HW6 solution

(1)

$$\langle V\rangle = \sum_V \int \frac{d^{3N}q\, d^{3N}p}{N!\, h^{3N}}\, \rho\, V$$

where ~~generalized partition fun~~ probability density function at constant T, N, P is

$$\rho = \frac{\exp\{-\beta H - \beta P V\}}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_V \int \frac{d^{3N}q\, d^{3N}p}{N!\, h^{3N}}\, e^{-\beta H - \beta P V}$$

Clearly
$$\langle V\rangle = -\frac{1}{\mathcal{Z}\beta}\frac{\partial}{\partial P} \sum_V \int \frac{d^{3N}q\, d^{3N}p}{N!\, h^{3N}}\, e^{-\beta H - \beta P V}$$

$$= -\frac{1}{\mathcal{Z}\beta}\frac{\partial}{\partial P}\mathcal{Z}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial P}\ln \mathcal{Z}$$

because
$$\mathcal{Z} = \sum_V e^{-\beta P V} Z(T,V,N)$$

where $Z(T,V,N)$ is the canonical partition function at constant V, T, N.

$$Z(T,V,N) = \frac{V^N}{N!\,\lambda^{3N}}$$

$$\mathcal{Z} = \sum_V e^{-\beta P V}\frac{V^N}{N!\,\lambda^{3N}}$$

$$= \frac{1}{V_0} \int_0^\infty dV \; e^{-\beta P V} \frac{V^N}{N! \lambda^{3N}}$$

(V_0 is a constant with unit of volume)

$$= \frac{1}{V_0} \frac{1}{N! \lambda^{3N}} \frac{1}{(\beta P)^{N+1}} \underbrace{\int_0^\infty d(\beta P V)\, e^{-\beta P V} (\beta P V)^N}_{= \Gamma(N+1) = N!}$$

$$= \frac{1}{V_0} \frac{1}{\lambda^{3N} (\beta P)^{N+1}}$$

Thus

$$\langle V \rangle = -\frac{1}{\beta} \frac{\partial}{\partial P} \ln \mathcal{Z}$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial P} \left(-(N+1) \ln P \right)$$

$$= (N+1) \frac{1}{\beta P} = \frac{(N+1) k_B T}{P}$$

$N \gg 1$

$$\boxed{\langle V \rangle = \frac{N k_B T}{P}}$$

⟨2⟩, ⟨3⟩, ⟨4⟩ See textbook.