HW 8 Solution
The following solution is without any cheating (mathematically respectable), but I do not demand math precision, but demand sound physics intuition and reasonable (if not correct) answers.

1. [Van der Waals gas]
(1) We know the van der Waals equation of state may be obtained from the gas made of hard spheres interacting with the Kac potential. If we approximate the hard sphere gas as an ideal gas moving in the free volume (= the volume - the total excluded volume due to the cores), then we can obtain its Helmholtz free energy using the following ideas:
(i) Since the attractive interaction is infinite-ranged and independent of the distance and direction, the Kac potential never depends on actual particle configuration details other than on the number density. Each particle has a potential energy of $-2an$, where n is the number density.
(ii) The excluded volume due to a single particle is b.
Write down the canonical partition function for the van der Waals gas.

Solution.
The system Hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m} - anN. \tag{1}$$

To understand the potential part, let us look at it in more detail: The total potential energy can be written as

$$\Phi = \sum_{i>j} \phi_{ij}. \tag{2}$$

The potential energy of the ith particle is

$$\Phi_i = \sum_{j \neq i} \phi_{ij}. \tag{3}$$

In our case the interactions are uniform and long ranged, so infinitely may particles contribute and consequently fluctuation disappears. Can we obtain Φ as $\sum_i \Phi_i$? No, because of double counting. That is, $\Phi = (1/2) \sum_i \Phi_i$. This explains why the total potential energy is not $-2naN$ but $-naN$.

The canonical partition function reads

$$Z(T, V) = \frac{1}{h^{3N} N!} \int_{V-Nb} d^3\boldsymbol{r}_1 \cdots \int_{V-Nb} d^3\boldsymbol{r}_N \int d^3\boldsymbol{p}_1 \cdots \int d^3\boldsymbol{p}_N e^{-\beta H} = Z_{ideal}(T, V-Nb)e^{\beta anN} \tag{4}$$

(2) Write down the Helmholtz free energy [Extra: and write it in term of $n = 1/V_r - 1$ and $\tau = T_r - 1$ introduced in Problem 4.2 (and its solution in Chapter 6)].

Solution.
Using (2.2.3), we have

$$Z(T, V) = \left(\frac{n_Q e(V - Nb)}{N} e^{\beta an} \right)^N. \tag{5}$$

Therefore, we obtain

$$A = -Nk_B T \log \left[\frac{n_Q e}{N} (V - Nb) \right] - \frac{aN^2}{V}. \tag{6}$$

1

(Later I will give the expression in terms of n, τ, etc.)

2. [Takahashi nearest neighbor gas][1]
Consider a one-dimensional fluid whose binary interaction potential ϕ is effective only for the nearest neighbor particles, and depends only on the distance. That is, if r_i denotes the position of the ith particle, the total potential energy of the system reads (notice that $0 \leq r_1 \leq \cdots \leq r_N \leq V$)

$$\Phi = \sum_{i=1}^{N-1} \phi(r_{i+1} - r_i).$$

(1) Write down the configurational partition function $Q(T, V)$ for this system confined in a 1D box of length V at temperature T. [Introduce $x_i = r_{i+1} - r_i$.]

Solution.

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\begin{aligned}
Q(T, V) &= \frac{1}{V^N} \int dr_1 \cdots \int dr_N \, e^{-\beta\Phi} && (7) \\
&\quad {}_{0 \leq r_1 \leq \cdots \leq r_N \leq V} \\
&= \frac{1}{V^N} \int dr_1 \int dx_1 \cdots \int dx_{N-1} \, e^{-\beta \sum \phi(x_i)} && (8) \\
&\quad {}_{0 \leq r_1 + x_1 + \cdots + x_{N-1} \leq V}
\end{aligned}
$$

Here, all the integrating variables are non-negative.

This is not easy to compute, but if we consider the same problem with the pressure ensemble formalism, then we can write it in the following 'non-interacting particle form.'

$$Y(T, P) = \int_0^\infty dV \, Z_{ideal}(T, V) Q(T, V) e^{-\beta PV} = [y(P, T)]^N.$$

(2) Write down the formula for $y(P, T)$ and show that there cannot be any phase transition (i.e., as a function of P and T it is holomorphic on the positive real half plane). You may assume that the binary interaction potential is a physically reasonable one.

Solution.
It is convenient to recall convolution defined as follows

$$(f * g)(x) = \int_0^x dy f(x - y) g(y) = \int dx_1 \int dx_2 \, f(x_1) g(x_2). \qquad (9)$$
$$\quad {}_{x_1 + x_2 = x}$$

This can be generalized to m functions as

$$(f_1 * f_2 * \cdots * f_m)(x) = \int dx_1 \cdots \int dx_m \, f_1(x_1) \cdots f_m(x_m). \qquad (10)$$
$$\quad {}_{x_1 + \cdots + x_m = x}$$

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[1]H. Takahashi, Proc. Phys.-Math. Soc. Jpn. **24** 60 (1942); Lieb, Mattis, *Mathematical Physics in One Dimension* (Academic Press, 1966) Chapter 1. If more neighbors are included, see L. van Hove, Physica **16**, 137 (1950).

Here, all variables are non-negative. We are interested in the Laplace transformation of f defined as

$$\mathcal{L}f(s) = \int_0^\infty f(t)e^{-st} \tag{11}$$

We can easily demonstrate (this is a fundamental relation for the Laplace transformation you should remember)

$$\mathcal{L}(f * g)(s) = \mathcal{L}f(s)\mathcal{L}g(s). \tag{12}$$

It is clear that $Z = Z_{ideal}Q$ has almost the convolution structure.

$$Z_{ideal}Q = \left(\frac{n_Q e}{N}\right)^N \int dr_1 \int dx_1 \cdots \int_{0 \leq r_1 + x_1 + \cdots + x_N \leq V} dx_N \, e^{-\beta \sum_i \phi(x_i)} \tag{13}$$

$$= \left(\frac{n_Q e}{N}\right)^N \int_0^V dR \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_N} dx_N \, e^{-\beta \sum_i \phi(x_i)} \tag{14}$$

Thus,

$$Y(T, P) = \left(\frac{n_Q e}{N}\right)^N \int_0^\infty dV \int_0^V dR \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} x_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta PV} \tag{15}$$

$$= \left(\frac{n_Q e}{N}\right)^N \int_0^\infty dR \int_R^\infty dV \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} x_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta PV} \tag{16}$$

$$= \left(\frac{n_Q e}{N}\right)^N \int_0^\infty dR \int_0^\infty dV' \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} x_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta P(V'+R)} \tag{17}$$

$$= \left(\frac{n_Q e}{N}\right)^N \int_0^\infty dV' e^{-\beta PV'} \int_0^\infty dR \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} x_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta PR}$$

$$\tag{18}$$

$$= \left(\frac{n_Q e}{N}\right)^N \frac{1}{\beta P} \int_0^\infty dR \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} dx_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta PR} \tag{19}$$

Now, we can exploit the above mentioned property of the Laplace transformation:

$$\left(\frac{n_Q e}{N}\right)^N \frac{1}{\beta P} \int_0^\infty dR \int dr_1 \int dx_1 \cdots \int_{R = r_1 + x_1 + \cdots + x_{N-1}} dx_{N-1} \, e^{-\beta \sum_i \phi(x_i)} e^{-\beta PR} \tag{20}$$

$$= \left(\frac{n_Q e}{N}\right)^N \left(\frac{1}{\beta P}\right)^2 \left[\int_0^\infty dx \, e^{-\beta \phi(x) - \beta Px}\right]^{N-1}. \tag{21}$$

The above calculation is an honest one, but you can ignore some prefactors and also use the fact $N \gg 1$.

From the result we can obtain the Gibbs free energy

$$G = -k_BT \log Y(T,P) = -Nk_BT \log(n_Q e/N) + 2k_BT \log(\beta P) - Nk_BT \log \left[\int_0^\infty dx\, e^{-\beta\phi(x) - \beta Px} \right].$$
(22)

To demonstrate that the system does not have any phase transition for the usual binary interaction potential (like the Lenard-Jones interaction), we should show that G/N in the thermodynamic limit is a holomorphic function of P and T and is not zero. Therefore, we have only to show the holomorphy of

$$q(P,T) = \int_0^\infty dx\, e^{-\beta\phi(x) - \beta Px}$$
(23)

For a fixed x which is outside the hardcore (if any), this is a holomorphic function of β (or T) and P (if their real part is positive). For large x ϕ vanishes, so $q \sim e^{-\beta Px}$. Now, we use the following elementary fact:

Theorem.[2] For the following integral, where S is the integration range and $z \in D$ a certain domain on the complex plane,

$$F(z) = \int_{x \in S} dx f(x, z)$$
(24)

If
(i) For each $z \in D$ f is integrable,
(ii) f is holomorphic on D for any x,
(iii) For any compact subset of D, there is an integrable function Φ such that $|f(x,z)| < \Phi(x)$,
then F is holomorphic on D.

Therefore, it is easy to see that as a function of T or P the Gibbs free energy density is holomorphic, so there cannot be any phase transition.

Some people confuses holomorphy and monotonicity of the PV-curve. If you honestly compute the partition function, then the monotonicity of the PV curve is never violated; the violation is due to approximation. Here, we calculate the partition function exactly. The positivity of y does not imply its holomorphy. If holomorphy is state without any reason, I gave -2 penalty.

(3) When the ϕ is a hard core potential, demonstrate that we get the Tonks gas equation of state.

Solution.
For the hard core potential of radius σ,

$$q(P,T) = \int_0^\infty dx\, e^{-\beta\phi(x) - \beta Px} = \int_\sigma^\infty dx\, e^{-\beta Px} = \frac{e^{-\beta P\sigma}}{\beta P}.$$
(25)

We know $dG = -SdT + VdP$, so ($N \gg 1$ is used)

$$V = \frac{Nk_BT}{P} + N\sigma,$$
(26)

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[2]This is a theorem for Lebesgue integration theory, so a slightly more careful statement is desirable, but for physicists this should be enough; basically, if the integration converges clearly, then holomorphy survives integration. Those who wish to be theoreticians must learn Lebesgue integrals.

so

$$P = \frac{Nk_BT}{V - N\sigma}.$$ (27)

It is a nice math exercise, but I wish you to remember how I 'derived' this equation chasing the trajectories of the particles.