Physics 112 Solution Set # 8 Winter 2000

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① RB Chapter 12, problem 5

We need to first compute the pressure at the top of Mt. Everest. In this course, we have studied two different models for the atmosphere: (i) the isothermal atmosphere [see, e.g. RB Chapter 7, problem 1 which we examined in problem set #6] and (ii) the adiabatic atmosphere, which we studied on the second midterm exam.

Case 1: isothermal atmosphere

In RB Chapter 7, problem 1 we derived the following result for the pressure as a function of the altitude z:

$$P(z) = P(0)\, e^{-mgz/kT}$$

For definiteness, take $T = 300\,\mathrm{K}$. The height of Mt. Everest is 8848 m [I don't know where Baierlein found his value!]. Then, with $P(0) = 1$ atm pressure, the pressure at the top of Mt. Everest would be:

$$\exp\left[\frac{-(4.8\times10^{-26}\,\mathrm{kg})(9.8\,\mathrm{m\,s^{-2}})(8848\,\mathrm{m})}{(1.381\times10^{-23}\,\mathrm{J/K})(300\,\mathrm{K})}\right]\ \mathrm{atm}$$

$$= 0.366\ \mathrm{atm}$$

where the mass of an air molecule has been taken from Table 5.2 on p107 of RB.

Case 2: adiabatic atmosphere

Using the results obtained in problem 1 on the second midterm exam,

$$\frac{dP}{dz} = \frac{-mg}{kT}P$$

where

$$\frac{dT}{dz} = -\frac{mg}{k}\left(\frac{\gamma-1}{\gamma}\right)$$

with $\gamma = \frac{7}{5}$. Solving for $T(z)$:

$$T(z) = T_0 - \frac{mg}{k}\left(\frac{\gamma-1}{\gamma}\right)z$$

For ease in notation, let us denote $c \equiv \frac{mg}{k}\left(\frac{\gamma-1}{\gamma}\right)$.

If we take $m = 4.8\times10^{-26}\,\mathrm{kg}$ for air molecules [on the exam, we took $m = m_{N_2}$ which is slightly less than m_{air}],

$$c = \frac{(4.8\times10^{-26}\,\mathrm{kg})(9.8\,\mathrm{m\,s^{-2}})}{1.381\times10^{-23}\,\mathrm{J\,K^{-1}}}\ \frac{(2/5)}{(7/5)}$$

$$= 9.732\times10^{-3}\,\mathrm{K\,m^{-1}}$$

As in case 1, we take $T_0 = 300\,\mathrm{K}$. Then,

$$\frac{dP}{dz} = \frac{-mg}{k(T_0 - cz)}P$$

$$\int\frac{dP}{P} = \frac{-mg}{k}\int\frac{dz}{T_0 - cz}$$

$$\ln\left[\frac{P(z)}{P_0}\right] = \frac{mg}{kc}\ln\left(\frac{T_0 - cz}{T_0}\right)$$

Thus,

$$P(z) = P_0\left(1 - \frac{cz}{T_0}\right)^{mg/kc}$$

However, one should note that $\frac{mg}{kc} = \frac{\gamma}{\gamma-1}$ by definition of c.

So,

$$P(z) = P_0\left(1 - \frac{cz}{T_0}\right)^{\gamma/\gamma-1}$$

In fact, there is a simpler way to obtain the same result without solving the differential equation for $P(z)$. Recall that for a (quasi-static) adiabatic process involving a classical ideal gas

$$P^{1-\gamma}T^{\gamma} = \text{constant}$$

(This follows from PV^{γ} = constant and the ideal gas law.)
In particular,

$$[P(z)]^{1-\gamma}[T(z)]^{\gamma} = P_0^{\,1-\gamma}T_0^{\,\gamma}$$

for any altitude z, where $P_0 = 1\,\text{atm}$ and T_0 is the temperature at sea-level. Solving for $P(z)$,

$$P(z) = P_0\left(\frac{T_0}{T(z)}\right)^{\frac{\gamma}{1-\gamma}}$$

But we saw on the previous page that $T(z) = T_0 - cz$. Thus,

$$\frac{T(z)}{T_0} = 1 - \frac{cz}{T_0}$$

and we recover the previous result for $P(z)$. To compute the pressure at the top of Mt. Everest, take $T_0 = 300\,K$. Then,

$$T_{\text{everest}} = 300\,K - (9.732\times 10^{-3}\,K\,m^{-1})(8848\,K)$$
$$= 213.9\,K$$

Note that $T_0 - T_{\text{everest}} = 86.1\,K$ differs slightly with the result obtained in problem 1 on the second midterm. This difference is due to the fact that on the midterm, we chose $m = m_{N_2}$ which is slightly less than m_{air} used in this problem.

Finally, the pressure at the top of Mt. Everest is

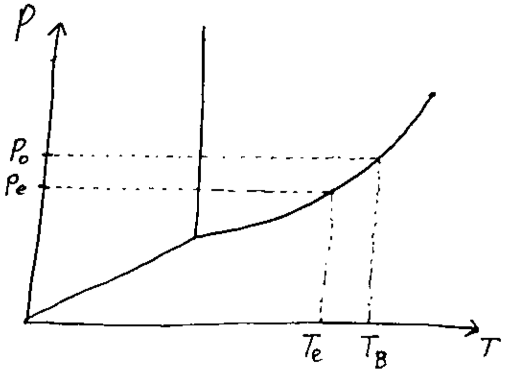
$$P_e = (1\,\text{atm})\left(\frac{300\,K}{213.9\,K}\right)^{-7/2}$$
$$= 0.306\ \text{atm}$$

The pressure is not very different in the two models.

To find the boiling point of water at this reduced pressure, we examine the vaporization curve of H_2O:

In the graph at the right, $P_0 = 1\,\text{atm}$ and $T_B = 373\,K$ is the boiling point of water at sea-level.

Let $P_e = 0.306\,\text{atm}$ be the pressure at the top of Mt. Everest. Then, T_e is the corresponding boiling point of water at this reduced pressure.



Our goal is to compute T_e. There are two methods of approximation.

Method 1:

Under the assumption that $v_g \gg v_\ell$, where v_g is determined by the ideal gas law ($v_g = kT/P$) and assuming that the latent heat is constant over the range of interest, one can integrate the Clausius-Clapeyron equation to give: [RB eq (12.30) on p 281]

$$P = \frac{P_e}{\exp[-L_{vap}/kT_e]} \exp[-L_{vap}/kT]$$

Here, $L_{vap} = 0.42\,eV/molecule$ [see Table 12.2 on p274 of RB].
We wish to solve for T_e.

Thus, $\exp[-L_{vap}/kT_e] = \frac{P_e}{P}\exp[-L_{vap}/kT]$.

Taking logs of both sides,

$$-\frac{L_{vap}}{kT_e} = \ln\frac{P_e}{P} - \frac{L_{vap}}{kT}$$

$$T_e = \frac{L_{vap}/k}{\frac{L_{vap}}{kT} - \ln\frac{P_e}{P}}$$

Since Lvap is given in eV units, we use $k = 8.617\times10^{-5}\,eV/K$.
We take $p = 1$ atm and $T = 300\,K$. Then,

$$T_e = \frac{\frac{0.42\,eV}{8.617\times10^{-5}\,eV/K}}{\frac{0.42\,eV}{(8.617\times10^{-5}\,eV/K)(373\,K)} - \ln P_e}$$

$$= \frac{4874\,K}{13.067 - \ln P_e}$$

where p_e is given in units of atm.

We consider the two models of the atmosphere:

(i) isothermal: $P_e = 0.366$ atm

$T_e = 346\,K$ (or $\Delta T = T_e - T = -27\,K$)

(ii) adiabatic: $P_e = 0.306$ atm

$T_e = 342\,K$ (or $\Delta T = -31\,K$)

Method 2:

The Clausius-Clapeyron equation states that

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_\ell)}$$

At $T = 373\,K$, we have [see RB Chapter 12, problem 8]

$$V_\ell = 3.12\times10^{-29}\,m^3/molecule$$

$$V_g = 1600\,V_\ell = 4.99\times10^{-26}\,m^3/molecule$$

and

$$L = 0.42\,eV/molecule$$

$$= 6.728\times10^{-20}\,J/molecule$$

Thus, at $T = 373\,K$,

$$\frac{dP}{dT} = \frac{6.728\times10^{-20}\,J}{(373\,K)[4.99\times10^{-26}\,m^3 - 3.12\times10^{-29}\,m^3]}$$

$$= 3616\,J\,m^{-3}\,K^{-1}$$

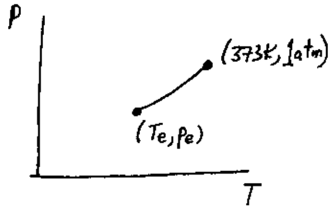
$$= 3616\,N\,m^{-2}\,K^{-1}$$

Using 1 atm = $1.013\times10^{5}\ \text{N m}^{-2}$,

$$\frac{dP}{dT} = 3.57\times10^{-2}\ \text{atm K}^{-1}$$

at $T = 373\text{K}$.

We now look again at the vaporization curve:



In the approximation that the curve is an approximate straight line, we can use the result above for the slope of that line. Thus,

$$3.57\times10^{-2}\text{atm K}^{-1} = \frac{1\ \text{atm} - P_e}{373\text{K} - T_e}$$

Consider again the two cases:

(i) isothermal: $p_e = 0.366$ atm.

$$\Delta T = T_e - 373\text{K} = \frac{0.366-1}{3.57\times10^{-2}} = -17.8\ \text{K}$$

(ii) adiabatic: $p_e = 0.306$ atm

$$\Delta T = T_e - 373\text{K} = \frac{0.306-1}{3.57\times10^{-2}} = -19.4\ \text{K}$$

The difference of the two methods arises from the fact that in method 1, L is assumed constant over the range of interest while in method 2, dP/dT is assumed constant over the range of interest. The truth probably lies somewhere in between.

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② RB Chapter 12, problem 8

(a) $W = P\Delta V$. For one molecule of water,

$$\Delta V = V_g - V_\ell$$

where $V_g = 4.99\times10^{-26}\ \text{m}^3$
$V_\ell = 3.12\times10^{-29}\ \text{m}^3$

and $P = 1\ \text{atm} = 1.013\times10^{5}\ \text{N m}^{-2}$. Thus,

$$W = (1.013\times10^{5}\ \text{N m}^{-2})(4.99\times10^{-26} - 3.12\times10^{-29}\ \text{m}^3)$$
$$= 5.05\times10^{-21}\ \text{J}$$
$$= 3.15\times10^{-2}\ \text{eV}$$

(b)
$$s_g - s_\ell = \frac{L_{vap}}{T} = \frac{0.42\ \text{eV/molecule}}{373\ \text{K}}$$
$$= 1.126\times10^{-3}\ \text{eV/K}$$
$$= 1.804\times10^{-22}\ \text{J/K}$$

(c) By the first law of thermodynamics,

$$\Delta E = L_{vap} - W = 0.39\ \text{eV/molecule}$$

(d) The Gibbs free energy per molecule is just the chemical potential. But in phase equilibrium, $\mu_g = \mu_\ell$. Hence $\Delta G = 0$.

We can also check that $\Delta G = \Delta E - T\Delta S + P\Delta V$. Since $W = P\Delta V$ and $T\Delta S = (373\text{K})(1.126\times10^{-3}\text{eV/K}) = 0.42\text{eV} = L_{vap}$, we indeed find that $\Delta G = 0.39\text{eV} - 0.42\text{eV} + 0.03\text{eV} = 0$.

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③ RB Chapter 12, problem 12

(a) Start from RB eq (12.49)

$$p = \frac{NkT}{V-Nb} - a\left(\frac{N}{V}\right)^2$$

Rewrite this as:

$$p = \frac{NkT}{V}\left[\frac{1}{1-\frac{bN}{V}} - \frac{a(N/V)}{kT}\right]$$

For individual corrections of 1%, one needs:

$$\frac{bN}{V} = 0.01 \qquad \text{since } \frac{1}{1-x} \simeq 1+x \quad \text{for } |x| \ll 1$$

and

$$\frac{a(N/V)}{kT} = 0.01$$

(b) Since about 80% of air is N_2, we shall use the data for N_2 given in Table 12.5:

$$a = 2.36 \times 10^{-30}\ \text{eV-m}^3$$
$$b = 64.3 \times 10^{-30}\ \text{m}^3$$

We need $\frac{N}{V}$. Since the ideal gas approximation is pretty good (as we shall see momentarily), let us compute for $T = 300K$ at $p = 1$ atm pressure:

$$\frac{N}{V} \simeq \frac{p}{kT} = \frac{1.013 \times 10^5\ \text{N m}^{-2}}{(1.381 \times 10^{-23}\ \text{J/K})(300\text{K})}$$

$$= 2.45 \times 10^{25}\ \text{molecules/m}^3.$$

Then,

$$\frac{bN}{V} = (64.3 \times 10^{-30}\text{m}^3)(2.45 \times 10^{25}\ \text{m}^{-3})$$

$$= 1.57 \times 10^{-3}$$

$$\frac{a(N/V)}{kT} = \frac{(2.36 \times 10^{-30}\text{eV-m}^3)(2.45 \times 10^{25}\text{m}^{-3})}{(8.617 \times 10^{-5}\text{eV/K})(300\text{K})}$$

$$= 2.23 \times 10^{-3}$$

Both are clearly small corrections. Since $\frac{bN}{V} \ll 1$, we can write

$$\frac{1}{1-\frac{bN}{V}} \simeq 1 + \frac{bN}{V}.$$

So,

$$p = \frac{NkT}{V}\left[1 + \frac{bN}{V} - \frac{a(N/V)}{kT}\right]$$

$$= \frac{NkT}{V}\left[1 - 6.6 \times 10^{-4}\right]$$

which is clearly a small correction to the ideal gas law. This also provides an a posteriori justification for using the ideal gas law to compute N/V. Our result is consistent.

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④ RB Chapter 12, problem 13

(a) In class, we wrote down the Helmholtz free energy for a van der Waals gas:

$$F = -NkT\left[\ln\left(\frac{\lambda_{th}^{-3}(V-Nb)}{N}\right) + 1 + \frac{Na}{VkT}\right]$$

The entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Keep in mind that λ_{th}^{-3} depends on temperature

$$\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$$

Thus,

$$\frac{\partial F}{\partial T} = -Nk\left[\ln\left(\frac{\lambda_{th}^{-3}(V-Nb)}{N}\right) + 1\right] - \frac{3}{2}Nk$$

and therefore,

$$S = Nk\left[\ln\left(\frac{\lambda_{th}^{-3}(V-Nb)}{N}\right) + \frac{5}{2}\right]$$

Comparing this with the ideal gas case (set $a=b=0$):

$$S_{ideal} = Nk\left[\ln\left(\frac{\lambda_{th}^{-3}V}{N}\right) + \frac{5}{2}\right]$$

$$S - S_{ideal} = Nk\left[\ln(V-Nb) - \ln V\right]$$

or

$$\boxed{S - S_{ideal} = Nk\ln\left(1 - \frac{Nb}{V}\right)}$$

Heating from temperature T_i to T_f at constant V,

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V(T)}{T}\,dT$$

[see RB eq (3.9) on p62]. This is equivalent to

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

But $S - S_{ideal}$ is independent of T. Thus, the ideal gas and the van der Waal's gas have the same heat capacity at constant volume. It follows that the entropy change of a van der Waal's gas when heated at constant volume is exactly the same as that of an ideal gas.

If the gas is monatomic, then $C_V = \frac{3}{2}Nk$ and

$$\Delta S = \frac{3}{2}Nk\ln\left(\frac{T_f}{T_i}\right)$$

(b) Using the result for $S - S_{ideal}$ obtained in part (a), if V_i changes to V_f at fixed T, then the difference in the entropy change of a van der Waals gas and that of an ideal gas is

$$\Delta S - \Delta S_{ideal} = Nk\left[\ln\left(1 - \frac{Nb}{V_f}\right) - \ln\left(1 - \frac{Nb}{V_i}\right)\right]$$

We can rewrite this as

$$\Delta S = \Delta S_{ideal} + kN \ln\left[\frac{1-b(N/V_f)}{1-b(N/V_i)}\right]$$

We can easily evaluate ΔS_{ideal}:

$$\Delta S_{ideal} = Nk \ln\left(\frac{V_f}{V_i}\right)$$

which follows from the volume dependence of the ideal gas entropy.

(c) In a slow adiabatic expansion (i.e. quasi-static), assuming there is no dissipation (e.g. friction), the entropy remains constant, since in this case

$$q = T\Delta S$$

and $q=0$ for an adiabatic process. This applies to any substance, gases and anything else.

⑤ (a) In free expansion, no work is done. Since the system is thermally isolated, no heat is exchanged. By the first law of thermodynamics, $q = \Delta E + w$. Thus, $\Delta E = 0$.

For a classical monatomic ideal gas, $E = \frac{3}{2}NkT$. Thus, since N is fixed, $\Delta E = 0$ implies that $\Delta T = 0$. Defining $\Delta T = T_2 - T_1$, we conclude that $T_1 = T_2$

(b) For a van der Waals gas, we need to work out an expression for E. Here is one method. Use the following results

$$E = kT^2 \frac{\partial}{\partial T} \ln Z$$

$$F = -kT \ln Z$$

Thus,

$$E = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

Using the previous problem,

$$\frac{F}{T} = -Nk\left[\ln\left(\frac{\lambda_{th}^{-3}(V-Nb)}{N}\right) + 1 + \frac{Na}{VkT}\right]$$

where $\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mkT}}$. Thus,

$$\frac{F}{T} = -\frac{3}{2}Nk\ln T - \frac{N^2a}{VT} + \text{terms independent of } T$$

It follows that

$$E = \frac{3}{2}NkT - \frac{N^2a}{V}$$

Since $\Delta E = 0$ in free expansion,

$$\frac{3}{2}NkT_1 - \frac{N^2a}{V_1} = \frac{3}{2}NkT_2 - \frac{N^2a}{V_2}$$

Therefore,

$$\boxed{T_2 - T_1 = \frac{2Na}{3k}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

The parameter a is positive. Since $V_2 > V_1$ by assumption, we see that $T_2 - T_1 < 0$. That is

$$\boxed{T_2 < T_1}$$

The temperature of a van der Waals gas drops during free expansion.

Note: We could have also computed E using the formula

$$F = E - TS$$

We have expressions for F and S for a van der Waals gas in the previous problem. Solving for E gives

$$E = \frac{3}{2}NkT - \frac{N^2a}{V}$$

in agreement with the result obtained previously.

ⓑ RB Chapter 9, problem 1

We are given $(V/N)^{1/3} = 1.97 \times 10^{-10}$ m and $T = 300K$ for metal zinc, which provides two conduction electrons per atom.

(a) The Fermi energy is given by [see RB eq (9.10) on p185]

$$\epsilon_F = \frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3}$$

where $n \equiv \frac{N}{V}$. Plugging in the numbers:

$$\epsilon_F = \frac{(1.055 \times 10^{-34}\,J \cdot s)^2}{2(9.109 \times 10^{-31}\,kg)} \; \frac{(3\pi^2)^{2/3}}{(1.97 \times 10^{-10}\,m)^2}$$

$$= 1.507 \times 10^{-18}\,J$$

$$= 9.4\,eV$$

(b) The Fermi temperature is obtained from $\epsilon_F = kT_F$.

$$T_F = \frac{9.4\,eV}{8.617 \times 10^{-5}\,eV/K} = 1.09 \times 10^5\,K$$

(c) The fractional shift in the chemical potential is [see RB eq. (9.16) on p188]

$$\frac{\mu(T) - \mu(0)}{\mu} = \frac{\mu(T) - \epsilon_F}{\epsilon_F} = -\frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2$$

$$= -\frac{\pi^2}{12}\left(\frac{300\,K}{1.09 \times 10^5\,K}\right)$$

$$= -6.23 \times 10^{-6}$$

(d) Using RB eq (9.19) on p189

$$\frac{C_V}{\frac{3}{2}Nk} = \frac{\pi^2}{3}\left(\frac{T}{T_F}\right)$$

$$= \frac{\pi^2}{3}\left(\frac{300\text{ K}}{1.09\times10^5\text{ K}}\right)$$

$$= 9.05\times10^{-3}$$

(e) According to Table 6.2 on p137 of RB, for zinc the Debye temperature is $\Theta_D = 327\text{ K}$. According to the graph shown in Figure 6.8 on p136 of RB, the contribution of the lattice to the heat capacity is

$$C_{lattice} \simeq 3N_{atoms}k$$

This result becomes exact when $T \gg \Theta_D$, but is still a very good approximation for $T \simeq \Theta_D$. This should be compared to

$$C_{electrons} = \frac{\pi^2}{2} N_{electrons} k \frac{T}{T_F}$$

For zinc, $N_{electrons} = 2N_{atoms}$. Therefore:

$$\frac{C_{electrons}}{C_{lattice}} = \frac{\pi^2}{3}\frac{T}{T_F} = 9.05\times10^{-3}$$

Since $C_V = C_{electrons} + C_{lattice}$, we see here that the contributions to the heat capacity from the lattice dominates when $T \gtrsim \Theta_D$.

⑦ RB Chapter 9, problem 7

Once again, we examine free expansion of a thermally isolated system. As in problem 5, $Q = W = 0$ which implies that $\Delta E = 0$. In this problem $\Delta E = E_f - E_i$, where E_i is the energy of an ideal fermi gas at $T=0$ and E_f is the energy of a classical ideal gas.

(a) According to eq (9.12) of RB on p186, the energy of an ideal fermi gas at $T=0$ is given by

$$E_i = \frac{3}{5}N\varepsilon_F$$

where

$$\varepsilon_F = \frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V_i}\right)^{2/3}$$

The energy of a classical ideal gas (assumed to be monatomic) is

$$E_f = \frac{3}{2}NkT_f$$

Thus,

$$\frac{3}{2}NkT_f = \frac{3}{5}N\frac{\hbar^2}{2m_e}\left(\frac{3\pi^2 N}{V_i}\right)^{2/3}$$

or

$$\boxed{T_f = \frac{\hbar^2}{5k m_e}\left(\frac{3\pi^2 N}{V_i}\right)^{2/3}}$$

(b) The classical ideal gas approximation is valid if

$$\lambda_{th} \ll \left(\frac{V}{N}\right)^{1/3}, \qquad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{m_e k T}}$$

Apply this inequality to the final state, and use the value of T_f obtained in part (a):

$$\left(\frac{2\pi\hbar^2}{m_e k T_f}\right)^{3/2} \ll \frac{V_f}{N}$$

with $T_f^{3/2} = \left(\frac{\hbar^2}{5 k m_e}\right)^{3/2}\left(\frac{3\pi^2 N}{V_i}\right)$. Then,

$$(10\pi)^{3/2} \ll 3\pi^2 \frac{V_f}{V_i}$$

Thus,

$$\frac{V_f}{V_i} \gg \frac{10}{3}\left(\frac{10}{\pi}\right)^{1/2} = 5.947$$

(c) The problem's title is "heating by adiabatic expansion". Technically, adiabatic means $q=0$ so no heat enters or leaves the system during the expansion. Nevertheless, the outcome of the expansion is an increase in temperature (which should be contrasted with the results of problem 5).

In the English language, if the result of some process is the increase in its temperature, then one often says that the system has been heated up. Nevertheless, in this problem the temperature has increased without adding or subtracting heat energy. This is a consequence of the fact that an ideal fermi gas possesses internal energy even at zero temperature. The latter is a consequence of the Pauli exclusion principle. That is, for a gas consisting of N fermions, only one can occupy the ground state. Thus the total energy of the gas is non-zero even at $T=0$.

See also the discussion in RB section 1.6.