HOMEWORK

7.1 Solved in Class

7.2 $\mathcal{H}_{\text{molecule}}(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m}(\vec{p}_1^{\,2} + \vec{p}_2^{\,2}) + \frac{1}{2}K|\vec{r}_1 - \vec{r}_2|^2$

For a classical system of N noninteracting diatomic molecules

$$\mathcal{H} = \sum_{i=1}^{N}\left\{\frac{1}{2m}\left[\vec{p}_{1i}^{\,2} + \vec{p}_{2i}^{\,2}\right] + \frac{1}{2}K|\vec{r}_{1i} - \vec{r}_{2i}|^2\right\}$$

$$Q_N(V,T) = \frac{1}{h^{3N}}\int d^3r_{11}\, d^3r_{21} \dots d^3r_{1N}\, d^3r_{2N}\, d^3p_{11}\, d^3p_{21} \dots d^3p_{1N}\, d^3p_{2N} \times e^{-\beta\mathcal{H}} =$$

$$= \frac{1}{h^{3N}} \iint d^3r_{11}\, d^3r_{21}\, e^{-\frac{\beta K}{2}|\vec{r}_{11} - \vec{r}_{21}|^2} \dots \iint d^3r_{1N}\, d^3r_{2N}\, e^{-\frac{\beta K}{2}|\vec{r}_{1N} - \vec{r}_{2N}|^2}$$

$$\int d^3p_{11}\, e^{-\beta\frac{\vec{p}_{11}^{\,2}}{2m}} \int d^3p_{21}\, e^{-\beta\frac{p_{21}^2}{2m}} \dots \int d^3p_{1N}\, e^{-\beta\frac{\vec{p}_{1N}^{\,2}}{2m}} \int d^3p_{2N}\, e^{-\beta\frac{\vec{p}_{2N}^{\,2}}{2m}} =$$

$$= \frac{1}{h^{3N}}\left(\int d^3r_{11}\int d^3r_{21}\, e^{-\frac{\beta K}{2}|\vec{r}_{11} - \vec{r}_{21}|^2}\right)^N \left(\int d^3p_{11}\, e^{-\frac{\beta \vec{p}_{11}^{\,2}}{2m}}\right)^{2N} =$$

$\longrightarrow$ changing variables $\vec{r}_{11} - \vec{r}_{21} = \vec{r}\,'$

$$= \frac{1}{h^{3N}}\left(\int d^3r_{21} \int d^3r'\, e^{-\frac{\beta K}{2}|r'|^2}\right)^N \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N} =$$

$$= \frac{V^N}{h^{3N}}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N}\left(\int d^3r'\, e^{-\frac{\beta K}{2}|r'|^2}\right)^N = \frac{V^N}{h^{3N}}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N}\left(\sqrt{\frac{2\pi}{\beta K}}\right)^{3N} =$$

$$\ln Q = N\Big[\ln V + \frac{6}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{6}{2}\ln\beta - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\Big(\frac{2\pi}{K}$$

$$= N\left[\ln V + 3\ln\left(\frac{2\pi m}{h^2}\right) - \frac{9}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi}{K}\right)\right]$$

$$\Longrightarrow \quad A = -k_B T \ln Q =$$

$$= -k_B T N\Big[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{9}{2}\ln\beta + \frac{3}{2}\ln\Big(\frac{2\pi}{K}$$

(b) $$\langle E\rangle = U = -\left(\frac{\partial \ln Q}{\partial\beta}\right)_V = \frac{9}{2}N\frac{1}{\beta} = \frac{9}{2}Nk_BT$$

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = \frac{9}{2}Nk_B$$

(c) $$\langle|\vec{r}_1-\vec{r}_2|^2\rangle = -\left(\frac{2}{\beta}\right)\left(\frac{\partial\ln Q}{\partial K}\right) = +\frac{2}{\beta}\left(\frac{3}{2}\right)\frac{1}{K} = 3\,\frac{k_BT}{K}$$

7.3 As in Problem 7.2 one has

$$Q_N(V,T) = \frac{1}{h^{2N} N!}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N}\left(\int d^3r_1 \int d^3r_2 \; e^{-\beta\epsilon|r_{12}-r_0|}\right)^N =$$

$$= \frac{1}{h^{3N} N!}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N} V^N \left(\int d^3r \; e^{-\beta\epsilon|r-r_0|}\right)^N =$$

$$= \frac{1}{h^{3N} N!}\left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N} V^N (4\pi)^N \left[\underbrace{\int_0^\infty dr\, r^2 e^{-\beta\epsilon|r-r_0|}}\right]^N$$

Evaluation of the $I = \int_0^\infty r^2 e^{-\beta\epsilon|r-r_0|} dr$

$$I = \int_0^{r_0} r^2 e^{\beta\epsilon(r-r_0)} dr + \int_{r_0}^\infty r^2 e^{-\beta\epsilon(r-r_0)} dr =$$

$$= e^{-\beta\epsilon r_0}\int_0^{r_0} r^2 e^{\beta\epsilon r} dr + e^{\beta\epsilon r_0}\int_{r_0}^\infty r^2 e^{-\beta\epsilon r} dr =$$

$$= e^{-\beta\epsilon r_0}\left[+\frac{1}{\beta\epsilon} r_0^2 e^{+\beta\epsilon r_0} - \frac{2}{(\beta\epsilon)^2} r_0 e^{+\beta\epsilon r_0} + \frac{2}{(\beta\epsilon)^3}\left(e^{+\beta\epsilon r_0} - 1\right)\right]$$

$$+ e^{\beta\epsilon r_0}\left[+\frac{1}{\beta\epsilon} r_0^2 e^{-\beta\epsilon r_0} + \frac{2}{(\beta\epsilon)^2} r_0 e^{-\beta\epsilon r_0} + \frac{2}{(\beta\epsilon)^2} e^{-\beta\epsilon r_0}\right] =$$

$$= \frac{2}{\beta\epsilon} r_0^2 + \frac{4}{(\beta\epsilon)^3} - \frac{2 e^{-\beta\epsilon r_0}}{(\beta\epsilon)^3}$$

Thus $Q_N(V,T) = \frac{1}{h^{3N} N!} \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{6N} \frac{V^N (4\pi)^N}{(\beta\epsilon)^{3N}} \left[4 - 2e^{-\beta\epsilon r_0} + 2r_0^2(\beta\epsilon)^2\right.$

b) $\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V =$

$$= -\frac{\partial}{\partial\beta}\Big\{-\ln(h^{3N}N!) + \frac{6N}{2}\ln(2\pi m) - \frac{6N}{2}\ln\beta + N\ln V + N\ln L$$

$$- 3N\ln\beta - 3N\ln\epsilon + N\ln\left[4 - 2e^{-\beta\epsilon r_0} + 2r_0^2(\beta\epsilon)^2\right]$$

$$= 6Nk_BT - N\frac{+2\epsilon r_0 e^{-\beta\epsilon r_0} + 4r_0^2\epsilon^2\beta}{4 - 2e^{-\beta\epsilon r_0} + 2r_0^2(\beta\epsilon)^2}$$

$\rightarrow$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = -\frac{1}{k_BT^2}\frac{\partial}{\partial\beta}\langle E\rangle =$$

$$= 6Nk_B - \frac{N}{k_BT^2}\frac{\left(-2(\epsilon r_0)^2 e^{-\beta\epsilon r_0} + 4r_0^2\epsilon^2\right)\left(4 - 2e^{-\beta\epsilon r_0} + 2r_0^2(\beta\epsilon)^2\right)}{\left(4 - 2e^{-x} + 2x^2\right)^2}$$

$$+ \frac{N}{k_BT^2}\frac{\left(2\epsilon r_0 e^{-\beta\epsilon r_0} + 4r_0^2\epsilon^2\beta\right)\left(+2\epsilon r_0 e^{-\beta\epsilon r_0} + 4r_0^2\epsilon^2\beta\right)}{\left(4 - 2e^{-x} + 2x^2\right)^2}$$

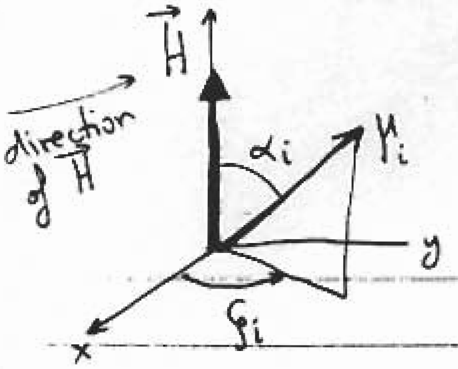
$$= 6Nk_B - Nk_B\frac{\left(-2x^2e^{-x} + 4x^2\right)\left(4 - 2e^{-x} + 2x^2\right) - \beta^2\left(2\frac{x e^{-x}}{\beta} + 4\frac{x^2}{\beta}\right)\left(2\frac{x}{\beta}e^{-x} + 4\frac{x}{\beta}\right)}{\left(4 - 2e^{-x} + 2x^2\right)^2}$$

$$\frac{C_v}{Nk_B} = 6 - \frac{4x^2(2-e^{-x})(2-e^{-x}+x^2) - 4x^2(e^{-x}+2x)(e^{-x}+2)}{4(2-e^{-x}+x^2)^2} =$$

$$= 6 - x^2 \frac{(2-e^{-x})(2-e^{-x}+x^2) - (e^{-x}+2x)(e^{-x}+2)}{(2-e^{-x}+x^2)^2}$$

? 7.5 $\mathcal{H}(p,q,H) = \mathcal{H}(p,q) - \mu H \sum_{i=1}^{N} \cos\alpha_i$

$\mathcal{H}$ in the absence of the field



$$Z_N(T,H) = \frac{1}{h^{3N}} \int dp\,dq \int d\Omega_1 \ldots d\Omega_N \; e^{-\beta\mathcal{H}(\ldots}$$

solid angle for the first moment

$$\Rightarrow Z_N(T,H) = \underbrace{\frac{1}{h^{3N}} \int dp\,dq \; e^{-\beta\mathcal{H}(p,q)}}_{Z_N(T,\,H=0)} \int d\Omega_1 \ldots d\Omega_N \; e^{+\beta\mu H \sum_{i=1}^{N} \cos\alpha\ldots}$$

$$\Rightarrow Z_N(T,H) = Z_N(T,H=0)\, Z'(T,H)$$

where
$$Z'(T,H) = \int d\Omega_1 \ldots d\Omega_N \; e^{\beta\mu H(\cos\alpha_1 + \ldots + \cos\alpha_N)} =$$

$$= \left(\int d\Omega_1 \, e^{\beta\mu H \cos\alpha_1} \right)^N = (2\pi)^N \left(\int_0^{\pi} \sin\alpha_1 \, d\alpha_1 \, e^{\beta\mu H \cos\alpha_1} \right)^N =$$

$$= -(2\pi)^N \left(\int_1^{-1} d(\cos\alpha_1) \, e^{\beta\mu H \cos\alpha_1} \right)^N = \frac{(2\pi)^N}{(\beta\mu H)^N} \left(e^{\beta\mu H} - e^{-\beta\mu H} \right)$$

$$= \left\{ 4\pi \, \frac{\sinh(\beta\mu H)}{\beta\mu H} \right\}^N$$

$$\langle M\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial H}\right) = \frac{1}{\beta}\frac{\partial}{\partial H}\left\{ N\left[\ln 4\pi + \ln \sinh(\beta\mu H) - \ln(\beta\mu H)\right]\right\}$$

$$= \frac{N}{\beta}\left\{ \beta\mu\,\frac{\cosh(\beta\mu H)}{\sinh(\beta\mu H)} - \frac{\beta\mu}{\beta\mu H}\right\} = N\mu\left[\coth \beta\mu H - \frac{1}{\beta\mu H}\right]$$

b) $$\chi = \frac{d\langle M\rangle}{dH} = N\mu\left[-\frac{(\beta\mu)}{\sinh^2(\beta\mu H)} + \frac{(\beta\mu)}{(\beta\mu H)^2}\right] =$$

$$= \frac{N\mu^2}{k_B T}\left[\frac{1}{(\beta\mu H)^2} - \frac{1}{\sinh^2(\beta\mu H)}\right]$$

c) High temperatures $\beta\mu H \ll 1$ $\quad \coth(\beta\mu H) \simeq \frac{1}{\beta\mu H} + \frac{\beta\mu H}{3}$

Thus from question (a) $\langle M\rangle \simeq N\mu\left[\cancel{\frac{1}{\beta\mu H}} + \frac{\beta\mu H}{3} - \cancel{\frac{1}{\beta\mu H}}\right]$

$$\Rightarrow \chi = \frac{d\langle M\rangle}{dH} = \frac{d}{dH}\left(\frac{N\mu^2 H}{3k_B T}\right) = \frac{N\mu^2}{3k_B T}$$

The proportionality constant $\frac{N\mu^2}{3k_B} = C$ is the Curie constant

P. 7.6 $\quad \mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} v_{ij}$ where $v_{ij} = v(r_{ij})$

$r_{ij} = |\vec{r}_i - \vec{r}_j|$

Define: $f(r_{ij}) \equiv f_{ij} \equiv e^{-\beta v(r_{ij})} - 1$

$$Q_N(V,T) = \frac{1}{h^{3N} N!} \int d^{3N}p \, d^{3N}q \, e^{-\beta \mathcal{H}} =$$

$$= \frac{1}{h^{3N} N!} \int d^3p_1 \dots d^3p_N \, e^{-\frac{\beta \vec{p}_1^{\,2}}{2m} - \dots - \frac{\beta \vec{p}_N^{\,2}}{2m}} \int d^3r_1 \dots d^3r_N \, e^{-\beta \sum_{i<j} v_{ij}} =$$

$$= \frac{1}{h^{3N} N!} \left(\sqrt{\frac{2\pi m}{\beta}} \right)^{3N} \int d^3r_1 \dots d^3r_N \prod_{i<j} \left[1 + f_{ij} \right]$$

Since $A = -k_B T \ln Q_N$ and $p = -\left(\frac{\partial A}{\partial V}\right)_T$

$$\Rightarrow p = k_B T \left(\frac{\partial \ln Q_N}{\partial V} \right)_T = k_B T \frac{\partial}{\partial V} \Big\{ -\ln\left(h^{3N} N!\right) + \frac{3N}{2} \ln\left(\frac{2\pi m}{\beta}\right)$$
$$+ \ln \int d^3r_1 \dots d^3r_N \prod_{i<j} (1 + f_{ij})$$

$$\rightarrow p = k_B T \frac{\partial}{\partial V} \left\{ \ln \frac{V^N}{V^N} \int d^3r_1 \dots d^3r_N \prod_{i<j} (1 + f_{ij}) \right\} =$$

$$= k_B T \frac{\partial}{\partial V} \left\{ N \ln V + \ln \frac{1}{V^N} \int d^3r_1 \dots d^3r_N \prod_{i<j} (1 + f_{ij}) \right\}$$

$$= k_B T \left\{ \frac{N}{V} + \frac{\partial}{\partial V} \ln \frac{1}{V^N} \int - - - - - \right\} =$$

$$= k_B T \left\{ \frac{1}{v} + \frac{v}{v} \frac{1}{N} \frac{\partial}{\partial v} \ln \left\{ \frac{1}{V^N} \int - - - - \right\} \right\}$$

Thus:

$$\frac{Pv}{k_B T} = 1 + v \frac{\partial}{\partial v}\left[\underbrace{\frac{1}{N} \ln\left\{ \frac{1}{V^N} \int d^3r_1 \ldots d^3r_N \prod_{i<j} (1+f_{ij}) \right\}}_{\text{Define } Z(v,T)} \right]$$

$$\longrightarrow \quad \frac{Pv}{k_B T} = 1 + v \frac{\partial Z(v,T)}{\partial v}$$

b) Expanding $\prod_{i<j}(1+f_{ij}) = 1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j\\ i'<j'}} f_{ij} f_{i'j'} + \ldots$

$$\Longrightarrow Z(v,T) = \frac{1}{N} \ln\left[\frac{1}{V^N} \int d^3r_1 \ldots d^3r_N \left(1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j\\ i'<j'}} f_{ij} f_{i'j'} \ldots \right.\right.$$

$$= \frac{1}{N} \ln\left\{ \frac{1}{V^N}\left(V^N + \sum_{i<j} \int d^3r_1 \ldots d^3r_N f_{ij} + \ldots \right) \right\} =$$

$$= \ln\left\{ 1 + \frac{1}{V^N} \sum_{i<j} \int d^3r_1 \ldots d^3r_N f_{ij} + \ldots \right\}^{1/N} =$$

There are $\frac{N(N-1)}{2} \approx$ identical terms. Since $N \to \infty$

$$= \ln\left\{ 1 + \frac{N^2 V^{N-2}}{2 V^N} \int d^3r_1 d^3r_2 f_{12} + \ldots \right\}^{1/N}$$

$$= \ln\left\{ 1 + \frac{N^2}{2V} \int d^3r f(r) + \ldots \right\}^{1/N}$$

(c) The virial expansion of the equation of state is

$$\frac{PV}{Nk_BT} = 1 + B_2(T)\frac{N}{V} + B_3(T)\frac{N^2}{V^2} + \cdots$$

where the functions $B_2(T)$, $B_3(T)$ are called virial coefficients.

$$\text{or} \quad \frac{Pv}{k_BT} = 1 + B_2(T)\frac{1}{v} + B_3(T)\frac{1}{v^2} + \cdots$$

Thus if $\frac{N}{V} << 1$ or $\frac{1}{v} << 1$ one can keep terms to linear order in the density

Thus:

$$\frac{Pv}{k_BT} = 1 + v\frac{\partial}{\partial v}\left[\frac{1}{N}\ln\left\{1 + \frac{N^2}{2V}\int d^3r\, f(r) + \cdots\right\}\right]$$

$$= 1 + v\frac{\partial}{\partial v}\left\{\frac{1}{N}\frac{N^2}{2V}\int d^3r\, f(r) + \cdots\right\} =$$

$$= 1 + v\left(-\frac{1}{2v^2}\right)\int d^3r\, f(r) =$$

$$= 1 - \frac{1}{2v}\int d^3r\, f(r) =$$

$$= 1 - \frac{1}{2v}\int_0^\infty 4\pi r^2 f(r)\, dr$$

Thus the second virial coeficient

$$B_2(T) = -\frac{1}{2}\int_0^\infty 4\pi r^2 f(r)\, dr \, .$$