Phys 430 - Solutions to the 2nd HOMEWORK

1. How do you interpret negative temperatures? Are you convinced that negative temperatures are hotter than positive temperatures? If yes, why? If no, why? Show that heat always flows from negative temperatures to positive temperatures. (10 points)

   Solution

   Formally speaking, temperature is a measure of how the entropy changes as the energy of a system is increasing. If a system has negative temperature, it means that the entropy of the system decreases as its energy is increasing. This is possible only if the system has a maximum possible energy level, and in general the maximum energy state will not be degenerate, and hence the entropy at that energy will be zero.

   From the definition of negative temperature, it is also obvious that negative energy states are states that have larger energy than positive energy states.

   To see that heat always from from negative temperature states to positive temperature states, consider a non-equilibrium system comsisting of a positive temperature subsytem A and a negative temperature subsystem B. Assume that initially they have energies E_A and E_B respectively. The total energy $E = E_A + E_B$ is conserved. The total entropy of the system will be $S(E) = S_A(E_A) + S_(B)(E_B)$. Since the system is not in equilibrium, as the system approaches equilibrium, the total entropy of the system has to increase (it can not remain zero as the process of heat flow between two reservoirs at different temperatures is not a reversible process). Hence

   $$\frac{d}{dt}S(E) = \frac{dS_A}{dE_A}\frac{dE_A}{dt} + \frac{dS_B}{dE_B}\frac{dE_B}{dt} > 0$$

   . Using the definition of temperature and the conservation of total enery, i.e.

   $$0 = \frac{dE}{dt} = \frac{dE_A}{dt} + \frac{dE_B}{dt}$$

   one obtains

   $$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\frac{dE_A}{dt} > 0$$

Since $T_A > 0$, $\frac{1}{T_A} < 0$. Subtracting a positive number from a negative number, one still has a negative number, hence

$$\frac{1}{T_A} - \frac{1}{T_B} < 0,$$

thus for the entropy to increase, we need to have

$$\frac{dE_A}{dt} < 0$$

i.e. the negative temperature system looses energy whereas the positive temperature system gains energy; i.e. heat flows from a negative temperature system to a positive temperature system.

2. Consider an ideal gas consisting of point particles whose energy momentum relation is given by $\varepsilon = cp$ whare c is some constant and p is the sum of the magnitudes of the components of the momentum of the particles; i.e. $p = |p_x| + |p_y| + |p_z|$. For this gas, calculate:

The number of states $\Gamma(E)$ that have energy less then or equal to E (10 points)

The entropy, S, of the system (5 points)

The temperature, T, of the system (5 points)

Calculate the thermodynamic potentials $E(S,V)$, $F(T,V)$, $W(S,P)$ and $\Phi(T,P)$ (10 points)

Calculate C_P and C_V (5 points)

Solution:

If we enclose this gas in a cube of side length L, the components of the momenta of the ith particle is given by $|p_j^i| = \frac{\hbar\pi}{L}n_j^i$, $j = x$, y, z, and the total energy of the system will be given by:

$$E = \frac{c\hbar\pi}{V^{1/3}} \sum_{i=1}^{N}(n_x^i + n_y^i + n_z^i) \tag{1}$$

where we have substituted $L = V^{1/3}$. In order to calculate $\Gamma(E)$, we need to find the number of sets of $3N$ integers ,$\{n_i\}$, such that

$$\frac{c\hbar\pi}{V^{1/3}} \sum_{i=1}^{3N} n_i \leq E \tag{2}$$

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or

$$\sum_{i=1}^{3N} n_i \leq \alpha = E \frac{V^{1/3}}{c\hbar\pi} \tag{3}$$

This determines a plane in the $3N$ dimensional space and we need to find the number of points under this plane that have integers for their coordinate. As we did in the class, we can imagine unit hyper-cubes, each having 1 for their volume, around each one of these points. These hyper-cubes will fill the volume under the plane. Then the question is transformed into finding the number of these unit hyper-cubes that one can fill under the plane. But this is nothing but the total volume under the plane devided by 1, the volume of each one of these unit cubes. Hence $\Gamma(E)$ is the volume under this hyper-plane.

The volume of this region can be obtained from the integral

$$A_{3N} = \int_0^\alpha dn_1 \int_0^{\alpha-n_1} dn_2 \int_0^{\alpha-n_1-n_2} dn_3 \cdots \int_0^{\alpha-\sum_{i=1}^{3N-1} n_i} dn_{3N} 1$$

We will prove that $A_n = \frac{\alpha^n}{n!}$ for any integer n using induction. For $n = 1$,

$$A_1 = \int_0^\alpha dn_1 = \alpha = \frac{\alpha^1}{1!},$$

hence our assertion is obviously true. Assume that it is true for $n-1$. Then

$$A_n = \int_0^\alpha A_{n-1}(\alpha - n_1) = \int_0^\alpha dn_1 \frac{(\alpha - n_1)^{n-1}}{(n-1)!} = - \left. \frac{(\alpha - n_1)^n}{n!} \right|_{n_1=0}^{n_1=\alpha} = \frac{\alpha^n}{n!} \tag{4}$$

Hence, our assertion is true for any finite integer n. Thus

$$\Gamma(E) = A_{3N}(\alpha) = \left(\frac{EV^{1/3}}{c\hbar\pi} \right)^{3N} \frac{1}{(3N)!N!} \tag{5}$$

where we have added an extra $N!$ in the denominator to take into account the fact that the particles are identical particles. From $\Gamma(E)$, one can obtain $\Delta\Gamma(E)$ by differentiating:

$$\begin{aligned}
\Delta\Gamma(E) &= \frac{\partial \Gamma(E)}{\partial E} \Delta E \\
&= \left(\frac{EV^{1/3}}{c\hbar\pi} \right)^{3N} \frac{1}{(3N-1)!N!} \frac{\Delta E}{E} \tag{6}
\end{aligned}$$

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and the entropy of the system becomes:

$$
\begin{aligned}
S(E) &= \ln \Delta\Gamma(E) = 3N \log\left(\frac{EV^{1/3}}{c\hbar\pi}\right) - \ln(3N-1)! - \ln N! + \ln\frac{\Delta E}{E} \\
&= 3N \log\left(\frac{EV^{1/3}}{c\hbar\pi}\right) - 3N\ln(3N) + 3N - N\ln N + N \\
&= 3N \ln\left(\frac{E}{N}\left(\frac{V}{N}\right)^{1/3}\frac{e^4}{c3\hbar\pi}\right) \tag{7}
\end{aligned}
$$

where $e = 2.71828\cdots$ is the logarithmic base; i.e. $\ln e = 1$. The expression for the entropy is clearly an additive expression.

The temperature T is obtained as

$$
T^{-1} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3N}{E} \tag{8}
$$

or $E = 3NT$.

Inverting the expression for entropy for the energy, we obtain

$$
E(S,V) = Ne^{\frac{S}{3N}}\left(\frac{N}{V}\right)^{1/3}\frac{3c\hbar\pi}{e^4} \tag{9}
$$

To obtain the free energy $F(T,V)$ we need to evaluate $F = E - TS$ in terms of temperature, T and the volume V. We have already shown that $E = 3NT$. Thus we only need to express S in terms of T and V. In the expression for entropy, substituting $E = 3NT$, we obtain

$$
S(T,V) = 3N \ln\left(T\left(\frac{V}{N}\right)^{1/3}\frac{e^4}{c\hbar\pi}\right) \tag{10}
$$

Thus

$$
\begin{aligned}
F(T,V) &= E(T,V) - TS(T,V) \\
&= 3NT - T3N\ln\left(T\left(\frac{V}{N}\right)^{1/3}\frac{e^4}{c\hbar\pi}\right) \\
&= -3NT\ln\left(T\left(\frac{V}{N}\right)^{1/3}\frac{e^3}{c\hbar\pi}\right) \tag{11}
\end{aligned}
$$

To obtain $W(S, P) = E(S, P) + PV(S, P)$, we first need to express the volume V in terms of the etropy S and the pressures P. The pressure is obtained as

$$P = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{1}{3}\frac{E}{V} \tag{12}$$

or $PV = E/3$. Hence

$$W(S, P) = E + PV = E + \frac{E}{3} = \frac{4}{3}E = 4N\left(\frac{c\hbar\pi}{e^4}\right)^{3/4}e^{\frac{S}{3N}}P^{1/4} \tag{13}$$

To obtain $\Phi(T, P)$, note that $PV = E/3 = NT$ is the equation of state. Hence

$$\begin{aligned}
\Phi(T, P) &= E - TS + PV = 3NT - TS + NT \\
&= 4NT - T3N\ln\left(T\left(\frac{V}{N}\right)^{1/3}\frac{e^4}{c\hbar\pi}\right) \\
&= 4NT - 3NT\ln\left(T\left(\frac{T}{P}\right)^{1/3}\frac{e^4}{c\hbar\pi}\right) \tag{14}
\end{aligned}$$

C_V can be obtained from the expression for E in terms of the parameter T and P, i.e. $E = 3NT$. Then

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N$$

. To calculate C_P, one can use the expression for $W(T, P) = E + PV = 3NT + NT = 4NT$. Hence

$$C_P = \left(\frac{\partial W}{\partial T}\right)_P = 4N$$

3. Consider again the system of N non-interacting dipoles that we have studied in the class. We had shown that if one takes only one of the dipoles, the probabilities that it will have energy $\pm\varepsilon$ are given by

$$P(\pm\varepsilon) = Z^{-1}e^{\mp\beta\varepsilon} \tag{15}$$

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where $\beta = T^{-1}$. Now, take two of the dipoles.

What are the possible states that the dipoles can be found in? (5 points)

Show explicitely (showing all your work) that the probability that these two dipoles are in the state n is given by

$$P_n = Z^{-1}e^{-\beta\varepsilon_n} \qquad (16)$$

where ε_n is the energy of the nth state and $Z = e^{-2\beta\varepsilon} + 2 + e^{2\beta\varepsilon}$ (15 points)

Solution:

There are 4 possible states for the dipoles:

State	d_1	d_2	Total Energy
1	ϵ	ϵ	2 ϵ
2	ϵ	- ϵ	0
3	$-\epsilon$	ϵ	0
4	$-\epsilon$	$-\epsilon$	-2 ϵ

Let $S(N, E)$ be the entropy of N dipoles when they have a total energy E. To find the required probabilities, let's devide the N dipole system into 2 subsystems: a subsystem A that contains the two dipoles and have energy ϵ_n and another subsystem B that contains the remaining $N - 2$ dipoles and has energy $E - \epsilon_n$. Then the probability P_n that the subsystem A is in the state n is given by

$$P_n = e^{S(N-2,E-\epsilon_n)-S(N,E)} \qquad (17)$$

Expanding $S(N - 2, E - \epsilon_n)$ around N and E, one obtains:

$$S(N - 2, E - \epsilon_n) = S(N, E) + \frac{\partial S}{\partial N}(-2) + \frac{\partial S}{\partial E}(-\epsilon_n) \qquad (18)$$

and hence

$$\ln P_n = -2\frac{\partial S}{\partial N} - \frac{\epsilon_n}{T} \qquad (19)$$

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and thus

$$P_n = \frac{e^{-\frac{\epsilon_n}{T}}}{\left(e^{\frac{\partial S}{\partial N}}\right)^2} \tag{20}$$

In the class, when we were discussing the probabilities of the single dipole, we had calculated that

$$e^{\frac{\partial S}{\partial N}} = e^{-\frac{\epsilon}{T}} + e^{\frac{\epsilon}{T}} \tag{21}$$

and hence

$$P_n = Z^{-1} e^{-\epsilon_n} \tag{22}$$

where

$$Z = \left(e^{-\frac{\epsilon}{T}} + e^{\frac{\epsilon}{T}}\right)^2 = e^{-2\frac{\epsilon}{T}} + 2 + e^{2\frac{\epsilon}{T}} \tag{23}$$

4. Express the following derivative in terms of derivatives of the equation of state and C_p or C_v. Find processes for which each derivative is relevant. (3 points each)

$$\left(\frac{\partial E}{\partial P}\right)_T, \left(\frac{\partial W}{\partial V}\right)_T, \left(\frac{\partial E}{\partial T}\right)_P, \left(\frac{\partial W}{\partial P}\right)_T, \left(\frac{\partial W}{\partial T}\right)_V$$

Solution:

Using $dE = TdS - PdV$,

$$\left(\frac{\partial E}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Using the fact that $d(E - TS + PV) = -SdT + VdP$ is a total differential, one can write:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P,$$

and hence

$$\left(\frac{\partial E}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

It is relevant e.g. in a system which is similar to the Joule Thomson process but instead of being isolated as in the JT process, the system is in contact with a heat reservoir.

Similar to the previous case, using $dW = TdS + VdP$,

$$\left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T$$

. Now using the fact that $d(E - TS) = -SdT - PdV$ is a total differential, one sees that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

and hence

$$\left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T.$$

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Note that similarity with the previous result. Except than a change in sign, the two results can be obtained from one another by exchanging P and V consistant with the general anology between W and E, i.e. The relation between E and V is the same as the relation between W and P.

This is relevant in a process in which we have a gas in a piston which is in contact with a heat reservoir.

Using $dE = TdS - PdV$,

$$\left(\frac{\partial E}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P = C_P - P\left(\frac{\partial V}{\partial T}\right)_P$$

where we have used

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

Consider a gas enclosed in a movable piston so that the pressure is kept constant. Then you heat the system, increasing the temperature.

Using $dW = TdS + VdP$, we obtain

$$\left(\frac{\partial W}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

and using the previous result for $\left(\frac{\partial S}{\partial P}\right)_T$,

$$\left(\frac{\partial W}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

The same process as in the first derivative: a JT process in contact with a heat reservoir.

Using $dW = TdS + VdP$, we obtain

$$\left(\frac{\partial W}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V = C_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

where we have used

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_V$$

The same as the third derivative but this time instead of a movable piston, we consider a gas enclosed in a fixed volume.

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5. Consider a system whose equation of state is given by

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NT$$

for some positive constants a and b (this is called the Van der Waals' equation of state). For this system

Calculate the derivatives

$$\left(\frac{\partial E}{\partial V}\right)_T$$

and

$$\left(\frac{\partial E}{\partial T}\right)_V$$

. (10 points)

By integrating you results, find $E(V,T)$ for this system upto a constant. (10 points)

In the limit $V \to \infty$, the van der Waals' equation of state reduces to the ideal gas equation of state. The energy of the Van der Waals' gas in this limit also reduces to the energy of the ideal gas. By considering this limit, and comparing the energy with the energy of the ideal gas, fix the constant in the expression for the energy of the Van der Waals' gas.(bonus: 10 points)
Solution:
By definition

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

. For the other derivative, using $dE = TdS - PdV$, we can write

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{24}$$

Using the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{25}$$

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one obtains

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{26}$$

Differentiating the Van der Waals equation of state with respect to T at constant V, one obtains

$$\left(\frac{\partial P}{\partial T}\right)_V (V - Nb) = N \tag{27}$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N}{V - Na} \tag{28}$$

Substituting, we obtain

$$\begin{aligned}\left(\frac{\partial E}{\partial V}\right)_T &= \frac{NT}{V - Na} - P \\ &= a\frac{N^2}{V^2} \tag{29}\end{aligned}$$

Integrating the results with respect to V at constant T, we obtain

$$E(V,T) = -a\frac{N^2}{V} + f(T) \tag{30}$$

where $f(T)$ is a yet unknown function of T only. For a given T, since the gas should become and ideal gas in the limit $V \to \infty$ at constant T and N, we have

$$E^{ideal\ gas}(T) = \lim_{V \to \infty} E(V,T) = f(T) \tag{31}$$

and hence $f(T) = \frac{3}{2}NT$. Thus for the Van der Waals gas

$$E(V,T) = \frac{3}{2}NT - a\frac{N^2}{V} \tag{32}$$