\frac{r}{r'}\right)^2 = \sigma T^4 \left(\frac{r}{r'}\right)^2 = (5.7 \times 10^{-5})(10^6)^4 \left(\frac{10}{10^5}\right)^2$$

$$= 5.7 \times 10^{11} \text{ergs/sec cm}^2 = 5.7 \times 10^4 \text{ watts/cm}^2$$

(c) The power spectrum has a maximum at

$$\frac{\hbar\omega_{max}}{kT} = \frac{hc}{kT \, \lambda_{max}} = 3$$

Thus

$$\lambda_{max} = \frac{(6.6 \times 10^{-27})(3 \times 10^{10})}{(3)(1.4 \times 10^{-16})(10^6)} = 47 \times 10^{-8} \text{ cm} = 47 \text{ Å}$$

9.13

(a) The power given off by the sun is

$$P = \sigma \, T_o^4 \, (4\pi \, R^2)$$

Half the earth's surface intercepts radiation from the sun at any time. Hence the power that the earth absorbs is

$$P_i = \sigma \, T_o^4 (4\pi R^2) \left(\frac{2\pi r^2}{4\pi L^2}\right)$$

The power that the earth emits is

$$P_e = \sigma \, T^4 (4\pi r^2)$$

In equilibrium, the power incident upon the earth is equal to the power it radiates, or $P_i = P_e$

Thus

$$\sigma T_o^4 (4\pi R^2)\left(\frac{2\pi r^2}{4\pi L^2}\right) = \sigma T^4 (4\pi \, r^2)$$

$$T = T_o \sqrt{\frac{R}{2L}} \tag{1}$$

(b) From Eq. (1)

$$T = (5500) \left[\frac{7 \times 10^{10}}{2(1.5 \cdot 10^{13})}\right]^{1/2} = 270^\circ K$$

9.14

We consider the liquid in equilibrium with its vapor (at vapor pressure p). By (7.12.13), the flux of molecules incident on the liquid is $p/\sqrt{2\pi \, m \, kT}$, and this must also be the flux $\mathcal{N}$ of particles escaping from the liquid. Since $\mathcal{N}$ cannot depend on the conditions outside the liquid, this is the escaping flux at all pressures.

Thus

$$\mathcal{N} = \frac{p}{\sqrt{2\pi \, m \, kT}}$$

The mass of a water molecule is $m = 18/6.02 \cdot 10^{23} = 2.99 \cdot 10^{-23}$. Thus for water at $25^\circ C$ where $p = 23.8 \text{ mm Hg} = 3.17 \cdot 10^4 \text{ dynes/cm}^2$ we have

$$\mathcal{N} = \frac{3.17 \cdot 10^4}{(2\pi \times 2.99 \times 10^{-23} \times 1.38 \times 10^{-16} \times 298)^{\frac{1}{2}}} = 1.14 \times 10^{22} \frac{\text{molecules}}{\text{sec} \cdot \text{cm}^2}$$

9.15

At the vapor pressure $p(T)$, the flux of molecules of the vapor incident on the wire is by (7.11.13), $\varphi_i = p/\sqrt{2\pi m kT}$. When the metal is in equilibrium with its vapor, the emitted flux must equal the incident flux, $\varphi_e = \varphi_i$. Then when the temperature is T, the number of particles emitted from the wire per unit length in time t is

$$N = \frac{p(T)\, 2\pi r\, t}{\sqrt{2\pi m\, kT}}$$

But $N = \Delta M/m$ where ΔM is the mass lost per unit length and m is the mass per molecule.

Thus
$$\frac{\Delta M}{m} = \frac{p(T)\, 2\pi r\, t}{\sqrt{2\pi m\, kT}}$$

or
$$p(T) = \frac{\Delta M}{rt}\sqrt{\frac{RT}{2\pi\mu}}$$

where we have used $\mu = mN_A$ and $R = N_A k$.

9.16

$\overline{v}_x = 0$ by symmetry.

By definition,
$$\overline{v_x^2} = \frac{\int d^3\underline{v}\, f(\underline{v})\, v_x^2}{\int d^3\underline{v}\, f(\underline{v})} \tag{1}$$

At absolute zero, the particles fill all the lowest states so that the distribution $f(\underline{v})$ is just a constant and cancels in (1). The maximum speed is at $\frac{1}{2}mv_F^2 = \mu$. By symmetry, $\overline{v_x^2} = \frac{1}{3}\overline{v^2}$ and (1) becomes

$$\overline{v_x^2} = \frac{\frac{4\pi}{3}\int_o^{v_F} v^4\, dv}{4\pi\int_o^{v_F} v^2\, dv} = \frac{1}{5}v_F^2 = \frac{2}{5}\frac{\mu}{m}$$

9.17
(a)
At T = 0 all states are filled up to the energy μ. Hence

the mean number of particles per state is just 1 and we have

$$\overline{E} = \int_o^\mu \epsilon\rho\,(\epsilon)\, d\epsilon$$

By (9.9.19)
$$\rho(\epsilon)d\epsilon = 2\frac{V}{4\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\epsilon^{\frac{1}{2}}\, d\epsilon$$

where the factor 2 is introduced since electrons have two spin states.

$$\overline{E} = \frac{V}{2\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\int_o^\mu \epsilon^{\frac{3}{2}}\, d\epsilon = \frac{V(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3}\mu^{\frac{5}{2}}$$

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(b)

Since $\mu = \frac{\hbar^2}{2m} (3\pi^2 \frac{N}{V})^{\frac{2}{3}}$ by (9.15.10), it follows that

$$\bar{E} = \frac{3}{5} N\mu \qquad (1)$$

(c) Substituting the expression for μ in (1) we have

$$\bar{E} = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2}{m} (\frac{N}{V})^{\frac{2}{3}} N \qquad (2)$$

As particles are added, each new particle can go only into an unfilled level of higher energy than the one before. Hence the energy is not proportional to N as it would be if particles were added to the same level.

9.18

(a) Differentiating $\bar{E}$ in 9.17 (c) gives

$$\bar{p} = - (\frac{\partial \bar{E}}{\partial V})_T = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m} (\frac{N}{V})^{5/3} \qquad (1)$$

(b) Again from 9.17 (c) we find

$$\bar{p} = \frac{2}{3} \frac{\bar{E}}{V} = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m} (\frac{N}{V})^{5/3}$$

(c) For Cu metal, $N/V = 8.4 \times 10^{22}$ electrons/cm^3. Substituting into (1) where m is the mass of the electron, we find $\bar{p} \approx 10^5$ atom. This enormous pressure shows that to confine a degenerate electron gas, a strong containing volume such as the lattice of a solid is required even at $0°K$.

9.19

From the general relation $TdS = \bar{d}Q = CdT$, we have that if the heat capacity is proportional to a power of the temperature, $C \propto T^a$

$$\Delta S = \int \frac{CdT}{T} \propto \int T^{a-1} dT \propto T^a$$

Thus the entropy is proportional to the same power of the temperature as is the heat capacity.

(a) The heat capacity and entropy of conduction electrons in a metal is proportional to T. Hence the ratio of the final and initial entropies is

$$\frac{S_f}{S_i} = \frac{400}{200} = 2$$

(b) The energy of the radiation field inside an enclosure is proportional to T^4, and the heat capacity has a T^3 dependence.

Thus

$$\frac{S_f}{S_i} = (\frac{2000}{1000})^3 = 8$$

9.20

(a) At $T = 0$, the total number of states within a sphere of radius κ_F must equal the total number of particles N.

Thus
$$2 \frac{V}{(2\pi)^3} \left(\frac{4}{3} \pi \kappa_F^3\right) = N$$

or
$$\kappa_F = \left(3\pi^2 \frac{N}{V}\right)^{\frac{1}{3}}$$

Substituting $\mu = \hbar^2 \kappa_F^2/2m$, we find
$$\mu = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V}\right)^{\frac{2}{3}} \tag{1}$$

The number of particles per cm^3, N/V, is $N_A \rho/\mu$ where N_A is Avogadro's number, $\rho = .95$ gm/cm^3, and $\mu = 23$. From (1) we find the Fermi temperature $T_F = \mu/k = 36,000°K$.

(b) To cool 100 cm^3 or 4.13 moles of Na from $1°K$ to $.3°K$, an amount of heat Q must be removed.

$$Q = \nu \int_1^{.3} c_V \, dT$$

where c_V is given by (9.16.23), $c_V = \frac{3}{2} R \left(\frac{\pi^2}{3} \frac{kT}{\mu}\right)$.

Thus
$$Q = (4.14)\left(\frac{3}{2} R\right)\left(\frac{\pi^2}{3} \frac{k'}{\mu}\right) \int_1^{.3} T \, dT = -.0022 \text{ joules}$$

Hence $.0022/.8 = .0027$ cm^3 of He^3 are evaporated. Note that a large amount of substance is cooled by a very small amount of helium.

9.21

(a) If electrons obeyed MB statistics, the susceptibility would be $\chi_{MB} = N\mu_m^2/kT$ where μ_m is the magnetic moment. In the actual case, most electrons cannot change their spin orientation when an external field is applied because the parallel states are already occupied. Only electrons near the top of the distribution can turn over and thus contribute to χ. We expect then, that the correct expression for χ is χ_{MB} with N replaced by the number of electrons in this region, N_{eff}.

$$N_{eff} = \left(\frac{kT}{\mu}\right)N = \left(\frac{T}{T_F}\right) N$$

where T_F is the Fermi temperature.

Thus
$$\chi = N_{eff} \frac{\mu_m^2}{kT} = \frac{N\mu_m^2}{kT_F} \tag{1}$$

(b) Since T_F is on the order of 10^4 or 10^5, (1) yields a χ per mole on the order of 10^{-6}. If electrons obeyed MB statistics, χ would be changed by the factor
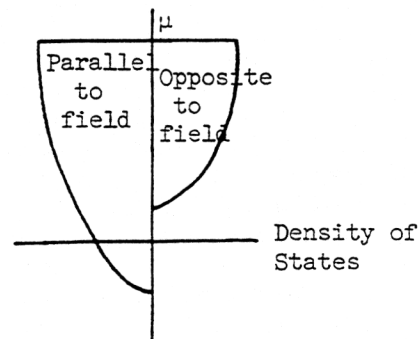
$$\frac{\chi_{MB}}{\chi} = \left(\frac{N\mu^2}{kT}\right) \Big/ \left(\frac{N\mu^2}{kT_F}\right) = \frac{T_F}{T}$$

This is on the order of 100 at room temperatures.

9.22

When the field H is turned on, the energy levels
of the parallel spins shift by $-\mu_m H$ while the
levels of the antiparallel spins shift by $+\mu_m H$.
The electrons fill up these states to the Fermi
energy μ as shown in the figure. The magnetic
moment is determined by the number of electrons
which spill over from antiparallel states to

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parallel states to minimize the energy. This is $(\mu_m H)\rho(\mu_o)$ where $\rho(\mu_o)$ is the density of states
at the Fermi energy μ_o. Consequently the magnetization is

$$M = 2\mu_m^2 \, \rho(\mu_o) \, H/V$$

But since $\rho(\mu_o) = \frac{3}{4}\frac{N}{\mu_o}$, we have

$$M = \frac{3}{2}\frac{\mu_m^2}{\mu_o}\frac{N}{V} H$$

and

$$\chi = \frac{M}{H} = \frac{3}{2}\frac{n\mu_m^2}{\mu_o} \quad \text{where } n = \frac{N}{V}$$

9.23

If we choose the zero of energy to be that of the electrons in the metal, the partition function
of an electron in the gas outside the metal is by (9.10.7)

$$\zeta = \frac{2V}{h^3}(2\pi\, m\, kT)^{\frac{3}{2}} e^{-V_o/kT}$$

where the factor 2 occurs because electrons have two spin states. The chemical potential μ_o is
found from the Helmholtz free energy.

$$F = -kT \ln Z = -kT\,[N \ln \zeta - N \ln N + N]$$

$$\mu_o = \frac{\partial F}{\partial N} = -kT \ln \frac{\zeta}{N} = -kT \ln \frac{2V}{Nh^3}(2\pi m\, kT)^{\frac{3}{2}} e^{-V_o/kT}$$

The chemical potential inside the metal is just $\mu = V_o - \Phi$, and in equilibrium the chemical
potentials inside and outside are equal, i.e., $\mu = \mu_o$.

Thus

$$e^{-\mu/kT} = e^{(\Phi-V_o)/kT} = \frac{2V}{Nh^3} (2\pi m\ kT)^{\frac{3}{2}} e^{-V_o/kT}$$

Hence the mean number of electrons per unit volume outside the metal is

$$n = \frac{N}{V} = \frac{2}{h^3} (2\pi\ m\ kT)^{\frac{3}{2}} e^{-\Phi/kT} \tag{1}$$

9.24

Consider a situation in which the metal is in equilibrium with an electron gas. Then the emitted flux is related to the incident flux by

$$\Phi_e = (1-r)\ \Phi_i \tag{1}$$

The electron gas outside the metal may be treated as a classical ideal gas from which it follows that the incident flux is

$$\Phi_i = \frac{1}{4} n\bar{v} = \frac{1}{4} \left[\frac{2}{h^3} (2\pi m\ kT)^{\frac{3}{2}} e^{-\Phi/kT} \right] \left[\frac{8\ kT}{\pi m} \right]^{\frac{1}{2}}$$

where we haved used (1) of problem 9.23. The emitted flux is then given by (1). But since the emitted flux cannot depend on the conditions outside the metal, this is also the flux where equilibrium does not prevail. Thus the current density is

$$J = e\Phi_e = \frac{4\pi\ m\ e(1-r)}{h^3} (kT)^2\ e^{-\Phi/kT}$$

where e is the electronic charge.

9.25

There are $(2\pi)^{-3}\ d^3\underline{\kappa}$ states per unit volume in the range $(\kappa:d\kappa)$ and with a particular direction of spin orientation. Since the mean number of electrons with one value of $\underline{\kappa}$ is $1/[e^{\beta(\epsilon-\mu)} + 1]$ where $\epsilon = \hbar^2\kappa^2/2m$, we obtain

$$f(\underline{\kappa})d^3\underline{\kappa} = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \frac{d^3\underline{\kappa}}{(2\pi)^3}$$

If we take the z direction to be the direction of emission, the number of electrons with wave vector in the range $(\underline{\kappa}:d\underline{\kappa})$ and of either spin direction which strike unit area of the surface of the metal per unit time is

$$\Phi(\underline{\kappa})\ d^3\underline{\kappa} = 2f(\underline{\kappa})\ v_z\ d^3\underline{\kappa} \tag{1}$$

Then the total current density emitted is given by summing (1) over all values of $\underline{\kappa}$ which will allow the electrons to escape. That is, the part of the kinetic energy resulting from motion in the z direction must be greater than V_o, or $\hbar^2\kappa_z^2/2m > V_o$, where we use the notation of problem

9.23. In addition, we assume that a fraction **r** of electrons of all energies are reflected. Thus the electron current density is

$$J = e\Phi_e = \frac{2e(1-r)}{(2\pi)^3} \int_{-\infty}^{\infty} d\kappa_x \int_{-\infty}^{\infty} d\kappa_y \int_{\sqrt{2mV_o}/\hbar}^{\infty} \frac{(\hbar\kappa_z/m)\, d\kappa_z}{1 + \exp\left[\frac{\beta\hbar^2}{2m}(\kappa_x^2+\kappa_y^2+\kappa_z^2) -\beta\mu\right]}$$

where e is the electronic charge. The integral over κ_z is of the form

$$\int \frac{x\,dx}{1+e^{x^2-\alpha}} = \int \frac{xe^{-x^2+\alpha}}{e^{-x^2+\alpha}+1} = -\frac{1}{2}\ln[1+e^{-x^2+\alpha}]$$

Hence
$$J = \frac{2e(1-r)}{(2\pi)^3}\frac{\hbar}{m}\frac{m}{\hbar^2\beta} \int_{-\infty}^{\infty} d\kappa_x \int_{-\infty}^{\infty} d\kappa_y\ \ln\left(1 + \exp\left[\beta(\mu-V_o)-\beta\hbar^2(\kappa_x^2+\kappa_y^2)/2m\right]\right)$$

Since $V_o > \mu$ and, in general, $|\beta(\mu-V_o)| \gg 1$, we can use $\ln(1+x) \approx x$ to expand the logarithm and obtain

$$J = \frac{2e(1-r)}{(2\pi)^3}\frac{e^{\beta(\mu-V_o)}}{\hbar\beta} \int_{-\infty}^{\infty} e^{-\beta\hbar^2\kappa_x^2/2m}\,d\kappa_x \int_{-\infty}^{\infty} e^{-\beta\hbar^2\kappa_y^2/2m}\,d\kappa_y$$

Each of these integrals is $(2\pi m/\beta\hbar^2)^{1/2}$ by appendix A.4, and

$$J = \frac{4\pi\,me\,(1-r)}{h^3}(kT)^2\,e^{-\Phi/kT}$$

9.26

(a) Since the integrand in (9.17.9) is even, one can write

$$I_2 = \int_{-\infty}^{\infty} \frac{e^x x^2}{(e^x+1)^2}\,dx = 2\int_o^{\infty} \frac{e^x\,x^2}{(e^x+1)^2}$$

$$= 2\left[-\frac{x^2}{e^x+1}\right]_o^{\infty} + 4\int_o^{\infty} \frac{x\,dx}{e^x+1}$$

where we have integrated by parts. Since the first term on the right vanishes

$$I_2 = 4\int_o^{\infty} \frac{x\,dx}{e^x+1} \qquad (1)$$

(b) This expression can be evaluated by series expansion. Since $e^{-x} < 1$ one can write

$$\frac{x}{e^x+1} = \frac{e^{-x}\,x}{1+e^{-x}} = e^{-x}x\,[1 - e^{-x}+e^{-2x}-e^{-3x}\ldots]$$

$$= \sum_{n=0}^{\infty} (-1)^n\,e^{-(n+1)x}\,x\,dx$$

Hence (1) becomes

$$I_2 = 4 \sum_{n=0}^{\infty} (-1)^n \int_0^{\infty} e^{-(n+1)x} \, x \, dx = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)^2} \int_0^{\infty} e^{-y} \, y \, dy$$

The integral is, by appendix A.4, equal to unity. Thus

$$I_2 = 4 \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)^2} = 4 \left[1 - \frac{1}{2^2} + \frac{1}{3^2} - \frac{1}{4^2} \cdots \right] \equiv 4S \qquad (2)$$
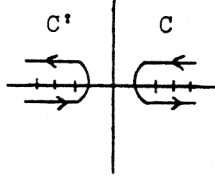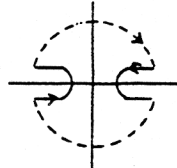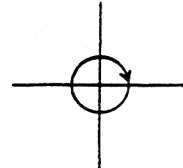
(c)

Fig. 1   Fig. 2   Fig. 3

One can use the contour C of Fig. (1) to write

$$\int_C \frac{1}{z^2 \sin \pi z} \, dz = 2\pi i \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2 \pi} = 2i \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \qquad (3)$$

or

$$\int_C \frac{dz}{z^2 \sin \pi z} = -2i \, S \qquad (4)$$

Here the integrand $\to 0$ for $z \to \infty$. The sum in (2) is unchanged if $n \to -n$. Hence one could equally well write the symmetric expression

$$\int_{C'} \frac{dz}{z^2 \sin \pi z} = -2i \, S \qquad (5)$$

along the contour C' of Fig. (1). Adding (3) and (4) one gets then

$$\int_{C+C'} \frac{dz}{z^2 \sin \pi z} = -4i \, S \qquad (6)$$

But here the contour can be completed along the infinite semi-circles as shown in Fig. (2) since the integrand vanishes as $|z| \to \infty$. Except for $z = 0$, there is no other singularity in the enclosed area so that the contour can be shrunk down around an infinitesimal circle C_0 surrounding $z = 0$ as shown in Fig. (3). For $z \approx 0$,

$$\frac{1}{z^2 \sin \pi z} = \frac{1}{z^2 [\pi z - \frac{1}{6}\pi^3 z^3 \cdots]} = \frac{1}{\pi z^3} [1 - \frac{1}{6}\pi^2 z^2 \cdots]^{-1}$$

$$= \frac{1}{\pi z^3} [1 + \frac{1}{6}\pi^2 z^2 \cdots] = \frac{1}{\pi z^3} + \frac{\pi}{6z} + \cdots$$

Hence

$$\int_{C_0} \frac{dz}{z^2 \sin \pi z} = (-2\pi i)\left(\frac{\pi}{6}\right) = -\frac{i\pi^2}{3}$$

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Thus it follows by (5) that

$$-\frac{i\pi^2}{3} = -4iS$$

or

$$S = -\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} = \frac{\pi^2}{12}$$
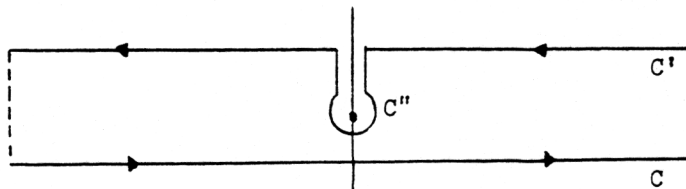
and by (2), $I_2 = \pi^2/3$.

9.27

(a) We expand e^{ikx} in the integral

$$J(k) = \int_{-\infty}^{\infty} \frac{e^{ikx}\,dx}{(e^x+1)(e^{-x}+1)} = \int_{-\infty}^{\infty} \frac{e^x\,e^{ikx}\,dx}{(e^x+1)^2} \tag{1}$$

$$= \int_{-\infty}^{\infty} \frac{e^x\,dx}{(e^x+1)^2} \sum_{m=0}^{\infty} \frac{(ik)^m}{m!}\, x^m$$

Interchanging the sum and integral yields

$$J(k) = \sum_{m=0}^{\infty} \frac{(ik)^m}{m!} \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\, x^m\, dx = \sum_{m=0}^{\infty} \frac{(ik)^m}{m!}\, I_m \tag{2}$$

(b) Putting $x=z$ in (1) to denote a complex variable, we evaluate the integral on the closed contour shown in the figure. Here C' is the path where z is increased by $2\pi i$ and C" is a small circle around the singularity at $i\pi$. Then the integral on the complete path is zero since there are no singularities in the region bounded by the contour.

But the integral is 0 at $x = \pm \infty$ and cancels along the imaginary axis. Hence

$$\int_C \frac{e^{ikz}\,dz}{(e^z+1)(e^{-z}+1)} = \int_{C'+C''} \frac{e^{ikz}\,dz}{(e^z+1)(e^{-z}+1)} \tag{3}$$

where both integrals are evaluated from left to right. Along C' where $z = x + 2\pi i$, we have since $e^{x+2\pi i} = e^x$

$$\int_{C'} \frac{e^{ikz}\,dz}{(e^z+1)(e^{-z}+1)} = \int_{-\infty}^{\infty} \frac{e^{ik(x+2\pi i)}}{(e^x+1)(e^{-x}+1)}\, dx = e^{-2\pi k} \int_{-\infty}^{\infty} \frac{e^{ikx}\,dx}{(e^x+1)(e^{-x}+1)}$$

The last integral is just $J(k)$. Thus from (3) we have

$$(1-e^{-2\pi k}) \int_C \frac{e^{ikz} \, dz}{(e^z+1)(e^{-z}+1)} = \int_{C''} \frac{e^{ikz} \, dz}{(e^z+1)(e^{-z}+1)} \tag{4}$$

To evaluate the integral around the small circle C'', we put $z = \pi i + \zeta$ and expand the integrand in terms of ζ

$$\int_{C''} \frac{e^{ikz} \, dz}{(e^z+1)(e^{-z}+1)} = e^{-\pi k} \int_{C''} \frac{e^{ik\zeta}}{(-\zeta)(\zeta)} \, d\zeta = e^{-\pi k} \int_{C''} \frac{[1+ik\zeta+\ldots]}{-\zeta^2} \, d\zeta$$

$$= e^{-\pi k} \Big[0 + (2\pi i)(-ik) \Big] = 2\pi k e^{-\pi k} \tag{5}$$

where we have used $e^x = 1+x+\ldots$ and the residue theorem. Then combining (4) and (5) we find

$$\int_{-\infty}^{\infty} \frac{e^{ikx} \, dx}{(e^x+1)(e^{-x}+1)} = \frac{2\pi k \, e^{-\pi k}}{1-e^{-2\pi k}} = \frac{\pi k}{\sinh \pi k} \tag{6}$$

(c) Expanding (6), we find

$$J(k) = \frac{\pi k}{\sinh \pi k} = 1 - \frac{(\pi k)^2}{6} + \frac{7(\pi k)^4}{360} - \ldots$$

Then comparing coefficients with the series in (2) we can read off the I_m's. We find $I_2 = \pi^2/3$.

9.28

(a) According to equation (6.9.4), the probability of state r of the system is

$$P_r \propto e^{-\beta E_r - \alpha N_r}$$

Then the mean number of particles in the state s is

$$\bar{n}_s = \frac{\sum_r n_s \exp\left[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots) - \alpha(n_1+n_2+\ldots)\right]}{\sum_r \exp\left[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots) - \alpha(n_1+n_2+\ldots)\right]}$$

where the sum is over all $n_1, n_2, \ldots$ without restriction.

Letting
$$\mathcal{Z} = \sum_r \exp\left[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots) - \alpha(n_1+n_2+\ldots)\right] \tag{1}$$

we have
$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln \mathcal{Z}$$

where the partial denotes taking the derivative where ϵ_s occurs explicitly. Evaluating the sum (1) in the usual way, we obtain

$$\mathcal{Z} = \left(\sum_{n_1} \exp\left[-(\alpha+\beta\epsilon_1)n_1\right] \right)\left(\sum_{n_2} \exp\left[-(\alpha+\beta\epsilon_2)n_2\right] \right) \cdots \qquad (2)$$

$$= \left(\frac{1}{1-e^{-(\alpha+\beta\epsilon_1)}} \right)\left(\frac{1}{1-e^{-(\alpha+\beta\epsilon_2)}} \right)\cdots$$

Thus

$$\ln \mathcal{Z} = -\sum_r \ln\left(1-e^{-\alpha-\beta\epsilon_r}\right)$$

and

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_s}\ln \mathcal{Z} = \frac{1}{e^{\alpha+\beta\epsilon_s}-1}$$

(b) Using the same argument which leads to (9.2.10) with the function $\mathcal{Z}$ we obtain

$$\overline{(\Delta n_s)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_s}{\partial\epsilon_s}$$

where again the differentiation is performed where ϵ_s occurs explicitly. Thus

$$\overline{(\Delta n_s)^2} = \frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s}-1)^2} = \bar{n}_s^{\,2}\left(1+\frac{1}{\bar{n}_s}\right)$$

$$= \bar{n}_s\left(1+\bar{n}_s\right)$$

The correction term in (9.6.18) is absent showing that if only the mean number of particles is fixed, the dispersion is greater than if the total number is known exactly.

(c) For FD statistics, the sums in (2) become

$$\mathcal{Z} = \left[1 + e^{-(\alpha+\beta\epsilon_1)}\right]\left[1 + e^{-(\alpha+\beta\epsilon_2)}\right]\cdots$$

$$\ln \mathcal{Z} = \sum_r \ln\left(1 + e^{-\alpha-\beta\epsilon_r}\right)$$

Thus

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_s}\ln \mathcal{Z} = \frac{1}{e^{\alpha+\beta\epsilon_s}+1}$$

and

$$\overline{(\Delta n)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_s}{\partial\epsilon_s} = \frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s}+1)^2} = \bar{n}_s^{\,2}\left(\frac{1}{\bar{n}_s}-1\right)$$

$$= \bar{n}_s\left(1-\bar{n}_s\right)$$

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We can remove the restrictions on the sum over states by inserting the Kronecker δ function

$$Z = \sum \exp\left[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)\right]\,\delta_{N,\sum_r n_r}$$

$$= \sum \exp\left[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)\right]\left\{\frac{1}{2\pi}\int_{-\pi}^{\pi} \exp\left[(N - \sum_r n_r)(\alpha + i\alpha')\right]\,d\alpha'\right\}$$

where the sum is over $n_r = 0, 1, \dots$ for each r. Letting $\underline{\alpha} = \alpha + i\alpha'$ and interchanging the sum and integral yields

$$Z = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{\underline{\alpha}N}\,\mathcal{Z}(\underline{\alpha})\,d\alpha' \tag{1}$$

where

$$\mathcal{Z}(\underline{\alpha}) = \sum \exp\left[-(\underline{\alpha} + \beta\epsilon_1)n_1 - (\underline{\alpha} + \beta\epsilon_2)n_2 \dots\right]$$

This sum is easily evaluated as in section 9.6 and

$$\ln \mathcal{Z}(\underline{\alpha}) = -\sum_r \ln\left(1 - e^{-\underline{\alpha} - \beta\epsilon_r}\right) \tag{2}$$

To approximate (1) we expand the logarithm of the integrand about $\alpha' = 0$ where it contributes appreciably to the integral.

$$\ln e^{\underline{\alpha}N}\,\mathcal{Z}(\underline{\alpha}) = \underline{\alpha}N + \ln \mathcal{Z}(\underline{\alpha})$$

$$= (\alpha + i\alpha')N + \ln \mathcal{Z}(\alpha) + B_1(i\alpha') + \frac{1}{2}B_2(i\alpha')^2 + \dots$$

$$= \alpha N + \ln \mathcal{Z}(\alpha) + i(N + B_1)\alpha' - \frac{1}{2}B_2\alpha'^2 + \dots$$

where

$$B_k = \left[\frac{\partial^k \ln \mathcal{Z}(\underline{\alpha})}{\partial \underline{\alpha}^k}\right]_{\alpha'=0} = \frac{\partial^k \ln \mathcal{Z}(\alpha)}{\partial \alpha^k}$$

Hence

$$e^{\underline{\alpha}N}\,\mathcal{Z}(\underline{\alpha}) = e^{\alpha N}\,\mathcal{Z}(\alpha)e^{-\frac{1}{2}B_2\alpha'^2}\,e^{i(N + B_1)\alpha'} \tag{3}$$

As in section 6.8, we optimize the approximation by setting

$$N + B_1 = 0$$

or

$$N + \frac{\partial \ln \mathcal{Z}(\alpha)}{\partial \alpha} = 0 \tag{4}$$

and (3) becomes

$$e^{\underline{\alpha}N}\,\mathcal{Z}(\underline{\alpha}) = e^{\alpha N}\,\mathcal{Z}(\alpha)\,e^{-\frac{1}{2}B_2\alpha'^2}$$

Substitution into (1) yields

$$Z = \frac{e^{\alpha N}\mathcal{Z}(\alpha)}{2\pi}\int_{-\pi}^{\pi} e^{-\frac{1}{2}B_2\alpha'^2}\,d\alpha' \tag{5}$$

or

$$\ln Z \approx \alpha N + \ln \mathcal{Z}(\alpha) = \alpha N - \sum_r \ln\left(1 - e^{-\alpha - \beta\epsilon_r}\right)$$

where we have used (2). The value α is determined by (4)

$$N + \frac{\partial}{\partial \alpha} \ln \overline{Z}(\alpha) = N - \sum_r \frac{\partial}{\partial \alpha} \ln (1 - e^{-\alpha - \beta \epsilon_r}) = 0$$

which gives

$$\sum_r \frac{1}{e^{\alpha + \beta \epsilon_r} - 1} = N$$

CHAPTER 10

Systems of Interacting Particles

10.1

Since $\sigma(\omega)\, d\omega \propto \kappa^2 d\kappa$ and for spin waves $\omega = A\kappa^2$, it follows that

$$\sigma(\omega)\, d\omega \propto \omega^{\frac{1}{2}}\, d\omega$$

Then by (10.1.20)

$$C_V \propto \int_0^\infty \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} (\beta \hbar \omega)^2 \omega^{\frac{1}{2}}\, d\omega$$

Substituting the dimensionless variable $x = \beta \hbar \omega$ we obtain

$$C_V \propto \frac{1}{(\beta \hbar)^{3/2}} \int_0^\infty \frac{e^x}{(e^x - 1)^2} x^{5/2}\, dx$$

The integral is just a constant not involving β. Hence

$$C_V \propto \beta^{-3/2} \propto T^{3/2}$$

10.2

(a) By (10.1.18)

$$\ln Z = \beta N \eta - \int_0^\infty \ln (1 - e^{-\beta \hbar \omega})\, \sigma_D(\omega)\, d\omega$$

where

$$\sigma_D(\omega) = \begin{cases} \dfrac{3V}{2\pi^2 c^3} \omega^2 & \text{for } \omega < \omega_D \\[2mm] 0 & \text{for } \omega > \omega_D \end{cases}$$

But since $V = 6\pi^2 N \left(\dfrac{c}{\omega_D}\right)^3$, we find

$$\ln Z = \beta N \eta - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \ln (1 - e^{-\beta \hbar \omega})\, \omega^2\, d\omega$$

In terms of the dimensionless variables $x = \beta \hbar \omega$ and $y = \beta \hbar \omega_D$, this gives

$$\ln Z = \frac{y N \eta}{\hbar \omega_D} - \frac{9N}{y^3} \int_0^y \ln (1 - e^{-x})\, x^2\, dx$$

This expression can be put in terms of the function $D(y)$ by integration by parts.

Thus
$$\ln Z = y\,\frac{N\eta}{\hbar\omega_D} - \frac{9N}{y^3}\left[\ln(1-e^{-x})\,\frac{x^3}{3}\right]_0^y - \frac{1}{3}\int_0^y\frac{x^3dx}{e^x-1}$$

$$= y\,\frac{N\eta}{\hbar\omega_D} - 3N\ln(1-e^{-y}) + ND(y)$$

$$= \frac{N\eta}{\hbar\omega_D} - 3N\ln(1-e^{-\theta_D/T}) + ND(\theta_D/T) \tag{1}$$

where $k\theta_D = \hbar\omega_D$.

(b) The mean energy is

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = -\hbar\omega_D\frac{\partial}{\partial y}\ln Z$$

Thus
$$\bar{E} = -N\eta + \frac{3N\hbar\omega_D\,e^{-y}}{1-e^{-y}} + \frac{9N\hbar\omega_D}{y^4}\int_0^y\frac{x^3dx}{e^x-1} - \frac{3N\hbar\omega_D}{y^3}\left(\frac{y^3}{e^y-1}\right)$$

$$= -N\eta + \frac{3N}{\beta}D(y) = -N\eta + 3N\,kT\,D(\theta_D/T) \tag{2}$$

(c) The entropy may be found from the relation $S = k[\ln Z + \beta\bar{E}]$. Then from (1) and (2), we have

$$S = Nk\left[-3\ln(1-e^{-y}) + 4D(y)\right]$$

$$= Nk\left[-3\ln(1-e^{-\theta_D/T}) + 4D(\theta_D/T)\right]$$

10.3

For $y \gg 1$, the upper limit in the function $D(\eta)$ may be replaced by ∞.

$$D(y) = \frac{3}{y^3}\int_0^\infty\frac{x^3dx}{e^x-1}$$

The integral is shown to be $\pi^4/15$ in tables.

Hence
$$D(y) = \frac{\pi^4}{5y^3}\qquad y \gg 1$$

For $y \ll 1$, we can expand $e^x \approx 1+x$ in the denominator

$$D(y) = \frac{3}{y^3}\int_0^\eta x^2dx = 1\qquad y \ll 1$$

From the results of problem 10.2, we find for $y \gg 1$, or $T \ll \theta_D$ when we use $y = \beta\hbar\omega_D = \theta_D/T$

$$\ln Z = \frac{N\eta}{kT} + \frac{N\pi^4 T^3}{5\theta_D^3}$$

$$\overline{E} = -N\eta + \frac{3\pi^4}{5} \; \frac{NkT^4}{\theta_D^3}$$

$$S = \frac{4\pi^4}{5} \; Nk \; \left(\frac{T}{\theta_D}\right)^3$$

For $y \ll 1$ $(T \gg \theta_D)$ we find, using $e^y \approx 1 + y$

$$\ln Z = \frac{N\eta}{kT} - 3N \ln \theta_D/T + N$$

$$\overline{E} = -N\eta + 3N \; kT$$

$$S = Nk \; [-3 \ln \theta_D/T + 4]$$

10.4

The pressure is given in terms of the partition function by the relation $\overline{p} = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$ where by equation (1) of problem 10.2

$$\ln Z = \frac{N\eta}{kT} - 3N \ln (1-e^{-\theta_D/T}) + ND \; (\theta_D/T)$$

Thus

$$\overline{p} = N \frac{\partial \eta}{\partial V} + \frac{3N \; kT \; e^{-\theta_D/T}}{1-e^{-\theta_D/T}} \; \left(-\frac{1}{T} \frac{\partial \theta_D}{\partial V}\right) + N \; kT \left[\frac{\partial D(\theta_D/T)}{\partial(\theta_D/T)}\right]\left[\frac{d(\theta_D/T)}{dV}\right]$$

where

$$\frac{\partial D(\theta_D/T)}{\partial D(\theta_D/T)} = -\frac{9}{(\theta_D/T)^4} \int_0^{\theta_D/T} \frac{x^3 dx}{e^x-1} + \frac{3}{e^{\theta_D/T}-1}$$

$$\overline{p} = N \frac{\partial \eta}{\partial V} - \frac{3NkT}{\theta_D} \; D(\theta_D/T) \; \frac{d\theta_D}{dT}$$

In terms of $\gamma = -(V/\theta_D)(d\theta_D/dT)$, this becomes

$$\overline{p} = N \frac{\partial \eta}{\partial V} + \frac{3\gamma NkT}{V} \; D(\theta_D/T)$$

For $T \ll \theta_D$, $D(\theta_D/T) \to \frac{\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3$, and

$$\overline{p} = N \frac{\partial \eta}{\partial V} + \frac{3\pi^4}{5} \; \frac{\gamma \; N \; kT^4}{V \; \theta_D^3}$$

For $T \gg \theta_D$, $D(\theta_D/T) \to 1$

$$\overline{p} = N \frac{\partial \eta}{\partial V} + \frac{3\gamma \; N \; kT}{V}$$

10.5

Comparing the expression for the energy $\overline{E}$, equation (2) in problem 10.2, with equation (1) in problem 10.4, we obtain

$$\overline{p} = N \frac{\partial \eta}{\partial V} + \gamma \; \frac{(\overline{E}+N\eta)}{V}$$

Thus
$$\alpha = \kappa \left(\frac{\partial \bar{p}}{\partial T}\right)_V = \frac{\kappa \gamma}{V}\left(\frac{\partial \bar{E}}{\partial T}\right)_V = \kappa \gamma \frac{C_V}{V}$$

10.6

(a) From electrostatics, $\qquad E \propto R^{-3}$

(b) The induced dipole moment in terms of the polarizability α is

$$p_2 = \alpha E \propto R^{-3}$$

(c) The energy of a dipole $\underline{p}_2$ in a field $\underline{E}$ is

$$u = -\underline{p}_2 \cdot \underline{E} \propto p_2 E \propto R^{-6}$$

10.7

By equation (10.3.8) and (10.3.16), the log of the partition function is

$$\ln Z = \ln \frac{1}{N!}\left(\frac{2\pi m}{h^2 \beta}\right)^{\frac{3}{2}N} + N \ln V + \frac{1}{2} NnI\,(\beta)$$

where $n = N/V$. The first two terms are the ideal gas partition functions while the last is the contribution of the interaction. Since the interaction is represented by an additive term in $\ln Z$, it must also be represented by an additive term in the entropy, $S = k\left[\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z\right]$

Thus the entropy per mole is

$$S(T,n) = S_o(T,n) + S'(T,n)$$

where
$$S'(T,n) = k\left[\frac{1}{2} n\, I(\beta) - \beta \frac{\partial}{\partial \beta}\left(\frac{1}{2} n\, I(B)\right)\right] = n\frac{k}{2}\left[I(\beta) - \beta \frac{\partial}{\partial \beta} I\,(\beta)\right]$$

and
$$S'(T,n) = n\, A(T) = n\left[-\frac{k}{2}\beta^2 \frac{\partial}{\partial \beta}\left(\frac{I(\beta)}{\beta}\right)\right]$$

To show that $A(T)$ is negative, we must show that the derivative $\partial/\partial \beta\,[I(\beta)/\beta]$ is positive.

We have

$$\frac{\partial}{\partial \beta}\left(\frac{I(\beta)}{\beta}\right) = \frac{\partial}{\partial \beta}\int_0^\infty \frac{(e^{-\beta u}-1)}{\beta} 4\pi R^2 dR = \int_0^\infty \frac{-\beta u e^{-\beta u}-(e^{-\beta u}-1)}{\beta^2} 4\pi R^2\, dR$$

but
$$-\beta u e^{-\beta u} - e^{-\beta u} + 1 = 1 - \frac{(1+\beta u)}{e^{\beta u}} > 0$$

since $(1+\beta u)$ is just the first two terms in the expansion of $e^{\beta u}$. Thus the integral is positive and $A(T)$ is negative.

Also
$$A(T) = -\frac{k}{2}\int_0^\infty \left[1 - e^{-\beta u}(1+\beta u)\right] 4\pi R^2\, dR$$

10.8

From the arguments of section 10.6 we can write down the partition function for a two dimensional gas

$$Z = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta}\right)^N Z_U$$

where

$$\ln Z_U = N \ln A + \frac{1}{2} \frac{N^2}{A} I(\beta)$$

$$I(\beta) = \int_0^\infty (e^{-\beta u} - 1) 2\pi R \, dR$$

Denoting the film pressure by p_f, we have

$$p_f = \frac{1}{\beta} \frac{\partial}{\partial A} \ln Z$$

$$\frac{p_f}{kT} = \frac{N}{A} - \frac{1}{2} \frac{N^2}{A^2} I$$

or

$$\frac{p_f}{kT} = n + B_2(T) \, n^2$$

where $n = N/A$ and $B_2(T) = -\frac{1}{2} I$.

10.9

(a) One can write down the mean energy from (10.7.3) and (10.7.5)

$$\overline{E} = -N g \mu_o \, H_i \, \overline{S_{jz}} = -NS \, kTx \, B_s(x) \tag{1}$$

Here N is the total number of particles. The consistency condition is

$$B_s(x) = \frac{kT}{2n \, JS} \, x \tag{2}$$

We solve this equation in the given temperature limits using Fig.(10.7.1)

$T \ll T_c$

   Here the slope, $kT/2n \, JS$, of the straight line is small and the intersection with $B_s(x)$ is at large x where $B_s(x) \approx 1$. Thus (2) becomes

$$1 = \frac{kT}{2n \, JS} x \quad \text{or} \quad x = \frac{2n \, JS}{kT}$$

and

$$\overline{E} = -NS \, kT \left(\frac{2n \, JS}{kT}\right)(1) = -2n \, NS^2 \, J \tag{3}$$

$T \approx T_c$

   In this region $kT/2n \, JS$ is large and the intersection is at small x. We cannot, however, approximate $B_s(x)$ by the linear term $\frac{1}{3}(s+1)x$ (eq.10.7.12) since this would not cross the

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line $(kT/2n\ JS)x$. Hence we must evaluate the second term in the expansion of $B_s(x)$. For small x,

$$\coth x \rightarrow \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} \qquad\qquad x \ll 1$$

Substitution in $B_s(x) = \frac{1}{S}\left[(S+\frac{1}{2})\coth\ (S+\frac{1}{2})x - \frac{1}{2}\coth\ \frac{1}{2}\ x\right]$ yields

$$B_s(x) \approx \frac{1}{S}\left\{(S+\tfrac{1}{2})\left[\frac{1}{(S+\frac{1}{2})x} + \frac{1}{3}(S+\tfrac{1}{2})x - \frac{1}{45}(S+\tfrac{1}{2})^3 x^3\right] - \frac{1}{2}\left[\frac{2}{x} + \frac{x}{6} - \frac{x^3}{360}\right]\right\}$$

$$B_s(x) \approx \frac{1}{3}(S+1)x - (S^2+S+\tfrac{1}{2})\frac{(S+1)}{45}\ x^3$$

Then (2) becomes

$$\frac{kT}{2n\ JS}\ x = \frac{1}{3}(S+1)x - (S^2+S+\tfrac{1}{2})\frac{(S+1)}{45}x^3$$

or

$$x^2 = \frac{45}{S^2+S+\frac{1}{2}}\left[\frac{1}{3} - \frac{kT}{2n\ JS(S+1)}\right] \qquad\qquad (4)$$

In the energy (2) we substitute $B_s(x)$ to first order and use (4)

$$\overline{E} = -NS\ kT\ x\ B_s(x) = -\frac{1}{3}NS(S+1)\ kT\ x^2$$

$$= -\frac{5NS(S+1)kT}{S^2+S+\frac{1}{2}}\left[1 - \frac{3kT}{2n\ JS(S+1)}\right] \qquad T \approx T_c \qquad (5)$$
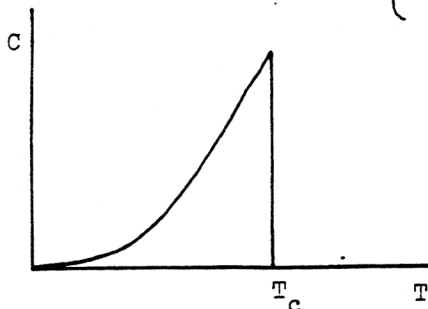
$T \gg T_c$

From (4) we see that $x=0$ at $kT = kT_c = \frac{2}{3}nJS(S+1)$, i.e., the energy becomes 0 at this point, and larger T gives imaginary x in this approximation.

Hence $\qquad\qquad\qquad\qquad\qquad\qquad \overline{E} = 0 \qquad\qquad\qquad T \gg T_c \qquad (6)$

(b) From equations (3), (5), and (6) we have

$$C = \frac{\partial\overline{E}}{\partial T} = \begin{cases} \rightarrow 0 & T \ll T_c \\[2mm] \dfrac{15N\ k^2 T}{nJ(S^2+S+\frac{1}{2})}\left[1 - \dfrac{1}{3}\dfrac{S(S+1)nJ}{kT}\right] & T \approx T_c \\[2mm] 0 & T > T_c \end{cases}$$

(c)

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CHAPTER 11

Magnetism and Low Temperatures

11.1

The mean magnetic moment is

$$\bar{M} = \frac{\sum_r (-\partial E_r / \partial H) \, e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H}$$

where $Z = \sum_r e^{-\beta E_r}$.

11.2

The change in entropy per unit volume is given by

$$\Delta S = \int_0^{H_o} \left(\frac{\partial S}{\partial H}\right)_T dH$$

But from the fundamental thermodynamic relation $d\bar{E} = TdS - \bar{M}dH$, we have the Maxwell relation

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial \bar{M}_o}{\partial T}\right)_H$$

where S and $\bar{M}_o$ are the entropy and magnetic moment per unit volume. Since $\bar{M}_o = XH$ and $X = A/(T-\theta)$ we obtain

$$\left(\frac{\partial \bar{M}_o}{\partial T}\right)_H = -\frac{AH}{(T-\theta)^2}$$

Thus

$$\Delta S = -\int_0^{H_o} \frac{AH}{(T-\theta)^2} dH = -\frac{A}{(T-\theta)^2} \frac{H_o^2}{2}$$

11.3

The change in the molar volume when the field is increased from $H=0$ to $H=H_o$ is

$$\Delta v = \int_0^{H_o} \left(\frac{\partial v}{\partial H}\right)_{T,p} dH$$

But from $d\bar{E} = TdS - \bar{p} \, dV - \bar{M}dH$, we see that

$$\left(\frac{\partial v}{\partial H}\right)_{T,\bar{p}} = - \left(\frac{\partial \bar{M}}{\partial \bar{p}}\right)_{T,H}$$

where v and $\bar{M}$ are the molar volume and magnetic moment. Since $\bar{M} = XH$ and $X = A/[T-\theta_o(1+\alpha\bar{p})]$ we find

$$\left(\frac{\partial \bar{M}}{\partial \bar{p}}\right)_{T,H} = \frac{A\theta_o \, \alpha \, H}{[T-\theta_o(1+\alpha\bar{p})]^2}$$

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and
$$\Delta v = -\int_o^{H_o} \frac{A\ \theta_o \alpha\ HdH}{[T-\theta_o(1+\alpha\ \overline{p})]^2} = -\frac{A\theta_o \alpha}{[T-\theta_o(1+\alpha\overline{p})]^2}\ \frac{H_o^2}{2}$$

11.4

(a) From the relation $d\overline{E}' = TdS - \overline{p}dV + Hd\overline{M}$ where $\overline{E}' = \overline{E} - v\overline{H}^2/8\pi$ we obtain

$$\left(\frac{\partial S}{\partial H}\right)_{V,T} = \left(\frac{\partial \overline{M}}{\partial T}\right)_{V,H}$$

In the normal state, $\overline{M} = VXH \approx 0$ since $X \approx 0$. Thus $(\partial S/\partial H)_{V,T} \approx 0$. In the superconducting state,

$$B = H + \frac{4\pi\overline{M}}{V} = 0$$

or

$$\overline{M} = -\frac{V}{4}H$$

Thus $\overline{M}$ is independent of temperature and $(\partial S/\partial H)_{V,T} = 0$

(b) Since the heat capacity is given by $C = T(\partial S/\partial T)$ we have from (11.4.18)

$$S_s - S_n = \frac{V}{4\pi}\ H\ \frac{dH}{dT}$$

$$C_s - C_n = T\frac{\partial}{\partial T}(S_s - S_n) = \frac{VT}{4\pi}\left(\frac{dH}{dT}\right)^2 + \frac{VTH}{4\pi}\left(\frac{d^2H}{dT^2}\right) \tag{1}$$

where H is the critical field.

(c) When $T = T_c$, the critical field is 0. Thus

$$C_s - C_n = \frac{VT_c}{4\pi}\left(\frac{dH}{dT}\right)^2$$

11.5

From (1) in problem 11.4 and $H = H_c[1-(T/T_c)^2]$ we obtain

$$C_s - C_n = -\frac{VH_c^2}{2\pi T_c^2}\ T + \frac{3VH_c^2}{2\pi T_c^4}\ T^3$$

But since $C_n = aT + bT^3$, we have

$$C_s = \left(a - \frac{VH_c^2}{2\pi T_c^2}\right)T + \left(b + \frac{3VH_c^2}{2\pi T_c^4}\right)T^3 \tag{1}$$

To satisfy the condition $C_s/T \to 0$ as $T \to 0$ we must set the coefficient of T in (1) equal to 0,

i.e., $a = VH_c^2/2\pi\ T_c^2$.

Thus
$$C_s = \left(b + \frac{3VH_c^2}{2\pi\, T_c^4} \right) T^3$$

11.6

(a) The entropy is related to the heat capacity, $dS = CdT/T$. Then since at $T=T_c$ and $T=0$ the entropy of the normal and superconducting states is the same, we have

$$S(T_c) - S(0) = \int_0^{T_c} \frac{C_n dT}{T} = \int_0^{T_c} \frac{C_s dT}{T}$$

or
$$\int_0^{T_c} \gamma\, dT = \int_0^{T_c} \alpha T^2\, dT$$

From which it follows that
$$\alpha = 3\gamma/T_c^2 \qquad\qquad (1)$$

(b) Since $dE = CdT$, the energy at $T=T_c$ and $T=0$ for the normal and superconducting states is

$$E_n(T_c) - E_n(0) = \int_0^{T_c} \gamma T\, dT = \frac{\gamma T_c^2}{2}$$

$$E_s(T_c) - E_s(0) = \int_0^{T_c} \alpha T^3\, dT = \frac{\alpha T_c^4}{4}$$

But $E_n(T_c) = E_s(T_c)$ and by (1) $\alpha = 3\gamma/T_c^2$.

Thus
$$E_s(0) - E_n(0) = -\frac{\gamma T_c^2}{4}$$

11.7

From the relation $dS = CdT/T$ we have for the entropy in the normal and superconducting states

$$S_n(T_c) - S_n(0) = \int_0^{T_c} \gamma\, dT = \gamma T_c$$

$$S_s(T_c) - S_s(0) = \int_0^{T_c} \alpha T^2\, dT = \frac{\alpha T_c^3}{3}$$

Since the entropy is the same for both states at $T=0$ and $T=T_c$, it follows that $\alpha = 3\gamma/T_c^2$.
Hence at $T=T_c$

$$\frac{C_n}{C_s} = \frac{\gamma T_c}{\alpha T_c^3} = \frac{1}{3}$$

Elementary Theory of Transport Processes

12.1

(a) 6   (b) 6   (c) 6

12.2

(a) ℓ (b) ℓ (c) ℓ

12.3

(a) The equation of motion for an ion in a field $\mathcal{E}$ is

$$m\ddot{x} = e\mathcal{E}$$

Hence

$$x = \frac{e\mathcal{E}}{m}\frac{t^2}{2} \quad \text{and} \quad \overline{x} = \frac{e\mathcal{E}}{m}\frac{\overline{t^2}}{2}$$

By (12.1.10),

$$\overline{t^2} = \int_0^\infty t^2 e^{-t/\tau}\frac{dt}{\tau} = 2\tau^2$$

and

$$\overline{x} = \frac{e\mathcal{E}}{m}\tau^2$$

(b) The time to travel a distance $\overline{x}$ is

$$t = \sqrt{\frac{2m}{e\mathcal{E}}}\ \overline{x}^{\frac{1}{2}} = \sqrt{2}\ \tau$$

Thus the fraction of cases in which the ion travels a distance less than $\overline{x}$ is

$$\xi = \int_0^{\sqrt{2}\ \tau} e^{-t/\tau}\frac{dt}{\tau} = 1 - e^{-\sqrt{2}} = .757$$

12.4

The differential cross section is given by
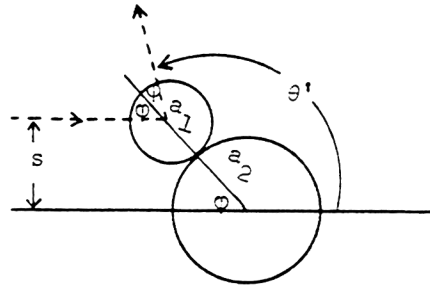
$$\sigma(\Omega) = -2\pi s\frac{ds}{d\Omega}$$

where $d\Omega$ is the element of solid angle and s is

the "inpact parameter" as shown.

From the sketch, $s = (a_1 + a_2)\sin\varphi$

$$\frac{ds}{d\Omega} = (a_1 + a_2)\cos\varphi\frac{d\varphi}{d\Omega}$$

Since $\varphi = 90 - \theta/2$ and $d\Omega = 2\pi\sin\theta'\ d\theta'$, it follows that

$$\frac{ds}{d\Omega} = \frac{-(a_1 + a_2)\sin\theta'/2}{4\pi\sin\theta'}$$

Hence
$$\sigma(\theta) = -2\pi s \frac{ds}{d\Omega} = \frac{(a_1 + a_2)^2 \sin \theta'/2 \cos \theta'/2}{2 \sin \theta'}$$

$$= \frac{1}{4}(a_1 + a_2)^2$$

12.5

By arguemnts similar to those of section 12.1, one has that the probability that a molecule travels a distance x without collision is

$$P = e^{-x/\ell}$$

where ℓ is the mean free path. Letting $P = .9$ and $\ell = (\sqrt{2}\, n\sigma)^{-1}$ yields

$$-\ln .9 = x\sqrt{2}\, n\sigma = x\sqrt{2}\, p\sigma/kT$$

Letting $x = 20$ cm and $T = 300^\circ K$ gives $p = 1.14 \times 10^{-4}$ mm Hg.

12.6

The coefficient of viscosity is

$$\eta = \frac{1}{3} n\, \bar{v}\, m\ell = \frac{1}{3\sqrt{2}}\; \frac{m}{\sigma_o}\sqrt{\frac{8}{\pi}\frac{kT}{m}} \qquad (1)$$

where we have used $\ell = (\sqrt{2}\, n\, \sigma_o)^{-1}$. To determine the cross section, we note that the volume per molecule is $A/N_A\rho$ where $A = 39.9$ gms, the atomic weight, and $\rho = 1.65$ gm cm^{-3}, the density in the solid state. Thus the radius of the molecule is

$$r = \left(\frac{3}{4\pi}\frac{A}{N_A\rho}\right)^{1/3}$$

and
$$\sigma_o = 4\pi r^2 = 5.6 \times 10^{-15}\ cm^2$$

From (1) we find $\eta = 1.1 \times 10^{-4}$ gm cm^{-1} sec^{-1}. Then the ratio of the calculated value of η to the observed value, $\eta = 2.27 \times 10^{-4}$ gm cm^{-1} sec^{-1}, is

$$\eta_{cal}/\eta_{obs} = .48$$

12.7

The coefficient of viscosity is proportional to $T^{\frac{1}{2}}$ since $\eta = m\bar{v}/3\sqrt{2}\, \sigma_o$ and $\bar{v} = (8kT/\pi m)^{\frac{1}{2}}$. Thus if the temperature increas s, the terminal velocity decreases. The velocity is independent of pressure.

12.8

The force on the inner cylinder is the pressure p times the area $A = 2\pi RL$.

$$\mathscr{F} = pA = 2\pi RL\, \eta\, \frac{\partial u}{\partial r}$$

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We make the approximation that the air at the outer cylinder is moving with it, i.e., at velocity $\omega(R+\delta) \approx \omega R$, and the air at the inner cylinder is stationary.

Thus
$$\frac{\partial u}{\partial r} \approx \frac{\omega R}{\delta}$$

and the torque is
$$G = \mathcal{F}R = \frac{2\pi R^3 L \, \eta \omega}{\delta}$$

(b) The viscosity is given by $\eta = m\bar{v}/3\sqrt{2}\,\sigma_o$. Since air is mainly composed of nitrogen, we let $m = 28/6.02 \times 10^{23}$, the mass of a nitrogen molecule. Putting $\sigma_o \approx 10^{-15}$ cm^2 and $T = 300^\circ$K, we find
$$\eta = 2 \times 10^{-4} \text{ gm cm}^{-1} \text{ sec}^{-1}$$

and
$$G = 8 \text{ dyne cm}$$

12.9

(a) We let
$$\sigma_o \propto v^x m^y C^z$$

where x,y, and z are to be determined. Letting L = length, T = time, and M = mass, the dimensional equation becomes
$$L^2 = L^x T^{-x} M^y C^z$$

But since $C = FR^s$, it has dimensions $MT^{-2}L^{s+1}$

Thus
$$L^2 = L^{x+(s+1)z} T^{-x-2z} M^{y+z}$$
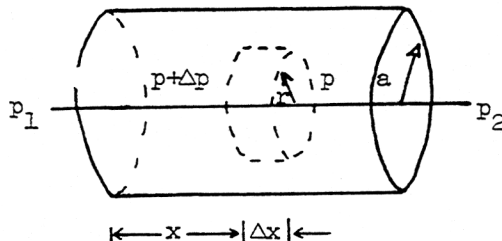
which gives $x+(s+1)z = 2$, $x+2z = 0$, $y + z = 0$.

On solving this system of equations, we find $x = 4/1-s$; hence the cross section σ_o is proportional to $v^{4/(1-s)}$.

(b) The viscosity is given by $\eta = m\bar{v}/3\sqrt{2}\,\sigma_o$ and here $\sigma_o \propto v^{4/1-s}$. Since velocity depends on the square root of the temperature, we have
$$\eta \propto T^{\frac{1}{2}}/T^{4/(1-s)} = T^{(s+7)/2(s-1)}$$

12.10

(a) Consider a disk of radius r and width Δx at the point x. There is a pressure difference Δp across the disk giving force $\pi r^2 \Delta p$ and a viscous retarding force $2\pi r \, \Delta x \eta \, \frac{\partial u(x,r)}{\partial r}$. Hence the condition that the disk moves without acceleration is

$$\pi r^2 \Delta p = -2\pi r \, \Delta x \, \eta \, \frac{\partial u(r,x)}{\partial r}$$

But since $\Delta p \approx -\frac{\partial p(x)}{\partial x} \Delta x$, where the minus sign is introduced because $p(x)$ is a decreasing function of x, we have

$$\pi r^2 \, \frac{\partial p(x)}{\partial x} = 2\pi \, r\eta \, \frac{\partial u(r,x)}{\partial r}$$

Assuming that the fluid in contact with the walls is at rest, it follows that

$$\int_0^{u(r)} du' = \frac{1}{2\eta} \, \frac{\partial p(x)}{\partial x} \int_a^r r'dr'$$

$$u(r,x) = \frac{1}{4\eta} \, \frac{\partial p(x)}{\partial x} \, (r^2-a^2)$$

For a liquid, $\frac{\partial p}{\partial x} = \frac{p_2 - p_1}{L}$. The mass flowing per second across a ring of radius r' and width dr' is $\rho u(r')2\pi r'dr'$ where ρ is the density. Then the total mass flow is

$$\dot{M} = \int_0^a \rho u(r')2\pi r'dr' = \frac{\pi}{2} \, \frac{\rho}{\eta L} \, (p_1-p_2) \int_0^a (a^2-r'^2)r'dr'$$

$$= \frac{\pi}{8} \, \frac{\rho}{\eta} \, \frac{a^4}{L} \, (p_1-p_2)$$

(b) For an ideal gas, the density is $\rho(x) = (\mu/RT)p(x)$ where μ is the molecular weight. Thus the mass flow is

$$\dot{M} = \frac{\pi}{2} \, \frac{\mu}{\eta RT} \, p(x) \, \frac{\partial p(x)}{\partial x} \int_0^a (r'^2-a^2) \, r'dr'$$

$$= -\frac{\pi}{8} \, \frac{\mu a^4}{\eta RT} \, p(x) \, \frac{\partial p(x)}{\partial x}$$

Since $\dot{M}$ is independent of x, we obtain

$$\dot{M} \int_0^L dx = -\frac{\pi}{8} \, \frac{\mu a^4}{\eta RT} \int_{p_1}^{p_2} p \, dp$$

which yields
$$\dot{M} = \frac{\pi}{16} \, \frac{\mu}{\eta RT} \, \frac{a^4}{L} \, (p_1^2 - p_2^2)$$

12.11

Let $T(z,t)$ be the temperature at time t and position z. We consider a slab of substance of thickness dz and area A. By conservation of energy, (the heat absorbed per unit time by the slab is equal to (the heat entering the slab per unit time through the surface at z) minus (the heat leaving per unit time through the surface at z+dz). Since the heat absorbed per unit time is $mc \, \partial T/\partial t = \rho A \, dzc \, \partial T/\partial t$, where c is the specific heat per unit mass and ρ is the density, we have

$$\rho A \, dz \, c \, \frac{\partial T}{\partial t} = A \left[Q_z - Q_{z+dz} \right]$$

$$= A \left[-\kappa \frac{\partial T}{\partial z} - \left(-\kappa \frac{\partial T}{\partial z} - \kappa \frac{\partial}{\partial z}\left(\frac{\partial T}{\partial z}\right) dz \right) \right]$$

and

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c} \frac{\partial^2 T}{\partial z^2}$$

12.12

The wire gives off heat I^2R per unit time and length. In order that the temperature be independent of time, a cylindrical shell between r and $r + dr$ must conduct all the incident I^2R heat.

Thus

$$I^2 R = -\kappa \, 2\pi r \, \frac{\partial T}{\partial r}$$

$$-\int_T^{T_o} dT = \frac{I^2 R}{2\pi\kappa} \int_a^b \frac{dr}{r}$$

or

$$\Delta T = T - T_o = \frac{I^2 R}{2\pi\kappa} \ln \frac{b}{a}$$

12.13

(a) The heat influx per cm height of the dewar across the space between the walls is

$$Q = -2\pi r \, \kappa \, \frac{\partial T}{\partial r} \tag{1}$$

where r is the radius, $r \approx 10$ cm.

We let

$$\frac{\partial T}{\partial r} \approx \frac{\Delta T}{\Delta r} = \frac{298 - 273}{10.6 - 10} = 42^\circ \text{K/cm}$$

by (12.4.9)

$$\kappa = \frac{1}{3\sqrt{2}} \frac{c}{\sigma_o} \bar{v}$$

The specific heat per molecule is $c = (3/2)k$ while $\sigma_o = 4\pi R^2 = 4\pi(10^{-8})^2 \text{ cm}^2$. The mean velocity is $\bar{v} = (8kT/\pi m)^{1/2}$. Choosing an intermediate temperature $T = 286^\circ$K, we find $\bar{v} = 1.2 \times 10^5 \text{cm/sec}$. Substitution of these values into (1) yields

$$Q = 1.2 \text{ watts/cm.}$$

(b) The thermal conductivity remains approximately constant until the pressure is such that the mean free path approaches the dimensions of the container, $L = .6$ cm. At lower pressures, the conductivity is roughly proportional to the number of molecules per unit volume n. Thus the heat influx is reduced by a factor of 10 when

$$n = \frac{1}{10\sqrt{2} \, L \, \sigma_o} \approx 10^{14} \text{ molecules/cm}^3$$

From $p = nkT$, we find $p \approx 3 \times 10^{-3}$ mm Hg.

12.14

(a) $\sigma_2/\sigma_1 = (\eta_1/\eta_2)(\mu_2/\mu_1)^{1/2}$

(b) $\kappa_2/\kappa_1 = \eta_2\mu_1/\eta_1\mu_2$

(c) $D_2/D_1 = \eta_2\mu_1/\eta_1\mu_2$

(d) $\sigma = \dfrac{2}{3\sqrt{\pi}} \dfrac{1}{\eta} \sqrt{\dfrac{\mu\, kT}{N_A}}$ gives $\sigma_1 = 1.1 \times 10^{-15}$ cm^2, $\sigma_2 = 2.8 \times 10^{-15}$ cm^2.

(e) $\sigma = \pi d^2$ gives $d_1 = 1.8 \times 10^{-8}$ cm, $d_2 = 3.0 \times 10^{-8}$ cm.

12.15

The gases are uniformly mixed when the mean square of the displacement is on the order of the square of the dimensions of the container. We have, after N collisions,

$$\overline{z^2} = \sum_i \overline{\zeta_i^2} + \sum_{i \neq j}\sum \overline{\zeta_i \zeta_j} = N\,\overline{\zeta^2}$$

since the second term is zero by statistical independence.

Then
$$\overline{\zeta^2} = \overline{v_z^2}\,\overline{t^2} = \tfrac{2}{3}\overline{v^2}\,\tau^2$$

$$\overline{z^2} = \tfrac{2}{3}\overline{v^2}\,\tau^2\,N = \tfrac{2}{3}\overline{v^2}\,\tau t$$

where $N = t/\tau$. Since $\tau = \ell/\overline{v} = 1/\sqrt{2}\, n\,\sigma\,\overline{v}$, one has on neglecting the distinction between $\overline{v}^2$ and $\overline{v^2}$,

$$\overline{z^2} = \dfrac{2}{3\sqrt{2}}\left(\dfrac{\overline{v}}{\sigma p}\,kT\right)t = \dfrac{\sqrt{2}}{3}\,\dfrac{kT}{\sigma p}\,\sqrt{\dfrac{8}{\pi}\dfrac{kT}{m}}\;t$$

Substitution of $\overline{z^2} = 10^4$ cm^2, $\sigma \approx 10^{-15}$ cm^2, and the given temperature and pressure yields $t \approx 10^4$ sec.

12.16

A molecule undergoes a momentum change of $2\mu v_z$ in a collision with the cube where $\mu = mM/m{+}M$, the reduced mass. Then the force is given by the momentum change per collision times the number of molecules which strike the cube per unit time, summed over all velocities.

$$\mathscr{F}_{tot} = 2\mu n \left(\dfrac{m\beta}{2\pi}\right)^{1/2} L^2 \int_0^\infty v_z^2\, e^{-\frac{\beta m}{2}(v_z - V)^2}\, dv_z$$

We may approximate the exponent since $\overline{v} \gg V$. Thus

$$e^{-\frac{\beta m}{2}(v_z - V)^2} \approx e^{-\frac{\beta m}{2}v_z^2 + \beta m v_z V} \approx e^{-\frac{\beta m}{2}v_z^2}(1 + \beta m v_z V)$$

and
$$\mathcal{F}_{tot} = 2\mu n \left(\frac{m\beta}{2\pi}\right)^{1/2} L^2 \int_0^\infty v_z^2 e^{-\frac{\beta m}{2}v_z^2}(1 + \beta m v_z V)\, dv_z$$

The first integral is just the force on a stationary wall as in section 7.14. The resistive force is then

$$\mathcal{F} = 2\mu n \left(\frac{m\beta}{2\pi}\right)^{1/2} L^2 \int_0^\infty \beta m V\, v_z^3 e^{-\frac{\beta m}{2}v_z^2} = 4\mu n \left(\frac{m\beta}{2\pi}\right)^{1/2} \frac{V}{\beta m} L^2$$

$$= \mu n\, \bar{v}\, V\, L^2$$

by Appendix A.4 and 7.11.13. Since we expect $M \gg m$, $\mu \approx m$, and the equation of motion becomes

$$M \frac{dV}{dt} = -mn\, \bar{v}\, V L^2$$

$$V = V_o \exp\left[-\frac{m}{M} n\, \bar{v}\, L^2 t\right]$$

The velocity is reduced to half its original value in time

$$c = \frac{M \ln 2}{mn\, \bar{v}\, L^2}$$

CHAPTER 13

Transport Theory using the Relaxation-Time Approximation

13.1

By (13.4.7)
$$\sigma_{el} = -e^2 \int d^3\underline{v}\, \frac{\partial g}{\partial \epsilon}\, \tau\, v_z^2$$

The value of the integral is unchanged if v_x^2 or v_y^2 is substituted for v_z^2. Hence since $v^2 = v_x^2 + v_y^2 + v_z^2$, we obtain

$$\sigma_{el} = -\frac{e^2}{3} \int d^3\underline{v}\, \frac{\partial g}{\partial \epsilon}\, \tau v^2$$

The quantities τ and $\partial g/\partial \epsilon$ are functions only of v. Thus the substitution $d^3\underline{v} = v^2 dv \sin\theta\, d\theta\, d\varphi$ yields

$$\sigma_{el} = -\frac{e^2}{3} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \int_0^\infty \frac{\partial g}{\partial \epsilon}\, \tau\, v^4\, dv = -\frac{4\pi}{3} e^2 \int_0^\infty \frac{\partial g}{\partial \epsilon}\, \tau\, v^4\, dv \qquad (1)$$

13.2

The function g becomes the Maxwell velocity distribution

$$\frac{\partial g}{\partial \epsilon} = n \left(\frac{m}{2\pi\, kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} \left(-\frac{1}{kT}\right)$$

In terms of $\hat{v} = (2kT/m)^{1/2}$, this is

$$\frac{\partial g}{\partial \epsilon} = -2\pi^{-3/2} \frac{n e^{-(v/\hat{v})^2}}{\hat{v}^5}$$

Substitution into (1) of problem 13.1 with $s = v/\hat{v}$ yields

$$\sigma = \frac{ne^2}{m} \langle \tau \rangle_\sigma$$

where

$$\langle \tau \rangle_\sigma = \frac{8}{3\sqrt{\pi}} \int_0^\infty ds\, e^{-s^2} s^4\, \tau(\hat{v}s)$$

13.3

Since $\epsilon = \frac{1}{2} mU^2 = \frac{1}{2}m\, (U_x^2 + U_y^2 + U_z^2)$, we have

$$\frac{\partial g}{\partial U_x} = \frac{\partial g}{\partial \epsilon}\, \frac{\partial \epsilon}{\partial U_x} = \frac{\partial g}{\partial \epsilon}\, mU_x$$

Thus

$$\eta = -m \int d^3\underline{U}\, \frac{\partial g}{\partial U_x}\, U_z^2\, U_x\, \tau = -m^2 \int d^3\underline{U}\, \frac{\partial g}{\partial \epsilon}\, U_z^2\, U_x^2\, \tau$$

In spherical coordinates, the components of velocity become

$$U_x = U \sin\theta \cos\varphi \qquad U_z = U \cos\theta$$

and

$$d^3\underline{U} = U^2 dU \sin\theta\, d\theta\, d\varphi$$

Therefore

$$\eta = -m^2 \int_0^{2\pi} \cos^2\varphi\, d\varphi \int_0^\pi \sin^3\theta \cos^2\theta\, d\theta \int_0^\infty dU\, \frac{\partial g}{\partial \epsilon}\, U^6\, \tau$$

$$= -m^2\pi \int_0^\pi [\cos^2\theta \sin\theta - \cos^4\theta \sin\theta]\, d\theta \int_0^\infty dU\, \frac{\partial g}{\partial \epsilon}\, U^6\, \tau$$

$$= -m^2 \frac{4\pi}{15} \int_0^\infty dU\, \frac{\partial g}{\partial \epsilon}\, U^6\, \tau \qquad\qquad (1)$$

But since $\int_0^\pi d\varphi \int_0^{2\pi} \sin\theta\, d\theta = 4\pi$, it follows that

$$\eta = -\frac{m^2}{15} \int_0^\pi d\varphi \int_0^{2\pi} \sin\theta\, d\theta \int_0^\infty dU\, \frac{\partial g}{\partial \epsilon}\, U^6\, \tau = -\frac{m^2}{15} \int d^3\underline{U}\, \frac{\partial g}{\partial \epsilon}\, U^4\, \tau$$

13.4

Substituting the expression

$$\frac{\partial g}{\partial \epsilon} = -2\pi^{-\frac{3}{2}} \frac{ne^{-(U/\hat{v})^2}}{\hat{v}^5}$$

from problem 13.2 where $\hat{v} = (2kT/m)^{1/2}$ into equation (1) of 13.3 yields

$$\eta = nkT \langle\tau\rangle_\eta$$

where

$$\langle\tau\rangle_\eta = \frac{16}{15\sqrt{\pi}} \int_0^\infty ds\, e^{-s^2} s^6 \tau(\hat{v}s), \qquad s = U/\hat{v}$$

13.5

Putting $\tau = (\sqrt{2}\, n\, \sigma_0 \bar{v})^{-1}$ into $\eta = nkT\,\tau$ and using $\bar{v} = (8kT/\pi m)^{1/2}$ gives

$$\eta = \frac{\sqrt{\pi}}{4} \frac{\sqrt{m\,kT}}{\sigma_0} = .443 \frac{\sqrt{mkT}}{\sigma_0}$$

This is larger by a factor of 1.18 than the mean free path calculation (12.3.18) and smaller than the result of the rigorous calculation (14.8.33) by a factor of 1.20.

13.6

We assume the local equilibrium distribution

$$g = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp\left[-\frac{1}{2}\beta m v^2\right] \tag{1}$$

where the temperature parameter β and the local density n are functions of z. Then in the notation of section 13.3,

$$\frac{df^{(0)}}{dt'} = -\frac{df^{(0)}}{dt_0} = -\frac{\partial g}{\partial n}\frac{\partial n}{\partial t_0} - \frac{\partial g}{\partial \beta}\frac{\partial \beta}{\partial t_0}$$

$$= -\frac{\partial g}{\partial n}\frac{\partial n}{\partial z}\frac{dz(t_0)}{dt_0} - \frac{\partial g}{\partial \beta}\frac{\partial \beta}{\partial z}\frac{dz(t_0)}{dt_0}$$

$$= -\frac{\partial g}{\partial n}\frac{\partial n}{\partial z}v_z - \frac{\partial g}{\partial \beta}\frac{\partial \beta}{\partial z}v_z$$

where the last follows since $dz(t_0)/dt_0 = v_z$. This expression is independent of t'. Thus (13.3.5) becomes

$$\Delta f = \frac{df^{(0)}}{dt'} \int_0^\infty e^{-t'/\tau}\, dt'$$

or

$$f = g - v_z\tau \left[\frac{\partial g}{\partial n}\frac{\partial n}{\partial z} + \frac{\partial g}{\partial \beta}\frac{\partial \beta}{\partial z}\right] \tag{2}$$

Using (1) this expression becomes

$$f = g - g\, v_z \tau \left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{3}{2\beta}\frac{\partial \beta}{\partial z} - \frac{mv^2}{2}\frac{\partial \beta}{\partial z}\right] \tag{3}$$

It remains to determine $\partial n/\partial z$ for which we use the condition

$$\bar{v}_z = \frac{1}{n}\int d^3\underline{v}\, f\, v_z = 0$$

or $\quad \displaystyle\int d^3\underline{v}\, g\, v_z - \int d^3\underline{v}\, v_z^2\, \tau g \left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{3}{2\beta}\frac{\partial \beta}{\partial z} - \frac{mv^2}{2}\frac{\partial \beta}{\partial z}\right] = 0$

The first integral is zero since the integrand is an odd function of v_z.

$$\int d^3\underline{v}\, v_z^2\, g \left[\frac{1}{n}\frac{\partial n}{\partial z} + \left(\frac{3}{2}\frac{1}{\beta} - \frac{mv^2}{2}\right)\frac{\partial \beta}{\partial z}\right] = 0$$

where we have assumed τ independent of v. By symmetry this equation also holds if v_z^2 in the integrand is replaced by v_x^2 or v_y^2. Then since $v^2 = v_x^2 + v_y^2 + v_z^2$, we have

$$\left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{3}{2\beta}\frac{\partial \beta}{\partial z}\right] \int d^3\underline{v}\, v^2 g - \frac{m}{2}\frac{\partial \beta}{\partial z}\int d^3\underline{v}\, v^4 g = 0$$

or $\quad \displaystyle\left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{3}{2\beta}\frac{\partial \beta}{\partial z}\right] \int_0^\infty v^4 e^{-\frac{1}{2}\beta mv^2}\, dv - \frac{m}{2}\frac{\partial \beta}{\partial z}\int_0^\infty v^6 e^{-\frac{1}{2}\beta mv^2}\, dv = 0$

on substituting (1) and $d^3\underline{v} = v^2 dv \sin\theta\, d\theta\, d\varphi$, and canceling common factors. The integrals are tabulated in appendix A.4

$$\left[\frac{1}{n}\frac{\partial n}{\partial z} + \frac{3}{2\beta}\frac{\partial \beta}{\partial z}\right]\frac{3}{8}\sqrt{\pi}\left(\frac{2}{\beta m}\right)^{5/2} - \frac{m}{2}\frac{\partial \beta}{\partial z}\frac{15}{16}\sqrt{\pi}\left(\frac{2}{\beta m}\right)^{7/2} = 0$$

or $$\frac{1}{n}\frac{\partial n}{\partial z} = \frac{1}{\beta}\frac{\partial \beta}{\partial z} \tag{4}$$

Substitution of the equation of state $n = p/kT = p\beta$ yields

$$\frac{1}{p\beta}\left(p\frac{\partial \beta}{\partial z} + \beta\frac{\partial p}{\partial z}\right) = \frac{1}{\beta}\frac{\partial \beta}{\partial z}$$

or $$\frac{dp}{dz} = 0$$

The pressure is independent of z. Then (3) and (r) give

$$f = g - g v_z \tau \frac{\partial \beta}{\partial z}\left[\frac{5}{2\beta} - \frac{mv^2}{2}\right]$$

$$= g + \frac{g v_z \tau}{T}\frac{dT}{dz}\left[\frac{5}{2} - \frac{1}{2}\frac{mv^2}{kT}\right]$$

13.7

Since there are no external forces and f is independent of time, the Boltzmann equation becomes

$$\underline{v}\cdot\frac{\partial f}{\partial \underline{v}} = v_z\frac{\partial f}{\partial z} = -\frac{f - f^{(0)}}{\tau}$$

where $f^{(o)} = g$ is the local Maxwell distribution of the previous problem. Letting $f = g+f^{(1)}$ where $f^{(1)} \ll g$ we have

$$v_z \frac{\partial g}{\partial z} = v_z \frac{\partial g}{\partial n} \frac{\partial n}{\partial z} + v_z \frac{\partial g}{\partial \beta} \frac{\partial \beta}{\partial z} = -\frac{f^{(1)}}{\tau}$$

Thus

$$f = g - v_z \tau \left[\frac{\partial g}{\partial n} \frac{\partial n}{\partial z} + \frac{\partial g}{\partial \beta} \frac{\partial \beta}{\partial z} \right]$$

This is identical to equation (2) of 13.6. The rest of this calculation proceeds as in that problem.

13.8

The heat flux in the z-direction is given by

$$Q_z = n \ \langle v_z (\tfrac{1}{2} mv^2) \rangle = \tfrac{1}{2} nm \langle v_z v^2 \rangle$$

$$= \tfrac{1}{2} m \int d^3\underline{v} \, f \, v_z v^2$$

where

$$f = g + \frac{g v_z \tau}{T} \frac{\partial T}{\partial z} \left[\frac{5}{2} - \frac{1}{2} \frac{mv^2}{kT} \right]$$

The integral over g is 0 since the integrand is an odd function of v_z. Consequently

$$Q_z = \frac{m\tau}{4} \frac{1}{T} \frac{\partial T}{\partial z} \left[n \left(\frac{m\beta}{2\pi} \right)^{3/2} \right] \int d^3\underline{v} \, v^2 v_z^2 \, e^{-\frac{1}{2}\beta mv^2} \left[5 - \beta mv^2 \right]$$

We can exploit the symmetry of the integral by replacing v_z^2 by $v^2/3$. Then the only angular dependence occurs in $d^3\underline{v} = v^2 dv \sin\theta \, d\theta \, d\varphi$ which yields $4\pi v^2 dv$ when the integration over angles is performed. Thus we obtain

$$Q_z = \frac{\pi}{3} \frac{m\tau}{T} \frac{\partial T}{\partial z} \left[n\left(\frac{m\beta}{2\pi}\right)^{3/2} \right] \left[5 \int_0^\infty dv v^6 e^{-\frac{1}{2}\beta mv^2} - \beta m \int_0^\infty dv v^8 e^{-\frac{1}{2}\beta mv^2} \right]$$

The integrals are tabulated in appendix A.4.

$$Q_z = \frac{\pi}{3} \frac{m\tau}{T} \frac{\partial T}{\partial z} \left[n \left(\frac{m\beta}{2\pi}\right)^{3/2} \right] \left[5 \cdot \frac{15}{16} \pi \left(\frac{2}{\beta m}\right)^{7/2} - \beta m \frac{105}{32} \pi \left(\frac{2}{\beta m}\right)^{9/2} \right]$$

$$= -\frac{5}{2} \frac{nk^2 T}{m} \tau \frac{\partial T}{\partial z}$$

Hence

$$\kappa = \frac{5}{2} \frac{nk^2 T}{m} \tau$$

13.9

The mean free path argument has

$$\kappa = \frac{1}{3} nc\bar{v}\ell = \frac{4}{\pi} \frac{nk^2 T}{m} \tau$$

since $\ell = \bar{v}\tau$ and $\bar{v} = (8kT/\pi m)^{1/2}$. Thus the constant relaxation time approximation yields a

result greater than the mean free path argument by $\frac{5/2}{4/\pi} = 1.96$.

13.10

From problems 13.4 and 13.8 we find

$$\frac{\kappa}{\eta} = \frac{(5/2)(nk^2T/m)\tau}{n \; kT \; \tau} = \frac{5}{2}\frac{k}{m} = \frac{5}{3}\frac{c}{m}$$

where $c = (3/2)k$, the specific heat per molecule. The simple mean free path argument gives

$$\frac{\kappa}{\eta} = \frac{c}{m}$$

Experiment shows that the ratio $(\kappa/\eta)(c/m)^{-1}$ lies between 1.3 and 2.5 (see discussion after (12.4.13)) so that the constant relaxation time approximation yields better agreement with experiment than does the mean free path argument.

13.11

In the absence of a temperature gradient, the equilibrium distribution of a Fermi-Dirac gas is

$$f^{(0)} = g(\epsilon) = \frac{2m^3}{(2\pi)^3 \hbar^3} \; \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \tag{1}$$

In the given situation, f is independent of time but will depend on z because of the temperature gradient $\partial T/\partial z$ along the z direction. This temperature gradient alone would cause the electrons to drift, but since no current can flow, there is a redistribution so as to set up a field $\mathcal{E}(z)$ to counter the effect of the temperature gradient and reduce the mean drift velocity $\bar{v}_z$ to zero. Thus the Boltzmann equation becomes

$$v_z \frac{\partial f}{\partial z} + \frac{e \; \mathcal{E}(z)}{m} \frac{\partial f}{\partial v_z} = -\frac{f-f_o}{\tau}$$

We will assume that the temperature gradient is sufficiently small so that f can be written $f = g+f^{(1)}$, $f^{(1)} \ll g$ where $f^{(1)}$ represents a small departure from local equilibrium.

Thus
$$v_z \frac{\partial g}{\partial z} + \frac{e\mathcal{E}}{m} \frac{\partial g}{\partial v_z} = -\frac{f^{(1)}}{\tau} \tag{2}$$

It is convenient to write this in terms of the dimensionless parameter

$$x = \beta(\epsilon-\mu) = \beta(\frac{1}{2} mv^2 -\mu) \tag{2}$$

Thus
$$\frac{\partial g}{\partial z} = \frac{\partial g}{\partial x} \frac{\partial x}{\partial z} = \frac{\partial g}{\partial x} (\epsilon-\mu) \frac{\partial \beta}{\partial z} = \frac{x}{\beta} \frac{\partial g}{\partial x} \; \frac{\partial \beta}{\partial z}$$

$$\frac{\partial g}{\partial v_z} = \frac{\partial g}{\partial x} \frac{\partial x}{\partial v_z} = \beta m v_z \frac{\partial g}{\partial x}$$

Then from (2) we find
$$f = g - v_z \tau \frac{\partial g}{\partial x} \left[\frac{1}{\beta} \frac{\partial \beta}{\partial z} x + \beta e \mathcal{E} \right] \qquad (4)$$

It remains to find $\mathcal{E}$ from the condition that $\bar{v}_z = \frac{1}{n} \int d^3\underline{v} \, f \cdot v_z = 0$ where f is given by (4). The integral over g is 0 since the integrand is odd. Letting $\tau = \tau_F = $ const. for electrons near the Fermi level, we have

$$\int d^3\underline{v} \, v_z{}^2 \frac{\partial g}{\partial x} \left[\frac{1}{\beta} \frac{\partial \beta}{\partial z} x + \beta e \mathcal{E} \right] = 0$$

or

$$\frac{1}{\beta} \frac{\partial \beta}{\partial z} \int d^3\underline{v} \, v_z{}^2 x \frac{\partial g}{\partial x} + \beta e \mathcal{E} \int d^3\underline{v} \, v_z{}^2 \frac{\partial g}{\partial x} = 0 \qquad (5)$$

The second integral can be expressed in terms of n, the total number of electrons per unit volume. Since $\frac{\partial g}{\partial x} = \frac{1}{\beta m v_z} \frac{\partial g}{\partial v_z}$

$$\int_{-\infty}^{\infty} dv_z \, v_z{}^2 \frac{\partial g}{\partial x} = \frac{1}{\beta m} \int_{-\infty}^{\infty} dv_z v_z \frac{\partial g}{\partial v_z} = \frac{1}{\beta m} \left[v_z g \right]_{-\infty}^{\infty} - \frac{1}{\beta m} \int_{-\infty}^{\infty} g \, dv_z$$

where we have integrated by parts. Since $g = 0$ at $\pm \infty$, it follows that

$$\int d^3\underline{v} \, v_z{}^2 \frac{\partial g}{\partial x} = - \frac{1}{\beta m} \int d^3\underline{v} \, g = - \frac{n}{\beta m} \qquad (6)$$

Proceeding to the evaluation of the first integral in (5), we note that x and $\partial g/\partial x$ are functions only of v^2 so that we can replace $v_z{}^2$ by $v^2/3$. The substitution $d^3v = v \, dv \sin \theta \, d\theta \, d\varphi$ yields $4\pi v^2 dv$ when the integration over angles is performed.

Thus
$$\int d^3\underline{v} \, v_z{}^2 x \frac{\partial g}{\partial x} = \frac{4\pi}{3} \int_0^{\infty} dv \, v^2 x \frac{\partial g}{\partial x}$$

Using $x = \beta(\frac{1}{2} mv^2 - \mu)$ this becomes

$$\frac{2\pi}{3} \left(\frac{2}{\beta m} \right)^{5/2} \int_{-\infty}^{\infty} dx \, x(x + \beta\mu)^{3/2} \frac{\partial g}{\partial x} \qquad (7)$$

From the properties of the Fermi distribution, we know that $\partial g/\partial x \approx 0$ except where $\epsilon \approx \mu$ or $x \approx 0$. The integrand contributes appreciably to the integral only in this region so we can expand the factor $x(x + \beta\mu)^{3/2}$ about $x = 0$ to approximate the integral. Also, the lower limit $-\beta\mu$ may be replaced by $-\infty$ with negligible error.

$$x(x + \beta\mu)^{3/2} \approx (\beta\mu)^{3/2} \left(x + \frac{3}{2} \frac{x^2}{\beta\mu} \right)$$

and,
$$\frac{\partial g}{\partial x} = - \frac{2m^3}{(2\pi)^3 \hbar^3} \frac{e^x}{(e^x + 1)^2} \qquad \text{from (1)}$$

Hence (7) becomes

$$\frac{2\pi}{3}\left(\frac{2}{\beta m}\right)^{5/2}\int_{-\infty}^{\infty}dx\ x(x+\beta\mu)^{1/2}\frac{\partial g}{\partial x} = -\frac{2^{3/2}}{3\pi^2}\frac{\mu^{3/2}m^{1/2}}{\beta\hbar^3}\left[\int_{-\infty}^{\infty}\frac{xe^x}{(e^x+1)^2}dx + \frac{3}{2\beta\mu}\int_{-\infty}^{\infty}\frac{x^2\ e^x}{(e^x+1)^2}\ dx\right] \quad (8)$$

These integrals are the I_1 and I_2 defined by equation (9.16.9). It is shown there that $I_1 = 0$ and $I_2 = \pi^2/3$. Combining the results of (5), (6), and (8), we obtain

$$-\frac{(2\mu m)^{1/2}}{\hbar^3}\ \frac{1}{\beta^3}\ \frac{\partial\beta}{\partial z} - \frac{ne\mathscr{E}}{m} = 0$$

and (4) becomes

$$f = g - v_z\ \tau_F\ \frac{\partial g}{\partial x}\left[x - \frac{(2\mu m^3)^{1/2}}{n\ \hbar^3\beta}\right]\ \frac{1}{\beta}\ \frac{\partial\beta}{\partial z} \quad (9)$$

Having found the distribution f, we can now calculate the heat flux Q_z.

$$Q_z = n\ \langle v_z(\tfrac{1}{2}\ mv^2)\rangle = \frac{1}{2}\ nm\ \langle v_z v^2\rangle$$

where

$$\langle v_z v^2\rangle = \frac{1}{n}\int d^3\underline{v}\ v_z v^2\ f$$

The integral over g is zero since the integrand is odd.

Hence

$$Q_z = -\frac{m\tau_F}{2}\frac{1}{\beta}\frac{\partial\beta}{\partial z}\left[\int d^3\underline{v}\ v_z^2 v^2 x\frac{\partial g}{\partial x} - \frac{1}{3}\ \frac{(2\mu m^3)^{1/2}}{n\ \hbar^3\beta}\int d^3\underline{v}\ v_z^2 v^2\frac{\partial g}{\partial x}\right] \quad (10)$$

The calculation of these integrals is similar to the steps leading to (8). Again v_z^2 can be replaced by $v^2/3$ and the integration over angles performed to yield 4π. The first integral in (10) becomes

$$\frac{4\pi}{3}\int_0^{\infty}dv\ v^6 x\ \frac{\partial g}{\partial x} = \frac{2\pi}{3}\left(\frac{2}{\beta m}\right)^{7/2}\int_{-\infty}^{\infty}x(x+\beta\mu)^{5/2}\frac{\partial g}{\partial x}\ dx$$

$$\approx -\frac{2^{5/2}}{3\pi^2}\frac{\mu^{5/2}m^{-1/2}}{\beta\hbar^3}\int_{-\infty}^{\infty}(x+\frac{5}{2}\frac{x^2}{\beta\mu})\frac{e^x}{(e^x+1)^2}\ dx$$

where we have expanded as before. The integral is $I_1 + (5/2\beta\mu)I_2 = 5\pi^2/6\beta\mu$.

Hence

$$\int d^3\underline{v}\ v_z^2 v^2\ x\ \frac{\partial g}{\partial x} = -\frac{5\cdot 2^{3/2}}{9}\ \frac{\mu^{3/2}m^{-1/2}}{\beta^2\ \hbar^3} \quad (11)$$

The second integral in (10) is

$$\int d^3\underline{v}\ v_z^2 v^2\ \frac{\partial g}{\partial x} = \frac{4\pi}{3}\int_0^{\infty}dv\ v^6\ \frac{\partial g}{\partial x}$$

$$= \frac{2\pi}{3}\left(\frac{2}{\beta m}\right)^{7/2}\int_{-\infty}^{\infty}(x+\beta\mu)^{5/2}\frac{\partial g}{\partial x}\ dx$$

$$\approx -\frac{2^{5/2}}{3\pi^2}\frac{\mu^{5/2}m^{-1/2}}{\beta\hbar^3}\int_{-\infty}^{\infty}\left(1+\frac{5x}{2\beta\mu}\right)\frac{e^x}{(e^x+1)^2}\,dx$$

Here we have neglected the squared term in the expansion since it is much less than 1. The integral is $I_0 + (5/2\ \beta\mu)\ I_1 = 1$.

Thus
$$\int d^3v\ v_z^2\ v^2\frac{\partial g}{\partial z}= -\frac{2^{5/2}}{3\pi^2}\frac{\mu^{5/2}m^{-1/2}}{\beta\hbar^3} \tag{12}$$

Combining the results of (10), (11), and (12) and using $\mu = (\hbar^2/2m)(3\pi^2 n)^{3/2}$, we find

$$Q_z = -\frac{m\tau_F}{2}\frac{1}{\beta}\frac{\partial\beta}{\partial z}\left[-\frac{5}{3}\frac{\pi^2 n}{m^2\beta^2}+\pi^2\frac{n}{m^2\beta^2}\right]$$

$$=\frac{\pi^2}{3}\frac{n\tau_F}{m}\frac{1}{\beta^3}\frac{\partial\beta}{\partial z}= -\frac{\pi^2}{3}\frac{nk^2T}{m}\ \tau_F\frac{\partial T}{\partial z}$$

Thus
$$\kappa = \frac{\pi^2}{3}\frac{nk^2T}{m}\ \tau_F$$

13.12

Combining the results of the previous problem and (13.4.12), we find

$$\kappa/\sigma_{el} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 T$$

At 273°K this becomes $\kappa/\sigma_{el} = 7.42\times10^{-11}$ erg cm^{-1} deg^{-1} or in more standard units $\kappa/\sigma_{el} = 6.68\times10^{-6}$ watt ohm deg^{-1}. Experimental values at 273°K are

element	Ag	Au	Cu	Pb	Pt	Sn	W	Zn
$\kappa/\sigma_{el}\times10^6$ watt ohm deg^{-1}	6.31	6.42	6.09	6.74	6.85	6.88	8.30	6.31

CHAPTER 14

Near-Exact Formulation of Transport Theory

14.1

The mean rate of momentum loss per unit volume due to collisions is, by (14.4.22)

$$\langle\Delta\underline{p}\rangle = \int_{\underline{v}}\int_{\underline{v}_1}\int_{\Omega} d^3\underline{v}\ d^3\underline{v}_1\ d\Omega'\ ff_1\ V\sigma\ (V,\theta')(\Delta\underline{p}) \tag{1}$$

where we assume central forces. We first perform the integration over angles by changing to center of mass coordinates.

Thus
$$(\Delta\underline{p}) = m\ (\underline{v}'-\underline{v})$$

becomes, since $\underline{v} = \underline{c} + \frac{\mu}{m}\underline{V}$ and $\underline{v}' = \underline{c} + \frac{\mu}{m}\underline{V}'$

$$(\Delta\underline{p}) = \mu(\underline{V}'-\underline{V})$$

where $\mu = \dfrac{mm_1}{m+m_1}$, m being the mass of the ions and m_1, the mass of the heavy molecules. Since the mean values $\bar{v}_x$ and $\bar{v}_y$ are zero, it is clear that $\langle\Delta p_x\rangle = \langle\Delta p_y\rangle = 0$. Hence we are left with $(\Delta p_z) = \mu(V_z' - V_z)$ and

$$\int_{\Omega'} d\Omega' \; \sigma(V,\theta')(\Delta p_z) \tag{2}$$

V_z' is given in terms of V_z and the scattering angles. Using the coordinate system illustrated in Fig. 14.8.1, we see that

$$V_z' = V'\cos(\underline{V}',\underline{z}) = V\cos(\underline{V}',\underline{z})$$

since $V' = V$. Inspection of Fig. 14.8.1 yields

$$V\cos(\underline{V}',\underline{z}) = V\left[\cos(\underline{V},z)\cos\theta' + \sin\theta'\cos\varphi'\sin(\underline{V},z)\right]$$

$$= V_z\cos\theta' + V\sin\theta'\cos\varphi'\sin(\underline{V},z)$$

and $\qquad \mu(V_z'-V_z) = \mu V_z(\cos\theta'-1) + \mu V\sin\theta'\cos\varphi'\sin(\underline{V},\underline{z})$

Substituting into (2) we obtain, since $\displaystyle\int_0^{2\pi}\cos\varphi'd\varphi' = 0$,

$$\int_0^{2\pi}\int_0^{\pi}\mu(V_z'-V_z)\sigma(V,\theta')\sin\theta'd\theta'd\varphi' = 2\pi\mu V_z\int_0^{\pi}(\cos\theta'-1)\sigma(V,\theta')\sin\theta'd\theta'$$

For hard spheres, σ is constant and

$$2\pi\mu V_z\sigma\int_0^{\pi}(\cos\theta'-1)\sin\theta'd\theta' = -4\pi\,\mu V_z\sigma = -\mu V_z\sigma_t$$

where σ_t is the total cross section. Equation (1) then simplifies to

$$-\langle\Delta p_z\rangle = \mu\sigma_t\iint_{\underline{v}\;\underline{v}_1} V_z V\, ff_1\, d^3\underline{v}\, d^3\underline{v}_1 \tag{3}$$

where
$$f_1 = n_1\left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\frac{\beta m_1}{2}v_1^2}$$

$$f = n\left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\beta\frac{m}{2}(v_x^2+v_y^2+(v_z-u)^2)}$$

Here u is the mean z component of velocity of the ions. To avoid carrying repititious constants we let

$$\alpha = \frac{m\beta}{2} \quad\text{and}\quad \alpha_1 = \frac{m_1\beta}{2} \tag{4}$$

f can be simplified by making the approximation that $v_z \gg u$, then

$$f \approx n\left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha v^2} e^{2\alpha u v_z} \approx n\left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha v^2}(1+2\alpha\, u\, v_z)$$

Equation (3) becomes

$$-\langle\Delta p_z\rangle = \mu\sigma_t n n_1 \left(\frac{\alpha_1\alpha}{\pi^2}\right)^{3/2} \iint e^{-(\alpha v^2 + \alpha_1 v_1^2)}(1+2\alpha\, u\, v_z) v_z V\, d^3\underline{v}\, d^3\underline{v_1} \qquad (5)$$

We again express $\underline{v}$ and $\underline{v_1}$ in relative coordinates

$$\underline{v} = \underline{c} + \frac{m_1}{m+m_1}\underline{V} \qquad \underline{v_1} = \underline{c} - \frac{m}{m+m_1}\underline{V}$$

Thus
$$\alpha v^2 + \alpha_1 v_1^2 = (\alpha+\alpha_1)c^2 + \frac{2(\alpha m_1 - \alpha_1 m)}{m+m_1}\underline{c}\cdot\underline{V} + \frac{(\alpha m_1^2 + \alpha_1 m^2)}{(m+m_1)^2}v^2$$

On completing the square this yields

$$= (\alpha+\alpha_1)\left[\underline{c} + \frac{(\alpha m_1 - \alpha_1 m)}{(\alpha+\alpha_1)(m+m_1)}\underline{V}\right]^2 - \frac{(\alpha m_1 - \alpha_1 m)^2}{(\alpha+\alpha_1)(m+m_1)^2}v^2 + \frac{(\alpha m_1^2 + \alpha_1 m^2)}{(m+m_1)^2}v^2$$

$$= (\alpha+\alpha_1)K^2 + \frac{\alpha\alpha_1}{\alpha+\alpha_1}v^2$$

where
$$\underline{K} = \underline{c} + \frac{(\alpha m_1 - \alpha_1 \underline{m})}{(\alpha+\alpha_1)(m+m_1)}\underline{V} \qquad (6)$$

Also
$$v_z = c_z + \frac{m_1}{m+m_1}V_z = K_z - \frac{(\alpha m_1 - \alpha_1 m)}{(\alpha+\alpha_1)(m+m_1)}V_z + \frac{m_1}{m+m_1}V_z$$

$$= K_z + \frac{\alpha_1}{\alpha+\alpha_1}V_z \qquad (7)$$

We wish to put the integral (5) in terms of $\underline{V}$ and the variable $\underline{K}$ defined by (6). It has been shown (14.2.6) that $d^3\underline{v_1}\, d^3\underline{v} = d^3\underline{c}\, d^3 V$. In terms of $\underline{K}$ we have

$$d^3\underline{c}\, d^3\underline{V} = J d^3\underline{K}\, d^3\underline{V}$$

It is easy to check from (6) that $J=1$. Thus (5) becomes

$$-\langle\Delta p_z\rangle = \mu\sigma_t\, n n_1 \left(\frac{\alpha_1\alpha}{\pi^2}\right)^{3/2}\iint e^{-(\alpha+\alpha_1)K^2} e^{-\frac{\alpha\alpha_1}{\alpha_1+\alpha}v^2}\left[1+2\alpha\, u\, K_z + 2u\frac{\alpha\alpha_1}{\alpha+\alpha_1}V_z\right]v_z V\, d^3\underline{K}\, d^3\underline{V}$$

The first two terms in the brackets give integrations over odd functions and hence do not contribute to the integral. Changing to spherical coordinates gives

$$-\langle\Delta p_z\rangle = \frac{2\mu u}{\pi^3}\sigma_t\, n n_1 \frac{(\alpha\alpha_1)^{5/2}}{(\alpha+\alpha_1)}\left[4\pi\int_0^\infty e^{-(\alpha+\alpha_1)K^2}K^2 dK\right]\left[\int_0^\infty e^{-\frac{\alpha\alpha_1}{\alpha+\alpha_1}v^2}v^5 dV\int_0^\pi 2\pi\cos^2\theta\,\sin\theta\, d\theta\right]$$

The integrals are found in appendix A.4 and we obtain

$$\langle \Delta p_z \rangle = -\frac{2uu}{\pi^3} \, \sigma_t \, nn_1 \, \frac{(\alpha\alpha_1)^{5/2}}{(\alpha+\alpha_1)} \left[4\pi \left(\frac{\sqrt{\pi}}{4} \, (\alpha+\alpha_1)^{-3/2} \right) \right] \left[\left(\frac{\alpha+\alpha_1}{\alpha\alpha_1} \right)^3 \frac{4\pi}{3} \right]$$

$$= -\frac{8}{3} \, u\sigma_t \, nn_1 \, \frac{mm_1}{m+m_1} \, \sqrt{\frac{2kT}{\pi} \left(\frac{1}{m} + \frac{1}{m_1} \right)}$$

$$= -\frac{8}{3} \, u\sigma_t \, nn_1 \, \sqrt{\frac{2\mu \, kT}{\pi}}$$

where $\mu = \dfrac{mm_1}{m+m_1}$. The momentum balance equation is then

$$ne\mathcal{E} + \langle \Delta p_z \rangle = 0$$

which gives

$$u = \frac{3}{8} \, \frac{e\mathcal{E}}{\sigma_t n_1 \sqrt{2\mu \, kT/\pi}}$$

Since $j = neu = \sigma_{el} \mathcal{E}$, we have

$$\sigma_{el} = \frac{3\sqrt{\pi}}{8} \, \frac{ne^2}{n_1 \sigma_t} \frac{1}{\sqrt{2\mu \, kT}}$$

14.2

(a) We will assume the distribution function

$$f = f^{(0)}(1+\Phi) \tag{1}$$

where

$$f^{(0)} = n(z) \, \left(\frac{m\beta(z)}{2\pi} \right)^{3/2} \exp \left[-\frac{m\beta(z)}{2} \, v^2 \right] \tag{2}$$

It is shown in problem 13.6 that the condition $\bar{v}_z = 0$ yields the relation

$$\frac{1}{n} \frac{\partial n}{\partial z} = \frac{1}{\beta} \frac{\partial \beta}{\partial z} \tag{3}$$

and that the pressure is independent of z.

(b) The Boltzmann equation (14.7.12) becomes

$$Df^{(0)} = \frac{\partial f^{(0)}}{\partial t} + \underline{v} \cdot \frac{\partial f^{(0)}}{\partial \underline{r}} + \frac{\underline{F}}{m} \cdot \frac{\partial f^{(0)}}{\partial \underline{v}} = \mathcal{L}_\Phi$$

Because the situation is time independent and there are no external forces, we are left with

$$v_z \frac{\partial f^{(0)}}{\partial z} = v_z \left(\frac{f^{(0)}}{n} \frac{\partial n}{\partial z} + \frac{3}{2} \frac{f^{(0)}}{\beta} \frac{\partial \beta}{\partial z} - f^{(0)} \frac{mv^2}{2} \frac{\partial \beta}{\partial z} \right) = \mathcal{L}_\Phi$$

or

$$\left(\frac{5}{2\beta} \frac{\partial \beta}{\partial z} \right) f^{(0)} \, v_z \left(1 - \frac{\beta mv^2}{5} \right) = \iint d^3\underline{v}_1 \, d\Omega \cdot f^{(0)} f_1^{(0)} v\sigma \, \Delta\Phi \tag{4}$$

on using (2),(3), and (14.7.10).

It remains to determine the function Φ. The left side of (4) leads us to expect that a good approximation will result if we choose

$$\Phi = Av_z \, (1-\alpha v^2)$$

where A and α are constants. Φ must satisfy the restrictions (14.7.14) to be a good approximation. These become

$$\int d^3\underline{v} \; f^{(0)} \; v_z(1-\alpha v^2) = 0$$

$$\int d^3\underline{v} \; f^{(0)} \; \underline{v} \; v_z(1-\alpha v^2) = 0$$

$$\int d^3\underline{v} \; f^{(0)} \; v^2 v_z(1-\alpha v^2) = 0$$

The first and third integrals are zero because the integrands are odd. Similarly only the v_z component of $\underline{v}$ in the second relation will give a non-zero integral. We use this condition to determine α. That is,

$$\int d^3\underline{v} \; f^{(0)} v_z{}^2 = \alpha \int d^3\underline{v} \; f^{(0)} v_z{}^2 \; v^2$$

$$\frac{nkT}{m} = \alpha \int_0^{2\pi} d\varphi \int_0^\pi \cos^2\theta \; \sin\theta \; d\theta \int_0^\infty n \; \left(\frac{m\beta}{2\pi}\right)^{3/2} v^6 e^{-\frac{\beta m v^2}{2}} dv$$

on using $v_z = v \cos\theta$ and $d^3\underline{v} = v^2 dv \sin\theta \; d\theta \; d\varphi$. Thus

$$\frac{kT}{m} = \alpha \; (2\pi)\left(\frac{2}{3}\right)\left(\frac{m\beta}{2\pi}\right)^{3/2}\left(\frac{15}{16}\pi\right)\left(\frac{2}{m\beta}\right)^{7/2}$$

$$\alpha = \frac{m\beta}{5}$$

and

$$\Phi = A \; v_z\left(1- \frac{m\beta}{5} v^2\right) \tag{5}$$

We will use the procedure of section 14.8 to evaluate the constant A. Multiplying (4) by Φ and integrating over $\underline{v}$ yields

$$\frac{5}{2\beta} \frac{\partial\beta}{\partial z} \int_{\underline{v}} d^3\underline{v} \; f^{(0)} v_z{}^2\left(1 - \frac{\beta m}{5} v^2\right)^2 = A \int_{\underline{v}} \int_{\underline{v}_1} \int_{\Omega'} d^3\underline{v} \; d^3\underline{v}_1 d\Omega' \; f^{(0)} f_1{}^{(0)} V\sigma v_z\left(1 - \frac{\beta m}{5} v^2\right) \Delta\left[v_z \; \left(1- \frac{\beta m}{5} v_z{}^2\right)\right] \tag{6}$$

The integral on the left is easily evaluated. We have

$$\int_{\underline{v}} d^3\underline{v} \; f^{(0)} \left[v_z{}^2 - \frac{2\beta m}{5} v_z{}^2 v^2 + \left(\frac{\beta m}{5}\right)^2 v_z{}^2 v^4\right] \tag{7}$$

$$= \frac{n}{\beta m} - \left(\frac{2\beta m}{5}\right)5n\left(\frac{1}{\beta m}\right)^2 + \left(\frac{\beta m}{5}\right)^2 \int_0^{2\pi} d\varphi \int_0^\pi \cos^2\theta \; \sin\theta d\theta \int_0^\infty n \; \left(\frac{m\beta}{2\pi}\right)^{3/2} v^8 e^{-\frac{\beta m v^2}{2}} dv$$

The integral of the second term in (7) was evaluated previously. The third term is easily shown to be $7n/5\beta m$. Thus the integral becomes

$$\frac{n}{\beta m} \; \left(1-2 + \frac{7}{5}\right) = \frac{2}{5} \frac{n}{\beta m} \tag{8}$$

We split the right side of (6) into an integration over the angle Ω' and over $\underline{v}$ and $\underline{v}_1$. We

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define

$$I = \int_{\underline{v}} \int_{\underline{v}_1} d^3\underline{v} \; d^3\underline{v}_1 \; f^{(0)} f_1^{(0)} v_z (1 - \frac{\beta m v^2}{5}) \; J$$

$$J = \int_{\Omega'} d\Omega' \; V \; \sigma \; \Delta\left[v_z \left(1 - \frac{\beta m}{5} v^2\right)\right]$$

Then using (8), equation (6) becomes

$$\left(\frac{5}{2\beta} \frac{\partial \beta}{\partial z}\right)\left(\frac{2}{5} \frac{n}{\beta m}\right) = \frac{n}{\beta^2 m} \frac{\partial \beta}{\partial z} = AI \tag{9}$$

To evaluate J, we express $\Delta\left[v_z(1-\alpha v^2)\right]$ in center of mass coordinates (we have reintroduced $\alpha = \beta m/5$). By (14.7.11),

$$\Delta\left[v_z(1-\alpha v^2)\right] = v_z'(1-\alpha v'^2) + v_{1z}'(1-\alpha v_1'^2) - v_z(1-\alpha v^2) - v_{1z}(1-\alpha v_1^2)$$

Using $\underline{v} = \underline{c} + \frac{1}{2} \underline{V}$, $v_1 = \underline{c} - \frac{1}{2} \underline{V}$, we have

$$v_z(1-\alpha v^2) + v_{1z}(1-\alpha v_1^2) = (c_z + \frac{1}{2}V_z)(1 - \alpha c^2 - \alpha\underline{c}\cdot\underline{V} - \frac{\alpha}{4} V^2) + (c_z - \frac{1}{2}V_z)(1 - \alpha c^2 + \alpha\underline{c}\cdot\underline{V} - \alpha\frac{V^2}{4})$$

$$= 2c_z - 2\alpha \; c_z c^2 - \frac{\alpha}{2} c_z V^2 - \alpha V_z \underline{c}\cdot\underline{V}$$

Then $\underline{c} = \underline{c}'$ and $|\underline{V}| = |\underline{V}'|$ gives

$$\Delta\left[v_z(1-\alpha v^2)\right] = -\alpha \; (V_z' \; \underline{c}\cdot\underline{V}' - V_z\underline{c}\cdot\underline{V}) \tag{10}$$

Carrying out the product in (10) we find

$$J = -\alpha \int_0^{2\pi} d\varphi' \int_0^{\pi} \sin\theta' d\theta' \sigma V \left[c_x(V_z'V_x'-V_zV_x) + c_y(V_z'V_y'-V_zV_y) + c_z(V_z'^2-V_z^2)\right]$$

where the coordinate system is shown in Fig. 14.8.1. We notice that, except for constants, the first integral is (14.8.7). The second integral involves only a change of the index x to y but is otherwise the same as the first. Consequently, by (14.8.20), these terms yield

$$\frac{3}{2} \alpha \; \sigma_\eta \; VV_z(c_x V_x + c_y V_y) \tag{11}$$

where σ_η is given by (14.8.21).

It remains to find

$$-\alpha \int_0^{2\pi} d\varphi' \int_0^{\pi} \sin\theta' d\theta' \sigma \; Vc_z(V_z'^2 - V_z^2) \tag{12}$$

By (14.8.18)

$$V_z'^2 - V_z^2 = V_z^2\cos^2\theta' + 2V_z V \sin\theta'\cos\theta'\cos\varphi' \; (\hat{\xi}\cdot\hat{z}) + V^2\sin^2\theta'\cos^2\varphi'(\hat{\xi}\cdot\hat{z})^2 - V_z^2$$

and
$$\int_0^{2\pi} d\varphi' (V_z'^2 - V_z^2) = 2\pi V_z^2(\cos^2\theta' - 1) + \pi V^2 \sin^2\theta' (\hat{\underline{\xi}}\cdot\hat{\underline{z}})^2 \tag{13}$$

To eliminate ξ, we write

$$\hat{\underline{z}}\cdot\hat{\underline{z}} = 1 = (\hat{\underline{\xi}}\cdot\hat{\underline{z}})^2 + (\hat{\underline{\eta}}\cdot\hat{\underline{z}})^2 + (\hat{\underline{\zeta}}\cdot\hat{\underline{z}})^2$$

or

$$(\hat{\underline{\xi}}\cdot\hat{\underline{z}})^2 = 1 - (\hat{\underline{\zeta}}\cdot\hat{\underline{z}})^2$$

and (13) becomes

$$\int_0^{2\pi} d\varphi' (V_z'^2 - V_z^2) = \pi V_z^2(2\cos^2\theta' - \sin^2\theta' - 2) + \pi V^2 \sin^2\theta'$$

$$= (-3\pi V_z^2 + \pi V^2) \sin^2\theta'$$

The last term in J is then

$$\frac{3}{2} \alpha \sigma_\eta V c_z \left(V_z^2 - \frac{V^2}{3}\right) \tag{14}$$

and (11) and (14) give

$$J = \frac{3}{2} \alpha \sigma_\eta V (c_x V_x V_z + c_y V_y V_z + c_z V_z^2 - c_z \frac{V^2}{3}) \tag{15}$$

$$= \frac{3}{2} \alpha \sigma_\eta V (V_z(\underline{c}\cdot\underline{V}) - c_z \frac{V^2}{3})$$

We now evaluate

$$I = \int_{\underline{v}} \int_{\underline{v}_1} d^3\underline{v}\, d^3\underline{v}_1\, f^{(o)} f_1^{(o)} v_z(1-\alpha v^2) J$$

The evaluation of this integral is straightforward though tedious. In the center of mass system

$$d^3\underline{v}\, d^3\underline{v}_1 = d^3\underline{c}\, d^3V \quad \text{by (14.2.6)}$$

$$f^{(o)} f_1^{(o)} = n^2 (\frac{m\beta}{2\pi})^3 \exp\left[-\frac{\beta m}{2}(v^2 + v_1^2)\right]$$

$$= n^2 (\frac{m\beta}{2\pi})^3 \exp\left[-\beta m (c^2 + \frac{V^2}{4})\right] \tag{16}$$

$$v_z(1-\alpha v^2) = c_z - \alpha c_z c^2 - \alpha c_z(\underline{c}\cdot\underline{V}) - \frac{\alpha}{4} c_z V^2 + \frac{1}{2} V_z - \frac{\alpha}{2} V_z c^2 - \frac{\alpha}{2} V_z \underline{c}\cdot\underline{V} - \frac{\alpha}{8} V^2 V_z$$

This expression is multiplied by J in the integrand. $f^{(o)} f_1^{(o)}$ is clearly an even function in c and V; hence we need keep only even terms in $v_z(1-\alpha v^2)J$. This yields explicitly

$$I = \int\int d^3\underline{c}\, d^3\underline{V}\, f^{(o)} f_1^{(o)} (\frac{3}{2}\alpha \sigma_\eta V) \left[c_z^2 V_z^2 - \alpha c^2 c_z^2 V_z^2 - \frac{\alpha}{4} c_z^2 V^2 V_z^2 - \frac{\alpha}{2}(c_x^2 V_x^2 V_z^2 + c_y^2 V_y^2 V_z^2 + c_z^2 V_z^4)\right.$$

$$\left. -c_z^2 \frac{V^2}{3} + \frac{\alpha}{3} c_z^2 c^2 V^2 + \frac{\alpha}{12} c_z^2 V^4 + \frac{\alpha}{6} c_z^2 V_z^2 V^2\right] \tag{17}$$

Since $f^{(o)} f_1^{(o)}$ has the simple form (16) all these integrals are the standard ones encountered in this theory. We quote the result of integrating over $\underline{c}$. In (18) the terms appear in the

order that they appear in (17)

$$I = \left[\frac{3}{2}\alpha\right]\left[n^2 \left(\frac{m\beta}{2\pi}\right)^3\right]\left[\frac{\pi^{3/2}}{2} \left(\frac{1}{\beta m}\right)^{5/2}\right] \times$$

$$\tag{18}$$

$$\int d^3\underline{v}\, e^{-\frac{\beta m V^2}{4}}\sigma_\eta \left[v v_z^2 - \frac{5\alpha}{2\beta m} v v_z^2 - \frac{\alpha}{4} v^3 v_z^2 - \frac{\alpha}{2} v_z^2 v^3 - \frac{v^2}{3} + \frac{5\alpha}{6\beta m} v^3 + \frac{\alpha}{12} v^5 + \frac{\alpha}{6} v^3 v_z^2\right]$$

The integral becomes on substituting $\alpha = \beta m/5$,

$$\int d^3\underline{v}\, e^{-\frac{\beta m V^2}{4}}\sigma_\eta \left[\frac{v v_z^2}{2} - \frac{7m\beta}{60} v_z^2 v^3 - \frac{v^3}{6} + \frac{m\beta}{60} v^5\right]$$

$$= \int_0^\infty v^5 \sigma_\eta e^{-\frac{\beta m V^2}{4}} dV\, 2\pi \int_0^\pi \left(\frac{\cos^2\theta}{2} - \frac{7m\beta}{60} v^2 \cos^2\theta - \frac{1}{6} + \frac{m\beta v^2}{60}\right)\sin\theta\, d\theta$$

$$= \frac{2\pi}{60}\left(-\frac{8}{3}\right)m\beta \int_0^\infty v^7 \sigma_\eta e^{-\frac{\beta m V^2}{4}} dV$$

We let $s = \frac{1}{2}\sqrt{m\beta}\, V$ and

$$= \frac{2\pi}{60}(-8\, m\beta)\left(\frac{2}{\sqrt{\beta m}}\right)^8 \frac{1}{3}\int_0^\infty ds\, e^{-s^2}\sigma_\eta \left(\frac{2s}{\sqrt{m\beta}}\right) s^7$$

$$= -\frac{1024\pi}{15}\frac{\bar\sigma_\eta}{(m\beta)^3}$$

where $\bar\sigma_\eta$ is given by (14.8.26). Substitution into (18) yields

$$I = -\frac{32}{25}\frac{n^2}{\pi^{1/2}(m\beta)^{3/2}}\bar\sigma_\eta$$

and by (9)

$$A = -\frac{25}{32\, n\, \bar\sigma_\eta}\left(\frac{m\pi}{\beta}\right)^{1/2}\frac{\partial\beta}{\partial z}$$

$$f = f^{(0)}\left[1 - \frac{25}{32\, n\bar\sigma_\eta}\left(\frac{m\pi}{\beta}\right)^{1/2} v_z\left(1 - \frac{m\beta}{5} v^2\right)\frac{\partial\beta}{\partial z}\right]$$

To find the coefficient of thermal conductivity, we evaluate the heat flux

$$Q_z = n \langle v_z(\tfrac{1}{2} m v^2)\rangle$$

$$= \tfrac{1}{2}m \int d^3\underline{v}\, f^{(0)}(1+\Phi)v_z v^2 = \tfrac{1}{2}m \int d^3\underline{v}\, f^{(0)}\Phi\, v_z v^2$$

$$= \tfrac{1}{2}m\, A \int d^3\underline{v}\, f^{(0)} v_z^2 v^2 \left(1 - \frac{m\beta}{5} v^2\right)$$

$$= \tfrac{1}{2}m\, A \left[\frac{5}{(m\beta)^2} - \frac{m\beta}{5}\left(\frac{35}{(m\beta)^3}\right)\right]$$

Thus
$$Q_z = -\frac{nk^2T^2}{m} A = \frac{25}{32\,\bar{\sigma}_\eta} \left(\frac{\pi}{m\beta^5}\right)^{1/2} \frac{\partial\beta}{\partial z}$$

$$= -\frac{25}{32} \frac{k}{\sigma_\eta} \sqrt{\frac{\pi\,kT}{m}}\ \frac{\partial T}{\partial z}$$

Therefore the coefficient of thermal conductivity is

$$\kappa = \frac{25}{32} \frac{k}{\sigma_\eta} \sqrt{\frac{\pi\,kT}{m}}$$

(c) By (14.8.32)
$$\bar{\sigma}_\eta = \frac{2}{3}\sigma_o$$

Hence
$$\kappa = \frac{75}{64} \frac{k}{\sigma_o} \sqrt{\frac{\pi\,kT}{m}}$$

14.3

(a)
$$\frac{\kappa}{\eta} = \frac{25}{32} \frac{k}{\sigma_\eta} \sqrt{\frac{\pi kT}{m}} \left[\frac{5}{24} \frac{\sqrt{\pi mkT}}{\bar{\sigma}_\eta}\right]^{-1} = \frac{15}{4} \frac{k}{m}$$

$$= 3.75\,\frac{R}{\mu}$$

(b) By (12.4.2), the simple mean free path argument gives

$$\frac{\kappa}{\eta} = \frac{c}{m} = 1.50\,\frac{R}{\mu}$$

Hence the Boltzmann equation gives a value for κ/η greater than the mean free path calculation
by a factor of 2.5

(c)

$\frac{\kappa}{\eta} \times 10^{-7}\,\mathrm{erg\,gm^{-1}\,deg^{-1}}$	Ne	A	Xe
Calculated	1.55	.780	.237
Experimental	1.55	.785	.250

14.4

Letting $f = n\left(\frac{m\beta}{2\pi}\right)^{3/2} \exp\left[-\frac{1}{2}\beta mv^2\right]$, we have

$$\int d^3\underset{\sim}{v}\ f\ \ln f = \int d^3\underset{\sim}{v}\ n\left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta mv^2}\left[\ln n\left(\frac{m\beta}{2\pi}\right)^{3/2} - \frac{\beta mv^2}{2}\right]$$

Performing the integration over angles yields

$$= 4\pi n \left(\frac{m\beta}{2\pi}\right)^{3/2} \int_o^\infty v^2 dv\ e^{-\frac{1}{2}\beta mv^2}\left[\ln n\left(\frac{m\beta}{2\pi}\right)^{3/2} - \frac{\beta mv^2}{2}\right]$$

and by appendix A.4 this is

$$\int d^3\underset{\sim}{v}\; f \ln f = 4\pi m \left(\frac{m\beta}{2\pi}\right)^{3/2} \left[\frac{\sqrt{\pi}}{4} \left(\frac{2}{m\beta}\right)^{3/2} \ln n \left(\frac{m\beta}{2\pi}\right)^{3/2} - \frac{3}{8}\sqrt{\pi} \left(\frac{2}{m\beta}\right)^{5/2} \frac{m\beta}{2} \right]$$

$$= -\frac{N}{V}\left[\ln \frac{V}{N} + \frac{3}{2} \ln T - \frac{3}{2} \ln \frac{m}{2\pi k} + \frac{3}{4}\right]$$

Comparison with (9.10.10) shows that except for a constant, this is -S/k where S is the entropy per unit volume of an ideal gas.

14.5

(a) Differentiating the function

$$H = \int d^3\underline{v}\; f \ln f$$

yields
$$\frac{dH}{dt} = \int d^3\underline{v}\; \frac{\partial f}{\partial t} (\ln f + 1) \tag{1}$$

$\partial f/\partial t$ can be found from the Boltzmann equation. We shall assume that there are no external forces so that the distribution function should depend only on the velocity and time. Then the Boltzmann equation becomes

$$\frac{\partial f}{\partial t} = \iint d^3\underline{v}_1\; d\Omega'\; V\sigma\; (f_1'f' - f_1 f) \tag{2}$$

Substitution of (2) into (1) yields

$$\frac{dH}{dt} = \iiint d^3\underline{v}\; d^3\underline{v}_1\; d\Omega'V\sigma(f_1'f'-f_1 f)(\ln f + 1) \tag{3}$$

This integral is invarient under the interchange of $\underline{v}$ and $\underline{v}_1$ because σ is invariant under this interchange. When the resulting expression is added to (3) we have

$$\frac{dH}{dt} = \frac{1}{2}\iiint d^3\underline{v}\; d^3\underline{v}_1\; d\Omega'\; V\sigma(f_1'f'-f_1 f)(\ln f_1 f + 2) \tag{4}$$

Similarly, this integral is invarient if the initial and final velocities are interchanged because σ is invariant under the inverse collision, i.e.,

$$\sigma(\underline{v}_1\underline{v} \to \underline{v}_1'\underline{v}') = \sigma(\underline{v}_1'\underline{v}' \to \underline{v}_1\underline{v})$$

Thus
$$\frac{dH}{dt} = \frac{1}{2}\iiint d^3\underline{v}'\; d^3\underline{v}_1'\; d\Omega'\; V'\sigma\; (f_1 f - f_1'f')(\ln f_1'f' + 2)$$

But V=V' and by (14.2.8), $d^3\underline{v}'d^3\underline{v}_1' = d^3\underline{v}\; d^3\underline{v}_1$

$$\frac{dH}{dt} = \frac{1}{2}\iiint d^3\underline{v}\; d^3\underline{v}_1\; d\Omega'\; V\sigma\; (f_1 f - f_1'f')(\ln f_1'f' + 2) \tag{5}$$

Adding (4) and (5) gives

$$\frac{dH}{dt} = -\frac{1}{4}\iiint d^3\underline{v}\; d^3\underline{v}_1\; d\Omega'\; V\sigma\; (f_1'f'-f_1 f)(\ln f_1'f'-\ln f_1 f) \tag{6}$$

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(b) Letting $f_1'f' = y$ and $f_1 f = x$, we see that since $(\ln y - \ln x)(y-x) \geq 0$, the integrand in (6) is greater than zero unless $f_1'f' = f_1 f$. Hence $dH/dt \leq 0$ where the equality holds when the integrand identically vanishes.

14.6

The equilibrium condition is

$$\ln f = Af \; B_x mv_x + B_y mv_y + B_z mv_z + C\tfrac{1}{2} mv^2 \qquad (1)$$

This can be written in the form

$$\ln f = -A'(\underline{v}-\underline{v}_0)^2 + \ln C'$$

where the constants A', C' and the constant vector $\underline{v}_0$ contain the constants in (1).

Hence $$f = C' \, e^{-A'(\underline{v}-\underline{v}_0)^2}$$

$\underline{v}_0$ is clearly the mean velocity which can be set equal to zero without loss of generality. To determine A', we find the mean energy of a molecule.

$$\bar{\epsilon} = \frac{\int d^3\underline{v} \; \tfrac{1}{2} mv^2 f}{\int d^3\underline{v} \; f} = \frac{4\pi \int_0^\infty v^2 dv \; \tfrac{1}{2} mv^2 \; e^{-A'v^2}}{4\pi \int_0^\infty v^2 dv \; e^{-A'v^2}}$$

$$\bar{\epsilon} = \frac{\tfrac{3}{8}\sqrt{\pi} \; A'^{-5/2} (\tfrac{1}{2} m)}{\tfrac{\sqrt{\pi}}{4} \; A'^{-3/2}} = \frac{3}{4}\frac{m}{A'}$$

Letting $\bar{\epsilon} = (3/2)kT$, we find $A' = m/2kT$. The constant C' is easily found from $n = \int d^3\underline{v} \; f$ which gives $C' = n(\tfrac{m}{2\pi kT})^{3/2}$ showing that f is the Maxwell distribution.

CHAPTER 15

Irreversible Processes and Fluctuations

15.1

Let the friction force depend on a, v, and η in the manner

$$f \propto a^x v^y \eta^z$$

Then the dimensional equation where L = length, T = time, and M = mass becomes

$$MLT^{-2} = (L)^x (LT^{-1})^y (ML^{-1}T^{-1})^z = L^{x+y-z} M^z T^{-y-z}$$

Thus $x+y-z = 1$, $z=1$, $-y-z = -2$. Solution of this system of equations yieldx $x=y=z=1$, and

$$f \propto \eta a v$$

15.2

Since $N_A k = R$ where N_A is Avogadro's number and R is the gas constant, we have from (15.6.11),

$$\langle x^2 \rangle = \frac{kT}{3\pi\eta a} t = \frac{RT}{3\pi\eta a N_A} t$$

or

$$N_A = \frac{RT}{3\pi\eta a \langle x^2 \rangle} t$$

Substituting $R = 8.32 \times 10^7$ ergs $mole^{-1}$ ${}^\circ K^{-1}$ and the given values yields $N_A = 7.0 \times 10^{23}$ molecules $mole^{-1}$.

15.3

(a) The energy of an ion in the field at point z is $- e\mathscr{E} z$.

Hence
$$\frac{n(z+dz)}{n(z)} = \frac{e^{\beta e \mathscr{E}(z+dz)}}{e^{\beta e \mathscr{E} z}} \approx 1 + \beta e \mathscr{E}\, dz \tag{1}$$

(b) The flux is given by

$$J_D = -D \frac{\partial n}{\partial z} \approx - \frac{D[n(z+dz) - n(z)]}{dz}$$

Then from (1)
$$J_D = -nD\,\beta e \mathscr{E}$$

(c)
$$J_\mu = nv = n\mu \mathscr{E}$$

(d)
$$J_D + J_\mu = -nD\beta\, e\mathscr{E} + n\mu \mathscr{E} = 0$$

Thus
$$\frac{\mu}{D} = \frac{e}{kT}$$

15.4

$$\frac{dv}{dt} = -\gamma v + \frac{1}{m} F'(t) \tag{1}$$

Substitution of $v(t) = u(t)e^{-\gamma t}$ into (1) gives

$$\frac{du}{dt} = \frac{1}{m} e^{\gamma t} F'(t)$$

Hence
$$u = u(o) + \frac{1}{m} \int_o^t e^{\gamma t'} F'(t') dt'$$

Since $u(o) = v(o)$ it follows that
$$v = v_o e^{-\gamma t} + \frac{1}{m} e^{-\gamma t} \int_o^t e^{\gamma t'} F'(t') dt' \tag{2}$$

15.5

By dividing the time interval t into N successive intervals such that $t = N\tau$, we can replace the integral in (2) of 15.4 by the sum of integrals over the intervals of length τ between t_k and

t_{k+1}. Then $t' = k\tau + s$ where k is an integer and $dt' = ds$.

Hence
$$v - v_0 e^{-\gamma t} = e^{-\gamma N\tau} \sum_{k=0}^{N-1} \frac{1}{m} \int_0^\tau e^{\gamma(k\tau+s)} F'(k\tau+s) \, ds$$

$$= \sum_{k=0}^{N-1} e^{-\gamma\tau(N-k)} \frac{1}{m} \int_0^\tau e^{\gamma s} F'(k\tau+s) \, ds$$

In the integral, $s \leq \tau$ or $e^{\gamma s} \leq e^{\gamma\tau} \approx 1$ since τ is chosen so that $\tau \ll \gamma^{-1}$. It follows that

$$v - v_0 e^{-\gamma\tau} = \sum_{k=0}^{N-1} e^{-\gamma\tau(N-k)} G_k$$

$$= \sum_{k=0}^{N-1} y_k = Y$$

where $G_k = \frac{1}{m} \int_0^\tau F'(k\tau+s) \, ds$.

15.7

We integrate the Langevin equation

$$\frac{dv}{dt} = -\gamma v + \frac{1}{m} F'(t)$$

over a time τ which is small compared to γ^{-1} but large compared to the correlation time τ^* of the random force

$$v(\tau) - v(0) = -\gamma v(0)\tau + \frac{1}{m} \int_0^\tau F'(t') dt' \qquad (1)$$

The time interval t is divided into N smaller intervals such that $t = N\tau$. Then in the kth subdivision $t' = k\tau + s$ and $dt' = ds$. Hence (1) becomes

$$v_k = (1-\gamma\tau) v_{k-1} + \frac{1}{m} \int_0^\tau F'[(k-1)\tau+s] \, ds$$

We can find the velocity at $t = N\tau$ by an iterative procedure. Defining G_k as in problem 15.6 we have

$$v_1 = (1-\gamma\tau) v_0 + G_0$$

$$v_2 = (1-\gamma\tau) v_1 + G_1$$

$$= (1-\gamma\tau) [(1-\gamma\tau)v_0 + G_0] + G_1$$

$$= (1-\gamma\tau)^2 v_0 + (1-\gamma\tau) G_0 + G_1$$

Continuing this way we see that

$$v_N = (1-\gamma\tau)^N v_0 + (1-\gamma\tau)^{N-1} G_0 + (1-\gamma\tau)^{N-2} G_1 + \ldots + G_{N-1}$$

Since $\gamma\tau \ll 1$, $e^{-\gamma\tau N} = (e^{-\gamma\tau})^N \approx (1-\gamma\tau)^N$ it follows that

$$v_N = e^{-\gamma\tau N} v_o + e^{-\gamma\tau(N-1)} G_o + e^{-\gamma\tau(N-2)} G_1 + \ldots + G_{N-1}$$

or

$$v_N - v_o e^{-\gamma t} = e^{\gamma\tau} \sum_{k=0}^{N-1} e^{-\gamma\tau(N-k)} G_k$$

$$\approx \sum_{k=0}^{N-1} e^{-\gamma\tau(N-k)} G_k$$

since $\gamma\tau \ll 1$. This result agrees with 15.5.

15.7

$$\overline{G}_k = \overline{G} = \int_o^\tau \langle F'(k+s) \rangle \, ds = 0$$

Hence

$$\overline{Y} = \sum_{k=0}^{N-1} \overline{y}_k = \sum_{k=0}^{N-1} e^{-\gamma\tau(N-k)} \overline{G} = 0$$

and

$$\overline{v} - v_o e^{-\gamma t} = \overline{Y} = 0$$

$$\overline{v} = v_o e^{-\gamma t}$$

Then as $t \to \infty$, $\overline{v} \to 0$.

15.8

From 15.5 we have

$$\overline{Y^2} = \sum_{k=0}^{N-1} \overline{y_k^2} + \sum_{k \neq j}^{N-1} \sum^{N-1} \overline{y_k}\,\overline{y_j}$$

It was shown in 15.7 that $\overline{y}_k = 0$.

Thus

$$\overline{Y^2} = \sum_{k=0}^{N-1} e^{-2\gamma\tau(N-k)} \overline{G_k^2} = \overline{G^2} e^{-2\gamma t} \sum_{k=0}^{N-1} e^{2\gamma\tau k}$$

Where we have used $N\tau = t$. The sum is just the geometric series and may be easily evaluated.

$$\overline{Y^2} = \overline{G^2} e^{-2\gamma t} \left[\frac{1-e^{2\gamma t}}{1-e^{2\gamma\tau}}\right] \approx \overline{G^2}\left[\frac{1-e^{-2\gamma t}}{2\gamma\tau}\right]$$

where $e^{2\gamma\tau} - 1 \approx 2\gamma\tau$ by series expansion since $\gamma\tau \ll 1$. To find $\overline{G^2}$ we note that

$$\overline{(v - v_o e^{-\gamma t})^2} = \overline{Y^2} = \overline{G^2}\,\frac{1-e^{-2\gamma t}}{2\gamma\tau}$$

Letting $t \to \infty$ yields, by equipartition,

$$\overline{v^2} = \frac{kT}{m} = \frac{\overline{G^2}}{2\gamma\tau}$$

Thus $\overline{G^2} = \dfrac{2kT\,\gamma\tau}{m}$

and $\overline{Y^2} = \dfrac{kT}{m}(1-e^{-2\gamma t})$.

15.9

Since $\overline{(\Delta Y)^2} = \overline{Y^2} - \overline{Y}^2 = \overline{Y^2}$, it follows immediately from the central limit theorem that

$$P(v,t|v_o) = \left[\frac{1}{2\pi\overline{Y^2}}\right]^{1/2} \exp\left[-\frac{(v-v_o e^{-\gamma t})^2}{2\overline{Y^2}}\right]$$

$$= \left[\frac{m}{2\pi kT(1-e^{-2\gamma t})}\right]^{1/2} \exp\left[-\frac{m(v-v_o e^{-\gamma t})^2}{2kT(1-e^{-2\gamma t})}\right]$$

15.10

From problem 15.5 we have

$$G_k = \frac{1}{m}\int_0^{\tau} F'(k\tau+t')\ dt'$$

and

$$\overline{G^2} = \frac{1}{m^2}\int_0^{\tau}dt'\int_0^{\tau}\langle F'(k\tau+t')F'(k\tau+t'')\rangle_o dt'' \qquad (1)$$

where we have changed the integration variable from s to t' to conform to the notation of the text. $\overline{G^2}$ is independent of k allowing the choice of k=0 in (1).

$$\overline{G^2} = \frac{1}{m^2}\int_0^{\tau}dt'\int_0^{\tau}\langle F'(t')\ F'(t'')\rangle_o\ dt''$$

The integrand is the correlation function of F' which depends only on the time difference s = t''−t'. Making this change of variable, we have

$$\overline{G^2} = \frac{1}{m^2}\int_0^{\tau}dt'\int_{-t'}^{\tau-t'}\langle F'(t')F'(t'+s)\rangle_o\ ds = \frac{1}{m^2}\int_0^{\tau}dt'\int_{-t'}^{\tau-t'}K(s)ds$$

where the last equality follows because $\langle F'(t')F'(t'+s)\rangle_o = \langle F'(o)F'(s)\rangle_o = K(s)$. Since K depends only on s, the integration over t' can be performed easily by interchanging the order of integration and reading off the limits from the figure.
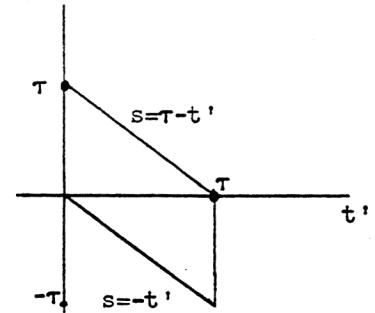
$$\overline{G^2} = \frac{1}{m^2}\left[\int_{-\tau}^{0}ds\int_{-s}^{\tau}K(s)\ dt' + \int_0^{\tau}ds\int_0^{\tau-s}K(s)\ dt'\right]$$

$$= \frac{1}{m^2}\left[\int_{-\tau}^{0}ds\ K(s)(\tau+s) + \int_0^{\tau}ds\ K(s)(\tau-s)\right]$$

Since $\tau \gg \tau^*$ and $K(s) \to 0$ for $s \gg \tau^*$, s can be neglected compared to τ and the limits replaced by $\pm\infty$.

Thus

$$\overline{G^2} = \frac{\tau}{m^2}\int_{-\infty}^{\infty}K(s)\ ds$$

By the results of 15.8, $\overline{G^2} = 2kT\,\gamma\tau/m$. It follows that

$$\gamma = \frac{1}{2mkT} \int_{-\infty}^{\infty} K(s)\, ds$$

15.11

(a) We integrate the Langevin equation

$$\frac{dv}{dt} = -\gamma v + \frac{1}{m} F'(t)$$

over the interval τ.

$$\int_{v_0}^{v(\tau)} dv = -\gamma \int_0^\tau v\, dt' + \frac{1}{m}\int_0^\tau F'(t')dt'$$

Since τ is small, we can replace v by the initial velocity v_0 in the first integral on the right

and obtain

$$\Delta v = v - v_0 = -\gamma v_0 \tau + \frac{1}{m}\int_0^\tau F'(t')dt'$$

$$= -\gamma v_0 \tau + G \tag{1}$$

and

$$\overline{\Delta v} = -\gamma v_0 \tau \qquad \text{since } \overline{G} = 0.$$

$$\overline{(\Delta v)^2} = (\gamma v_0 \tau)^2 - 2\gamma v_0 \tau\, \overline{G} + \overline{G^2}$$

$$\approx \overline{G^2} = 2kT\gamma\tau/m \tag{2}$$

where we have used the result of 15.8 and kept only terms to first order in τ.

(b) From (1), keeping terms to lowest order in τ and noting that odd moments of G are 0, we find

$$\overline{(\Delta v)^3} = -3\gamma\, v_0 \tau\, \overline{G^2}$$

$$\overline{(\Delta v)^4} = \overline{G^4}$$

Since $\overline{G^2} \propto \tau$, $\overline{G^4}$ should be proportional to τ^2. Hence $\overline{(\Delta v)^3}$ and $\overline{(\Delta v)^4}$ are proportional to τ^2.

(c) From (2), $\overline{(\Delta v)^3} = -6kT\,\gamma^2\tau^2 v_0/m$.

15.12

From eq. (2) of 15.4

$$\langle v(o)v(t)\rangle = \langle v^2(o)\rangle\, e^{-\gamma t} + \left\langle \frac{v(o)}{m} e^{-\gamma t} \int_0^t e^{\gamma t'} F'(t')dt' \right\rangle$$

$$= \langle v^2(o)\rangle\, e^{-\gamma t} + \frac{e^{-\gamma t}}{m}\langle v(o)\rangle \int_0^t \langle e^{\gamma t'} F'(t')\rangle\, dt'$$

But since $F'(t')$ is random, the second term on the right is 0. By equipartition

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$\langle v^2(o) \rangle = kT/m$

Thus
$$\langle v(o)v(t) \rangle = \frac{kT}{m} e^{-\gamma t}$$

and since $\langle v(o)v(-t) \rangle = \langle v(o)v(t) \rangle$, we have for all t
$$\langle v(o)v(t) \rangle = \frac{kT}{m} e^{-\gamma |t|}$$

15.13

Squaring equation (2) of 15.4 yields

$$v^2(t) = v_o^2 e^{-2\gamma t} + 2v_o \frac{e^{-2\gamma t}}{m} \int_o^t e^{\gamma t'} F'(t')dt' + \frac{e^{-2\gamma t}}{m^2} \int_o^t dt' \int_o^t e^{\gamma(t'+t'')} F'(t')F(t'')dt''$$

and
$$\overline{v^2(t)} = v_o^2 e^{-2\gamma t} + \frac{e^{-2\gamma t}}{m^2} \int_o^t dt' \int_o^t e^{\gamma(t'+t'')} \langle F'(t')F'(t'') \rangle \, dt'' \qquad (1)$$

since $\langle F'(t') \rangle = 0$. The correlation function in the integral is only a function of the time difference $s = t''-t'$. Making this change of variable yields

$$\int_o^t dt' \int_o^t e^{\gamma(t'+t'')} \langle F'(t')F'(t'') \rangle dt'' = \int_o^t dt' \int_{-t'}^{t-t'} ds \, e^{\gamma(2t'+s)} K(s)$$

where $K(s) = \langle F'(t')F'(t'+s) \rangle = \langle F'(o)F'(s) \rangle$. The evaluation of this integral is similar to that of problem 15.10. Thus interchanging the order of integration and reading the limits off the diagram of problem 15.10 with t substituted for τ yields

$$\int_o^t dt' \int_{-t'}^{t-t'} ds \, e^{\gamma(2t'+s)} K(s) = \int_{-t}^o ds \int_{-s}^t dt' e^{\gamma(2t'+s)} K(s) + \int_o^t ds \int_o^{t-s} dt' e^{\gamma(2t'+s)} K(s)$$

$$= \int_{-t}^o ds \, e^{\gamma s} K(s) \frac{(e^{2\gamma t} - e^{-2\gamma s})}{2\gamma} + \int_o^t ds \, e^{\gamma s} K(s) \frac{(e^{2\gamma(t-s)} -1)}{2\gamma}$$

Since $K(s)$ is only appreciable when $\gamma s \ll 1$, we can put $e^{\gamma s} \approx 1$ in the above and find

$$\int_{-t}^o ds \, K(s) \frac{(e^{2\gamma t}-1)}{2\gamma} + \int_o^t ds \, K(s) \frac{(e^{2\gamma t}-1)}{2\gamma} = \frac{(e^{2\gamma t}-1)}{2\gamma} \int_{-t}^t ds \, K(s) \approx \frac{(e^{2\gamma t}-1)}{2\gamma} \int_{-\infty}^\infty ds \, K(s)$$

Substitution in (1) yields
$$\overline{v^2(t)} = v_o^2 e^{-2\gamma t} + \frac{(1-e^{-2\gamma t})}{2\gamma m^2} \int_{-\infty}^\infty ds \, K(s)$$

as $t \to \infty$, $\overline{v^2(\infty)} = kT/m$ by equipartition and

$$\overline{v^2(\infty)} = \frac{kT}{m} = \frac{1}{2\gamma m^2} \int_{-\infty}^\infty ds \, K(s)$$

Hence
$$\gamma = \frac{1}{2mkT} \int_{-\infty}^\infty ds \, K(s) \qquad \text{as in (15.8.8)}$$

15.14

(a) We will denote the Fourier coefficient of $F'(t)$ by $F'(\omega)$ and that of $v(t)$ by $v(\omega)$. That is

$$F'(t) = \int_{-\infty}^{\infty} e^{i\omega t} F'(\omega)\ d\omega \quad \text{and} \quad v(t) = \int_{-\infty}^{\infty} e^{i\omega t} v(\omega)\ d\omega \tag{1}$$

Substitution in the Langevin equation gives

$$i\omega v(\omega) = -\gamma v(\omega) + \frac{1}{m} F'(\omega)$$

or

$$v(\omega) = \frac{1}{m(\gamma+i\omega)} F'(\omega)$$

Denoting the spectral densities of F' and v by $J_{F'}(\omega)$ and $J_v(\omega)$, we have from (15.15.11)

$$J_{F'}(\omega) = \frac{\pi}{\theta} |F'(\omega)|^2 = \frac{\pi}{\theta} |m(\gamma+i\omega)\ v(\omega)|^2$$

$$= m^2(\gamma^2+\omega^2)\ \frac{\pi}{\theta} |v(\omega)|^2$$

or

$$J_{F'}(\omega) = m^2(\gamma^2+\omega^2)\ J_v(\omega) \tag{2}$$

(b) By (15.10.9)

$$K(s) = \langle \mathbf{v}(o)v(s)\rangle = \frac{kT}{m} e^{-\gamma|s|} \tag{3}$$

Thus

$$J_v(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} K(s)\ e^{-i\omega s}\ ds$$

$$= \frac{kT}{2\pi m} \left[\int_{-\infty}^{0} e^{(-i\omega+\gamma)s}\ ds + \int_{o}^{\infty} e^{(-i\omega-\gamma)s} ds \right]$$

$$J_v(\omega) = \frac{kT}{2\pi m} \left[\frac{1}{(\gamma-i\omega)} - \frac{1}{(-\gamma-i\omega)} \right] = \frac{kT}{2\pi m} \left[\frac{2\gamma}{\gamma^2+\omega^2} \right] \tag{4}$$

(c) Substitution of (4) into (2) gives

$$J_F(\omega) = \frac{1}{\pi} mkT\ \gamma$$

or

$$J_{F'}^{(+)}(\omega) = 2J_F(\omega) = \frac{2}{\pi} mkT\ \gamma$$

This result depends on $\omega \ll (\tau^*)^{-1}$, where τ^* is the correlation time of the fluctuation force, since in deriving (3), one used a time scale such that $\tau \gg \tau^*$. Consequently, $\omega\tau \approx 1 \gg \omega\tau^*$.