

Gibbs classical statistical mechanics III

Grand canonical ensemble

- A grand canonical ensemble is relevant for systems which exchange not only energy with its environment but also particles. The ensemble is also useful for computational reasons.
- The microstate density of grand canonical ensemble is derived considering a small subsystem (labeled as 1) of the isolated system such that

$$N = N_1 + N_2, \quad \mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2, \quad (1)$$

and

$$N_1 \ll N_2, \quad \mathcal{H}_1 \ll \mathcal{H}_2. \quad (2)$$

One expects that

$$\rho(\mathbf{r}_1, \mathbf{p}_1, N_1) \sim \Gamma_{N-N_1}(U - U_1), \quad (3)$$

Using

$$S(U, V, N) \equiv k_B \ln \Gamma_N(U, V), \quad (4)$$

the relation (3) becomes

$$\rho(\mathbf{r}_1, \mathbf{p}_1, N_1) \sim \exp \left[\frac{1}{k_B} S(U - U_1, V_2, N - N_1) \right]. \quad (5)$$

Since $U \gg U_1$ and $N \gg N_1$, we expand $S(U - U_1, V_2, N - N_1)$ around U as

$$S(U - U_1, V_2, N - N_1) = S(U, V_2, N) - \frac{\partial S(U, V_2, N)}{\partial U} U_1 - \frac{\partial S(U, V_2, N)}{\partial N} N_1. \quad (6)$$

Using the identity

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N}, \quad (7)$$

and the definition of the chemical potential μ

$$\frac{\mu}{T} \equiv - \left(\frac{\partial S}{\partial N} \right)_{U, V}, \quad (8)$$

the formula (5) is written as

$$\rho(\mathbf{r}_1, \mathbf{p}_1, N_1) \sim \exp \left[\frac{1}{k_B} S(U, V, N) \right] \exp \left[- \frac{U_1 - \mu N_1}{k_B T} \right]. \quad (9)$$

The first term can be ignored and the density of microscopic states in the grand canonical ensemble is chosen as

$$\rho(\mathbf{r}, \mathbf{p}, N) = \exp \left[- \frac{\mathcal{H}(\mathbf{r}, \mathbf{p}, N) - \mu N}{k_B T} \right]. \quad (10)$$

The system 2 is treated here as a thermostat of the temperature T and a reservoir of particles.

Grand partition function

- The grand partition function is defined as

$$\Xi(T, V, \mu) \equiv \sum_{N=0}^{\infty} \frac{1}{N!} \int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \exp \left[-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p}, N) - \mu N}{k_B T} \right], \quad (11)$$

where $d^{3N}r \equiv d^3r_1 d^3r_2 \dots d^3r_N$, $\frac{d^{3N}p}{(2\pi\hbar)^{3N}} \equiv \frac{d^3p_1}{(2\pi\hbar)^3} \frac{d^3p_2}{(2\pi\hbar)^3} \dots \frac{d^3p_N}{(2\pi\hbar)^3}$.

- The equivalent definition is

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} z^N Q_N(T, V), \quad (12)$$

where $z \equiv e^{\beta\mu}$ is called the fugacity ($\beta \equiv \frac{1}{k_B T}$).

Relation with thermodynamics

- The first step to establish a relation with thermodynamics is to define the internal energy as the ensemble average of the Hamilton function

$$U(T, V, \mu) \equiv \langle \mathcal{H} \rangle \equiv \frac{1}{\Xi(T, V, \mu)} \sum_{N=0}^{\infty} \frac{1}{N!} \int d^{3N}r \frac{d^{3N}p}{(2\pi\hbar)^{3N}} \mathcal{H}(\mathbf{r}, \mathbf{p}, N) \times \exp \left[-\frac{\mathcal{H}(\mathbf{r}, \mathbf{p}, N) - \mu N}{k_B T} \right]. \quad (13)$$

- One observes that

$$U(T, V, \mu) \equiv \langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln \Xi(T, V, \mu) + \mu \langle N \rangle, \quad (14)$$

with

$$\langle N \rangle = \sum_{N=0}^{\infty} N \mathcal{P}_N, \quad (15)$$

where \mathcal{P}_N is the particle number distribution

$$\mathcal{P}_N = \frac{z^N Q_N(T, V)}{\Xi(T, V, \mu)}. \quad (16)$$

Due to Eq. (12) the distribution is normalized that is $\sum_{N=0}^{\infty} \mathcal{P}_N = 1$. One observes that

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(T, V, z). \quad (17)$$

- If the grand partition function is expressed not through μ but $z \equiv e^{\beta\mu}$, the formula (14) simplifies to

$$U(T, V, z) \equiv \langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \ln \Xi(T, V, z). \quad (18)$$

- The second step to establish the relation with thermodynamics is the definition of the grand thermodynamical potential

$$\Omega(T, V, \mu) \equiv -k_B T \ln \Xi(T, V, \mu). \quad (19)$$

- We are going to prove that

$$\Omega(T, V, \mu) = -pV, \quad (20)$$

but the proof is somewhat cumbersome.

- We start with the observation

$$\Omega(T, V, \mu) = F(T, V, \langle N \rangle) - \mu \langle N \rangle, \quad (21)$$

because $F = -k_B T \ln Q_N$ and the dominant contribution to the series (12) comes from $N = \langle N \rangle$.

- To check the equality (21) we derive the equation satisfied $\Omega(T, V, \mu)$. Computing the derivative of both sides of the definition (19), one gets

$$\left(\frac{\partial \Omega}{\partial T} \right)_{V, \langle N \rangle} = -k_B \ln \Xi(T, V, \mu) - k_B T \frac{\partial}{\partial T} \ln \Xi(T, V, \mu). \quad (22)$$

Using the definitions (19) and (14), we get

$$T \left(\frac{\partial \Omega}{\partial T} \right)_{V, \langle N \rangle} = \Omega(T, V, \mu) - U(T, V, \mu) + \mu \langle N \rangle. \quad (23)$$

- Substituting the expression (21) into Eq. (23) and using the definition $F \equiv U - TS$, one finds the thermodynamic identity

$$\left(\frac{\partial F}{\partial T} \right)_{V, \langle N \rangle} = -S(T, V, \langle N \rangle), \quad (24)$$

which has been already derived. So, the equality (21) is proven.

- To get the desired relation (20) we express the chemical potential (8) as

$$\mu \equiv -T \left(\frac{\partial S}{\partial \langle N \rangle} \right)_{U, V} = \left(\frac{\partial F}{\partial \langle N \rangle} \right)_{T, V}. \quad (25)$$

- To prove the relation (25) one computes TdS in two ways. The first one is

$$TdS = T \left(\frac{\partial S}{\partial U} \right)_{V, \langle N \rangle} dU + T \left(\frac{\partial S}{\partial V} \right)_{U, \langle N \rangle} dV + T \left(\frac{\partial S}{\partial \langle N \rangle} \right)_{U, V} d\langle N \rangle. \quad (26)$$

Taking into account the identity (7) one gets

$$TdS = dU + T \left(\frac{\partial S}{\partial V} \right)_{U, \langle N \rangle} dV + T \left(\frac{\partial S}{\partial \langle N \rangle} \right)_{U, V} d\langle N \rangle. \quad (27)$$

- The second method to compute TdS starts with $F \equiv U - TS$ and $dF = dU - TdS - SdT$ which gives

$$\begin{aligned} TdS &= dU - SdT - dF \\ &= dU - SdT - \left(\frac{\partial F}{\partial T} \right)_{V, \langle N \rangle} dT + \left(\frac{\partial F}{\partial V} \right)_{T, \langle N \rangle} dV + \left(\frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} d\langle N \rangle \\ &= dU + \left(\frac{\partial F}{\partial V} \right)_{T, \langle N \rangle} dV + \left(\frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} d\langle N \rangle, \end{aligned} \quad (28)$$

where the relation

$$S = -T \left(\frac{\partial F}{\partial T} \right)_V \quad (29)$$

has been used.

- Comparing the differentials (27) and (28) one finds the equality (25) and the expression (21) becomes

$$\Omega(T, V, \mu) = F(T, V, \langle N \rangle) - \left(\frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} \langle N \rangle. \quad (30)$$

- Since the pressure is given as

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T, \langle N \rangle}, \quad (31)$$

the derivative with respect to $\langle N \rangle$ has to be changed into the derivative with respect to V in Eq. (30). The result is

$$\left(\frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} = \frac{F}{\langle N \rangle} - \frac{V}{\langle N \rangle} \left(\frac{\partial F}{\partial V} \right)_{T, \langle N \rangle}. \quad (32)$$

- One proves the equality (32) writing down the free energy

$$F(T, V, \langle N \rangle) = \langle N \rangle f(T, v), \quad (33)$$

where $v \equiv \frac{V}{\langle N \rangle}$. The form is valid for any extensive quantity.

- Taking the derivative, one finds

$$\begin{aligned} \frac{\partial F(V, \langle N \rangle)}{\partial \langle N \rangle} &= f(v) + \langle N \rangle \frac{\partial f(v)}{\partial \langle N \rangle} = f(v) + \langle N \rangle \frac{\partial v}{\partial \langle N \rangle} \frac{\partial f(v)}{\partial v} \\ &= f(v) - v \frac{\partial f(v)}{\partial v} = f(v) - v \frac{\partial V}{\partial v} \frac{\partial f(\frac{\langle N \rangle}{V})}{\partial V} = f(v) - V \frac{\partial f(\frac{\langle N \rangle}{V})}{\partial V} \\ &= \frac{F(V, \langle N \rangle)}{\langle N \rangle} - \frac{V}{\langle N \rangle} \frac{\partial F(V, \langle N \rangle)}{\partial V}, \end{aligned} \quad (34)$$

where the argument T has been dropped to simplify the notation.

- With the definition of pressure (31) and the equality (32), Eq. (30) changes into the desired relation (20). Uff

Relation of grand potential with thermodynamics – summary

$$U = - \frac{\partial}{\partial \beta} \ln \Xi(T, V, z), \quad (35)$$

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(T, V, z), \quad (36)$$

$$pV = k_B T \ln \Xi(T, V, z). \quad (37)$$

Ideal gas

- Since

$$Q_N(T, V) = \frac{V^N}{N!} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3N}{2}}, \quad (38)$$

we have

$$\Xi(T, V, z) = \sum_{N=0}^{\infty} z^N Q_N(T, V) = \exp \left[zV \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} \right], \quad (39)$$

because

$$\sum_{n=1}^{\infty} \frac{x^n}{n!} = e^x. \quad (40)$$

- The thermodynamical quantities are

$$U = -\frac{\partial}{\partial \beta} \ln \Xi(T, V, z) = \frac{3}{2} zV \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} k_B T, \quad (41)$$

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \Xi(T, V, z) = zV \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}}, \quad (42)$$

$$pV = k_B T \ln \Xi(T, V, z) = zV \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{\frac{3}{2}} k_B T. \quad (43)$$

- Substituting $\langle N \rangle$ given by Eq. (42) into Eqs. (41) and (43), one gets the well-known formulas

$$U = \frac{3}{2} \langle N \rangle k_B T, \quad (44)$$

$$pV = \langle N \rangle k_B T, \quad (45)$$

but N is replaced by $\langle N \rangle$. It suggests that the fluctuations are small.

- The particle number distribution (16) is

$$\mathcal{P}_N = \frac{\langle N \rangle^N}{N!} e^{-\langle N \rangle}, \quad (46)$$

where z is expressed by $\langle N \rangle$.

- One recognizes in (46) the Poisson distribution. The variance is

$$\langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle. \quad (47)$$

- A typical deviation of N from $\langle N \rangle$ is

$$\Delta N \equiv \sqrt{\langle N^2 \rangle - \langle N \rangle^2} = \sqrt{\langle N \rangle}. \quad (48)$$

Therefore, the relative fluctuations are small

$$\frac{\Delta N}{\langle N \rangle} = \frac{1}{\sqrt{\langle N \rangle}} \ll 1. \quad (49)$$

Particle fluctuations in grand canonical ensemble

We are going to generalize the result obtained for the ideal gas.

- The particle number distribution (16) can be written as

$$\mathcal{P}_N \sim z^N Q_N(V, T) = z^N e^{-\beta F(T, V, N)}. \quad (50)$$

- We expand $F(T, V, N)$ around $\langle N \rangle$ as

$$F(T, V, N) = F(T, V, \langle N \rangle) + \frac{\partial F(T, V, \langle N \rangle)}{\partial \langle N \rangle} (N - \langle N \rangle) + \frac{1}{2} \frac{\partial^2 F(T, V, \langle N \rangle)}{\partial \langle N \rangle^2} (N - \langle N \rangle)^2. \quad (51)$$

- Using the chemical potential (25), the expansion is rewritten as

$$F(T, V, N) = F(T, V, \langle N \rangle) + \mu(N - \langle N \rangle) + \frac{1}{2} \frac{\partial^2 F(T, V, \langle N \rangle)}{\partial \langle N \rangle^2} (N - \langle N \rangle)^2 \quad (52)$$

and the particle number distribution (50) becomes

$$\mathcal{P}_N \sim \exp \left[-\frac{\beta}{2} \frac{\partial^2 F(T, V, \langle N \rangle)}{\partial \langle N \rangle^2} (N - \langle N \rangle)^2 \right]. \quad (53)$$

One should remember that $z \equiv e^{\beta\mu}$. The missing constant can be found from the normalization condition.

- Since $N \gg 1$ it can be treated as a continuous variable and the distribution (53) can be written as the Gauss distribution

$$\mathcal{P}_N \sim e^{-\frac{(N - \langle N \rangle)^2}{2\sigma^2}}, \quad (54)$$

with

$$\sigma^2 \equiv \langle N^2 \rangle - \langle N \rangle^2 = k_B T \left(\frac{\partial^2 F(T, V, \langle N \rangle)}{\partial \langle N \rangle^2} \right)^{-1}. \quad (55)$$

What is the meaning of the thermodynamical quantity (55)?

- Let us replace the derivative with respect of $\langle N \rangle$ into the derivative with respect of V . Writing again F as in Eq. (33) one finds

$$\frac{\partial^2 F(T, V, \langle N \rangle)}{\partial \langle N \rangle^2} = \frac{v^2}{\langle N \rangle} \frac{\partial^2 f(T, v)}{\partial v^2}. \quad (56)$$

Since

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T, \langle N \rangle} = - \frac{\partial f(T, v)}{\partial v}, \quad (57)$$

we have

$$\frac{\partial^2 F}{\partial \langle N \rangle^2} = - \frac{v^2}{\langle N \rangle} \frac{\partial p}{\partial v} = - \frac{V^2}{\langle N \rangle^2} \frac{\partial p}{\partial V}, \quad (58)$$

and

$$\sigma^2 \equiv - \frac{\langle N \rangle^2 k_B T}{V^2} \left(\frac{\partial p}{\partial V} \right)_T^{-1} = - \frac{\langle N \rangle^2 k_B T}{V^2} \left(\frac{\partial V}{\partial p} \right)_T. \quad (59)$$

- The quantity

$$\chi \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (60)$$

is called the isothermal compressibility. It says how the system's volume changes when the pressure grows.

- The variance of particle number distribution in grand canonical ensemble finally equals

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{\langle N \rangle^2 k_B T}{V} \chi. \quad (61)$$

- Let us estimate an order of magnitude of the terms in (61). Both terms in the left hand side are of order $\langle N \rangle^2$. The right hand side is of order $\langle N \rangle$ because χ and $\langle N \rangle/V$ are intensive quantities. So, as long as χ is finite the particle number fluctuations are small.
- At the first order phase transitions χ becomes infinite as the change of volume does not change the system's pressure. Then, the particle number fluctuations are large.

Application of grand canonical ensemble – mixture of atomic and molecular hydrogen

- What is a relative concentration of atomic hydrogen as function of T at fixed V ?
- There are reactions



where $\epsilon_B = 4.5$ eV and $N = N_1 + 2N_2 = \text{const}$.

-

$$\Xi(T, V, z_1, z_2) = \sum_{N_1, N_2=0}^{\infty} z_1^{N_1} z_2^{N_2} Q_{N_1, N_2}(T, V), \quad (63)$$

where

$$Q_{N_1, N_2}(T, V) \equiv \frac{1}{N_1! N_2!} \int d^{3N_1} r_1 d^{3N_2} r_2 \frac{d^{3N_1} p_1}{(2\pi\hbar)^{3N_1}} \frac{d^{3N_2} p_2}{(2\pi\hbar)^{3N_2}} \exp \left[-\frac{\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2)}{k_B T} \right], \quad (64)$$

with

$$\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \sum_{i=1}^{N_1} \left(m_1 c^2 + \frac{\mathbf{p}_i^2}{2m_1} \right) + \sum_{j=1}^{N_2} \left(m_2 c^2 + \frac{\mathbf{p}_j^2}{2m_2} \right). \quad (65)$$

- One finds

$$Q_{N_1, N_2}(T, V) = Q_{N_1}(T, V) Q_{N_2}(T, V) \quad (66)$$

$$= e^{-\beta N_1 m_1 c^2} \frac{V^{N_1}}{N_1!} \left(\frac{m_1 k_B T}{2\pi\hbar^2} \right)^{\frac{3N_1}{2}} e^{-\beta N_2 m_2 c^2} \frac{V^{N_2}}{N_2!} \left(\frac{m_2 k_B T}{2\pi\hbar^2} \right)^{\frac{3N_2}{2}}, \quad (67)$$

which gives

$$\Xi(T, V, z_1, z_2) = \exp \left[z_1 e^{-\beta m_1 c^2} V \left(\frac{m_1 k_B T}{2\pi\hbar^2} \right)^{3/2} + z_2 e^{-\beta m_2 c^2} V \left(\frac{m_2 k_B T}{2\pi\hbar^2} \right)^{3/2} \right]. \quad (68)$$

- The average numbers $\langle N_1 \rangle$ and $\langle N_2 \rangle$ are

$$\langle N_1 \rangle = z_1 \frac{\partial}{\partial z_1} \ln \Xi(T, V, z_1, z_2) = z_1 e^{-\beta m_1 c^2} V \left(\frac{m_1 k_B T}{2\pi \hbar^2} \right)^{3/2}, \quad (69)$$

$$\langle N_2 \rangle = z_2 \frac{\partial}{\partial z_2} \ln \Xi(T, V, z_1, z_2) = z_2 e^{-\beta m_2 c^2} V \left(\frac{m_2 k_B T}{2\pi \hbar^2} \right)^{3/2}. \quad (70)$$

- Since

$$\langle N \rangle = \langle N_1 \rangle + 2\langle N_2 \rangle, \quad (71)$$

we have

$$z_1 e^{-\beta m_1 c^2} V \left(\frac{m_1 k_B T}{2\pi \hbar^2} \right)^{3/2} + 2z_2 e^{-\beta m_2 c^2} V \left(\frac{m_2 k_B T}{2\pi \hbar^2} \right)^{3/2} = \langle N \rangle, \quad (72)$$

which can be rewritten as

$$z_1 + 2e^{-\beta(m_2 - m_1)c^2} \left(\frac{m_2}{m_1} \right)^{3/2} z_2 = e^{\beta m_1 c^2} \rho \left(\frac{2\pi \hbar^2}{m_1 k_B T} \right)^{3/2}, \quad (73)$$

where $\rho \equiv \frac{\langle N \rangle}{V}$.

- We need a relation which connects μ_1 to μ_2 which is found from the minimum of free energy

$$F(T, V, \langle N_1 \rangle, \langle N_2 \rangle) = F_1(T, V, \langle N_1 \rangle) + F_2(T, V, \langle N_2 \rangle). \quad (74)$$

Taking into account Eq. (71) it is rewritten as

$$F(T, V, \langle N_1 \rangle, \langle N_2 \rangle) = F_1(T, V, \langle N \rangle - 2\langle N_2 \rangle) + F_2(T, V, \langle N_2 \rangle). \quad (75)$$

- The condition of minimum reads

$$\frac{\partial F(T, V, \langle N_1 \rangle, \langle N_2 \rangle)}{\partial \langle N_2 \rangle} = \frac{\partial F_1(T, V, \langle N \rangle - 2\langle N_2 \rangle)}{\partial \langle N_2 \rangle} + \frac{\partial F_2(T, V, \langle N_2 \rangle)}{\partial \langle N_2 \rangle} = 0, \quad (76)$$

which gives

$$2 \frac{\partial F_1(T, V, \langle N_1 \rangle)}{\partial \langle N_1 \rangle} = \frac{\partial F_2(T, V, \langle N_2 \rangle)}{\partial \langle N_2 \rangle}. \quad (77)$$

Because of the definition (25), one finds the desired relation as

$$2\mu_1 = \mu_2, \quad (78)$$

or equivalently $z_2 = z_1^2$.

- Eq. (73) becomes the quadratic equation for z_1

$$az_1^2 + z_1 + c = 0, \quad (79)$$

where

$$a \equiv 2e^{-\beta(m_2 - m_1)c^2} \left(\frac{m_2}{m_1} \right)^{3/2}, \quad c \equiv -e^{\beta m_1 c^2} \frac{\langle N \rangle}{V} \left(\frac{2\pi \hbar^2}{m_1 k_B T} \right)^{3/2}. \quad (80)$$

The positive solution is

$$z_1 = \frac{\sqrt{1 - 4ac} - 1}{2a}. \quad (81)$$

- Keeping in mind that

$$m_2 c^2 = 2m_1 c^2 - \epsilon_B, \quad (82)$$

with $m_1 c^2 \gg \epsilon_B$, the solution (81) is

$$z_1 = \frac{e^{\beta(m_1 c^2 - \epsilon_B)}}{2^{7/2}} \left(\sqrt{1 + 2^{9/2} e^{\beta \epsilon_B} \rho \left(\frac{2\pi \hbar^2}{m_1 k_B T} \right)^{3/2}} - 1 \right). \quad (83)$$

- The complete analysis requires a numerical computation. We consider two extreme cases of high and low temperatures. At high temperatures the second term under the root in (83) is small. Expanding the root one gets

$$z_1 = e^{\beta m_1 c^2} \rho \left(\frac{2\pi \hbar^2}{m_1 k_B T} \right)^{3/2}. \quad (84)$$

Substituting the result (84) into Eq. (69) we find

$$\frac{\langle N_1 \rangle}{\langle N \rangle} = 1. \quad (85)$$

So, the hydrogen is almost completely in the atomic form. One finds a small admixture of molecules substituting the fugacity (84) in Eq. (70)

$$\frac{\langle N_2 \rangle}{\langle N \rangle} = e^{\beta \epsilon_B} \rho \left(\frac{4\pi \hbar^2}{m_1 k_B T} \right)^{3/2}. \quad (86)$$

The molecular admixture becomes smaller and smaller as the temperature grows.

- At low temperatures when $e^{\beta \epsilon_B} \gg 1$ which requires $k_B T \ll \epsilon_B$ the mixture should be dilute to remain classical. Then, the second term under the root in Eq. (83) is much bigger than unity and

$$z_1 = \frac{e^{\beta(m_1 c^2 - \epsilon_B/2)}}{2^{5/4}} \rho^{1/2} \left(\frac{2\pi \hbar^2}{m_1 k_B T} \right)^{3/4}. \quad (87)$$

Substituting the fugacity (87) into Eq. (70), one finds

$$\frac{\langle N_2 \rangle}{\langle N \rangle} = \frac{1}{2}, \quad (88)$$

which means that almost all hydrogen is in the molecular form. A small admixture of atoms is found substituting the fugacity (87) into Eq. (69)

$$\frac{\langle N_1 \rangle}{\langle N \rangle} = \frac{e^{-\frac{\beta \epsilon_B}{2}}}{4} \left(\frac{m_1 k_B T}{\pi \hbar^2 \rho^{2/3}} \right)^{3/4}. \quad (89)$$

The atomic admixture becomes bigger and bigger as the temperature grows.