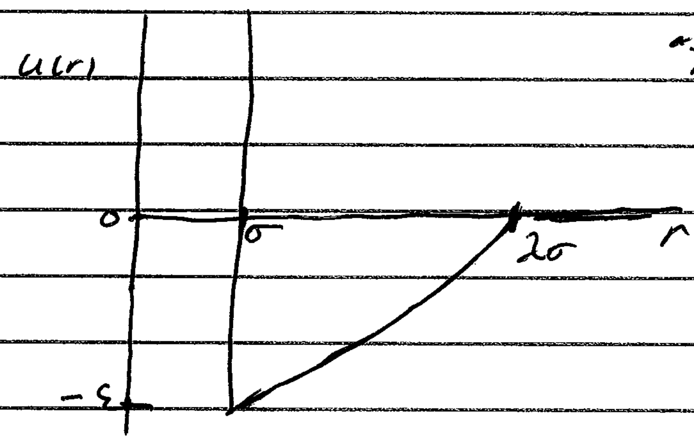
Q 12-9 I am just going to outline the solution

$$u = \infty \qquad r < \sigma$$
$$= \frac{\varepsilon}{\sigma(\lambda-1)}(r - \lambda\sigma) \qquad \sigma < r < \lambda\sigma$$
$$= 0 \qquad r > \lambda\sigma$$



"Triangle potential"

$$B_2(T) = \underbrace{-2\pi \int_0^{\sigma} (-1)\, r^2\, dr}_{\frac{2\pi\sigma^2}{3} = b_0} \underbrace{- 2\pi \int_{\sigma}^{\lambda\sigma} \left[e^{-\frac{\beta\varepsilon(r-\lambda\sigma)}{\sigma(\lambda-1)}} - 1 \right] r^2\, dr}_{A} \underbrace{- 2\pi \int_{\lambda\sigma}^{\infty} (0)\, r^2\, dr}_{0}$$

A is the tough part, but it is just integration

$$A = -2\pi\, e^{+\frac{\beta\varepsilon\lambda}{\lambda-1}} \int_{\sigma}^{\lambda\sigma} \left[e^{-\frac{\beta\varepsilon r}{\sigma(\lambda-1)}} - 1 \right] r^2\, dr$$

$$v = \frac{r}{\sigma} \qquad r = \sigma v \qquad dr = \sigma\, dv$$

$$A = -2\pi\, e^{\beta\varepsilon\lambda/\lambda-1}\, \sigma^3 \int_1^{\lambda} \left[e^{av} - 1 \right] v^2\, dv \quad \text{where } a = \frac{-\beta\varepsilon}{\sigma(\lambda-1)}$$

$$A = -2\pi\sigma^3 e^{\beta\varepsilon\lambda/\lambda-1}\Big[\underbrace{\int_1^\lambda e^{av} v^2\,dv}_{X} \underbrace{- \int_1^\lambda v^2\,dv}_{-\frac{1}{3}v^3\big|_1^\lambda = \frac{1}{3}(1-\lambda^3)}\Big]$$

Use: $\displaystyle\int x^m e^{ax}\,dx = e^{ax}\sum_{r=0}^{m}(-1)^r \frac{m!\,x^{m-r}}{(m-r)!\,a^{r+1}}$

$$X = e^{ax}\left[\frac{2v^2}{2a} - \frac{2v}{a^2} + \frac{2}{a^3}\right]_1^\lambda$$

Thus $B_2(T) = b_0 - 2\pi\sigma^3 e^{\beta\varepsilon\lambda/\lambda-1}\left(X + \frac{1}{3}(1-\lambda^3)\right)$

Evaluating X will give explicit solution

Q12-30 The general expression for $B_2(T)$ ~~[illegible]~~ for monatomic point particles is eq. 12-23 in the text, which can be converted to eq. 12-25:

$$B_2(T) = -2\pi \int_0^\infty [e^{-\beta u} - 1] r^2 dr$$

In our case, however, the molecules are not point particles. They also have dipole moments, and we need to consider the orientation of the dipole vectors. Each vector has a θ and a ϕ, hence $\theta_1, \phi_1, \theta_2, \phi_2$. The energy u depends on θ_1 and θ_2 explicitly, but only on the difference $\phi = \phi_2 - \phi_1$. Therefore $B_2(T)$ becomes:

$$B_2(T) = -2\pi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\phi_2=0}^{2\pi} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} [e^{-\beta u} - 1] r^2 \sin\theta_1 \sin\theta_2 \, dr \, d\theta_1 d\theta_2 \cdot d\phi \, d\phi_2$$

Since $u = u(\theta_1, \theta_2, \phi, r)$ is independent of ϕ_2, we can immediately integrate for a factor of 2π:

$$B_2(T) = -4\pi^2 \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{r=0}^{\infty} [e^{-\beta u} - 1] r^2 \sin\theta_1 \sin\theta_2 \, dr \, d\theta_1 d\theta_2 \, d\phi$$

Integrating directly using the exponential is tough – analytical solution not obvious. So we proceed by expanding exponential in power series:

$$e^{-\beta u} - 1 = -\beta u + \frac{1}{2}\beta^2 u^2 - \frac{1}{6}\beta^3 u^3 + \frac{1}{24}\beta^4 u^4 + \ldots$$

where $u = \infty \quad r < \sigma$

$$= -\frac{\mu^2}{r^3}\left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right] \quad r > \sigma$$

By symmetry, the positive and negative contributions cancel in the integrals of odd-power terms. The leading term is therefore the $\beta^2 u^2$ term:

$$e^{-\beta u} - 1 \approx \frac{\mu^4}{r^6}\left[4\cos^2\theta_1\cos^2\theta_2 - 4\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2\cos\phi + \sin^2\theta_1\sin^2\theta_2\cos^2\phi\right]$$

Thus:

$$B_2(T) = 4\pi^2 \int_{\theta_1=0}^{\pi}\int_{\theta_2=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{r=0}^{\sigma} r^2 \sin\theta_1 \sin\theta_2 \, dr\, d\theta_1\, d\theta_2\, d\phi$$

$$- 4\pi^2 \int_{\theta_1=0}^{\pi}\int_{\theta_2=0}^{\pi}\int_{\phi=0}^{2\pi}\int_{r=\sigma}^{\infty} \frac{1}{2}\beta^2 \frac{\mu^4}{r^6}\left[4\cos^2\theta_1\cos^2\theta_2 - 4\sin\theta_1\cos\theta_1\sin\theta_2\cos\theta_2\cos\phi + \sin^2\theta_1\sin^2\theta_2\cos^2\phi\right] \cdot r^2\, dr\, d\theta_1\, d\theta_2\, d\phi \sin\theta_1\sin\theta_2$$

+ higher-order terms

This reduces to

$$B_2(T) = \underbrace{\frac{2\pi}{3}\sigma^3}_{b_0}\left(1 - \frac{1}{3}\frac{\beta^2\mu^4}{\sigma^6} + \dots\right)$$

... <u>except</u> that I get an extra factor of 8π in my calculation