Post-Lecture Question 5

(a)

$$
\begin{aligned}
\beta A(\lambda) &= -\ln Q(\lambda) \\
&= \ln\big(\Lambda^{3N} N!\big) - \ln \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\};\lambda))
\end{aligned}
$$

(b)

$$
\begin{aligned}
\left(\frac{\partial A}{\partial \lambda}\right)_{N,V,T} &= -\frac{1}{\beta}\frac{\partial}{\partial \lambda} \ln \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\};\lambda)) \\
&= -\frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial}{\partial \lambda} \exp(-\beta U(\{\mathbf{r}_i\};\lambda))}{\beta \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\};\lambda))} \\
&= \frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial U(\{\mathbf{r}_i\};\lambda)}{\partial \lambda} \exp(-\beta U(\{\mathbf{r}_i\};\lambda))}{\beta \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\};\lambda))} \\
&= \left\langle \left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T} \right\rangle_{\lambda}
\end{aligned}
$$

(c)

$$
\begin{aligned}
A_1 - A_0 &= \int_0^1 \mathrm{d}\lambda \left(\frac{\partial A}{\partial \lambda}\right)_{N,V,T} \\
&= \int_0^1 \mathrm{d}\lambda \left\langle \left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T} \right\rangle_{\lambda} \\
&= \int_0^1 \mathrm{d}\lambda \, \langle -2(1-\lambda)U_0 + 2\lambda U_1 \rangle_{\lambda}
\end{aligned}
$$

(d)

$$
\begin{aligned}
\left(\frac{\partial^2 A}{\partial \lambda^2}\right)_{N,V,T} &= \left(\frac{\partial}{\partial \lambda}\right)_{N,V,T} \left[\frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial U}{\partial \lambda} \exp(-\beta U(\{\mathbf{r}_i\};\lambda))}{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U(\{\mathbf{r}_i\};\lambda))}\right] \\
&= \frac{1}{\left[\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U)\right]^2} \left[\left(\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial^2 U}{\partial \lambda^2} \exp(-\beta U) - \beta \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \left(\frac{\partial U}{\partial \lambda}\right)^2 \exp(-\beta U)\right)\right. \\
&\quad \left. \int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U) + \beta \left(\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U)\right)^2\right] \\
&= \frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial^2 U}{\partial \lambda^2} \exp(-\beta U)}{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U)} - \beta \frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \left(\frac{\partial U}{\partial \lambda}\right)^2 \exp(-\beta U)}{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U)} + \beta \left[\frac{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \frac{\partial U}{\partial \lambda} \exp(-\beta U)}{\int \prod_{i=1}^{N} \mathrm{d}\mathbf{r}_i \exp(-\beta U)}\right]^2 \\
&= \left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_{\lambda} - \beta \left\langle \left[\left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T}\right]^2 \right\rangle_{\lambda} + \beta \left\langle \left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T} \right\rangle_{\lambda}^2
\end{aligned}
$$

$$
\begin{aligned}
\left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_{\lambda} &= \langle 2U_0 + 2U_1 \rangle_{\lambda} \\
\left\langle \left[\left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T}\right]^2 \right\rangle_{\lambda} &= \langle (-2(1-\lambda)U_0 + 2\lambda U_1)^2 \rangle_{\lambda} \\
\left\langle \left(\frac{\partial U}{\partial \lambda}\right)_{N,V,T} \right\rangle_{\lambda}^2 &= \langle -2(1-\lambda)U_0 + 2\lambda U_1 \rangle_{\lambda}^2
\end{aligned}
$$

(e)

$$\frac{\partial^2 A}{\partial \lambda^2} = \left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_\lambda - \beta \left[\left\langle \left[\left(\frac{\partial U}{\partial \lambda} \right)_{N,V,T} \right]^2 \right\rangle_\lambda - \beta \left\langle \left(\frac{\partial U}{\partial \lambda} \right)_{N,V,T} \right\rangle_\lambda^2 \right]$$

$$= \left\langle \frac{\partial^2 U}{\partial \lambda^2} \right\rangle_\lambda - \beta \sigma^2 \left(\left(\frac{\partial U}{\partial \lambda} \right)_{N,V,T} \right),$$

where the latter term is non-negative, while the former term has unknown sign. The Gibbs-Bogoliubov inequality does not hold.