TSP-2022/23   —   Thermal and Statistical Physics (Part II)

Problem sheet III: questions 1-9

1. **Virial coefficient and radial distribution function**
   An inter-molecular potential takes the form

$$
\phi(r) \;=\; \begin{aligned}
&\infty &\quad& r < a \\
&-\epsilon && a < r < 2a \\
&0 && r > 2a.
\end{aligned}
$$

   Within the virial expansion the radial distribution function is expanded in powers of the density.
   (a) Sketch the form of the density-independent part of the radial distribution function versus r for $k_B T \gg \epsilon$ and $k_B T \ll \epsilon$.
   (b) Evaluate the 2nd virial coefficient, $B_2(T)$, and the Boyle temperature of the gas.
   (c) Identify a set of reduced units, v_0^* and T^*, for which $B_2(T^*)/v_0^*$ is independent of a and ϵ. Sketch $B_2(T^*)/v_0^*$ versus T^*.

   Solution: The virial expansion is:

$$
\begin{aligned}
g(r) &= g_0(r) + g_1(r)\,n + g_2(r)\,n^2 + \cdots \\
\frac{p}{k_B T} &= n + B_2(T)\,n^2 + B_3(T)\,n^3 + \cdots .\\
B_2(T) &= \int_0^\infty 2\pi r^2 \left(1 - \mathrm{e}^{-\phi/k_B T}\right) dr.
\end{aligned}
$$

   (a)

$$
g_0(r) = \mathrm{e}^{-\beta\phi(r)}.
$$

   (b)

$$
\begin{aligned}
B_2(T) &= \int_0^a 2\pi r^2 dr + \int_a^{2a} 2\pi r^2 \left(1 - e^{\beta\epsilon}\right) dr \\
&= \frac{2\pi}{3}a^3 + \frac{2\pi}{3}(8a^3 - a^3)\left(1 - e^{\beta\epsilon}\right) = \frac{16\pi}{3}a^3 - \frac{14\pi}{3}a^3 e^{\beta\epsilon}.
\end{aligned}
$$

   T_B is where $B_2(T) = 0$, i.e.

$$
T_B = \frac{\epsilon}{k_B \ln(8/7)}.
$$

   (c) We have

$$
\frac{B_2}{a^3} = \frac{16\pi}{3} - \frac{14\pi}{3}e^{\beta\epsilon} \quad \text{therefore} \quad \frac{B_2(T^*)}{v_0^*} = 4 - \frac{7}{2}e^{1/T^*},
$$

   where $v_0^* = 4/3\,\pi a^3$ and $T^* = k_B T/\epsilon$. Make the $B_2(T)$ sketch to see the high-T and low-T limits.

2. **Liquid crystal**
   The order parameter for a fluid of rod shaped molecules is their degree of alignment, Q,

with $Q = 0$ corresponding to a disordered fluid, and $Q \neq 0$ corresponding to a nematic liquid crystal. The free energy can be written as

$$F(Q,T) \;=\; a(T - T_c)Q^2 - bQ^3 + cQ^4,$$

where a, b, c and T_c are positive constants. This system shows a first order phase transition, at a temperature T^*, between two states with $Q = 0$ and $Q = Q^*$.
(a) Calculate Q^* and T^*, using the conditions that the free energies of the two states are equal at the transition and that the free energies are stationary in equilibrium.
(b) Calculate the latent heat of the transition.

Solution: (a) The free energy expansion suggests the 1st order transition since the cubic term is present: $F(Q,T) = a(T - T_c)Q^2 - bQ^3 + cQ^4$. The first step is to identify free energy minima:

$$\begin{aligned}
\frac{\partial F}{\partial Q} &= 2a(T - T_c)Q - 3bQ^2 + 4cQ^3 \\
&= \left[2a(T - T_c) - 3bQ + 4cQ^2\right]Q = 0
\end{aligned}$$

The disordered phase corresponds to $Q = 0$, $F = 0$. The condition that the free energies of the ordered and disordered phases are equal at the transition point $T = T^*$ leads to

$$a(T^* - T_c) - bQ^* + cQ^{*2} = 0.$$

The condition that the free energy is stationary (i.e. has a minimum at Q^*) leads to

$$2a(T^* - T_c) - 3bQ^* + 4cQ^{*2} = 0.$$

Solving these equations for Q^* and T^* leads to

$$\begin{aligned}
Q^* &= \frac{b}{2c} \qquad \text{(the jump of order parameter)} \\
T^* &= T_c + \frac{b^2}{4ac} \quad \text{(point of equilibrium transition)}
\end{aligned}$$

(b) The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_Q = -aQ^2.$$

You might be concerned that $Q = Q(T)$ itself, so why is there only the partial derivative here? The full expression is, of course, $S = (\partial F/\partial T)_{V,N} = (\partial F/\partial T)_Q + (\partial F/\partial Q)(\partial Q/\partial T)$. But the derivative $(\partial F/\partial Q) = 0$ in equilibrium, so the second (unpleasant) term drops out always.

For the disordered phase $S = 0$, while for the ordered phase $S = -ab^2/4c^2$, and therefore the latent heat of this phase transition is

$$L = T^* \Delta S = -\left(T_c + \frac{b^2}{4ac}\right)\frac{ab^2}{4c^2}.$$

The entropy of the ordered state is negative, but this should not worry us as there will be other contributions to the entropy which will ensure that the total entropy is positive. The fact that the jump in entropy is negative on entering the more ordered phase is, on the other hand, a natural expectation: the extra heat is released from the system (in contrast to requiring the heat, and thus cooling the vicinity environment, on entering the high-temperature disordered phase).

3. **Coupled order parameters**

The free energy of a ferroelectric crystal can be written as

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6 + D\varepsilon P^2 + E\varepsilon^2,$$

where P is the polarisation of the crystal and ε is the elastic strain. The coupling εP^2 can be found in most materials (in contrast to the linear 'piezoelectric' coupling εP that requires polar symmetry breaking). Show that the crystal will undergo a first order phase transition when $D^2/4E > b$, in spite of the even-power expansion required to make the scalar energy out of the vector P. Find the temperature of this first order transition.

Solution: It looks like the free energy expansion in powers of P is in even powers only, i.e. there is no cubic term and thus one expects the second-order transition. However, this depends on the sign of the coefficient of the 4th-order term. If this coefficient is positive then, in fact, we don't need the 6th-order term at all because at small $P \ll 1$ (which is the basis for the Landau series expansion) $bP^4 \gg cP^6$ and they both have the similar qualitative effect of increasing F at higher P.

Since we now have the free energy a function of two variables, but are only interested in one (the transition in P), we should equilibrate this microstate in the ε variable. That is:

$$\frac{dF}{d\varepsilon} = DP^2 + 2E\varepsilon = 0, \quad \text{so } \varepsilon^* = -\frac{DP^2}{2E}.$$

Now let's write the effective free energy

$$F(P, \varepsilon^*) = \alpha(T - T_c)P^2 + bP^4 + cP^6 - \frac{D^2P^4}{4E}$$

(note that the renormalisation is always negative: the 'best' configuration $\varepsilon^*(P)$ will surely lower the free energy of this microstate with respect to zero when both $\varepsilon = 0$, $P = 0$).

If the 4th order coefficient $(b - D^2/4E)$ is negative, the first order transition may occur depending on the relative magnitude of parameters. The plot (made at $b = -3$, $c = 3$, $a = 1$) illustrates the point: the solution is symmetric for $\pm P$ (as expected for even-power series), but has all the features of the ordinary 1st order transition.
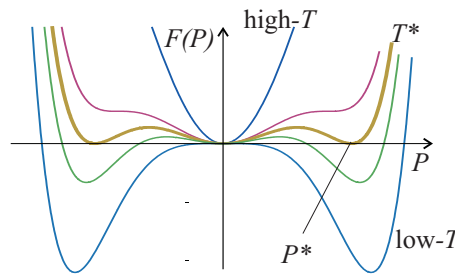
The analysis follows the standard steps: first identify free energy minima:

$$\frac{\partial F}{\partial P} = 0 \quad \text{so} \quad \left[2a(T - T_c) - 4|b - D^2/4E|P^2 + 6cP^4\right]P = 0$$

(taking the renormalised 4th order coefficient to be explicitly negative). The disordered phase corresponds to $P = 0$, $F = 0$, as always. Solving the bi-quadratic equation gives

$$P^2 = \frac{b \pm \sqrt{(b - D^2/4E)^2 - 3ac(T - T_c)}}{3c}$$

so the beginning of hysteresis region is when $(b - D^2/4E)^2 - 3ac(T - T_c) = 0$ or at $T_B = T_c + (b - D^2/4E)^2/3ac$.

At the thermodynamic equilibrium transition point $T = T^*$ the free energies of the ordered and disordered phases are equal, so

$$a(T^* - T_c) - |b - D^2/4E|P^{*2} + cP^{*4} = 0.$$

Solving this, together with the $\partial F/\partial P = 0$ equation, for P^* and T^* leads to

$$
\begin{aligned}
P^* &= \pm\sqrt{\frac{|b - D^2/4E|}{2c}} \quad \text{(the jump of order parameter)} \\
T^* &= T_c + \frac{(b - D^2/4E)^2}{4ac} \quad \text{(equilibrium transition point)}
\end{aligned}
$$

The entropy is, as in the previous question, $S = -aP^2$. For the disordered phase $S = 0$, while for the ordered phase $S = -ab/2c$ and therefore the latent heat of this transition is

$$L = T^*\Delta S = -\left(T_c + \frac{(b - D^2/4E)^2}{4ac}\right)\frac{ab}{2c}.$$

4. **Particle number fluctuations**
   Show that the fluctuations in particle number, N, at constant temperature, T, and volume, V, are given by

$$\langle \Delta N^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

Solution: We want to calculate

$$\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2.$$

Using the grand partition function we have

$$
\begin{aligned}
\langle N \rangle &= \frac{\sum_i N_i\, e^{-(E_i - \mu N_i)/k_B T}}{\sum_i e^{-(E_i - \mu N_i)/k_B T}} = \frac{k_B T}{\Xi}\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V}, \\
\langle N^2 \rangle &= \frac{\sum_i N_i^2 e^{-(E_i - \mu N_i)/k_B T}}{\sum_i e^{-(E_i - \mu N_i)/k_B T}} = \frac{(k_B T)^2}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,V}.
\end{aligned}
$$

(Note that I am now using the single index i to denote the microstates.) From the expression for $\langle N \rangle$ we have

$$
\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = -\frac{k_B T}{\Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V}^2 + \frac{k_B T}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,V} \tag{1}
$$

$$
= -\frac{\langle N \rangle^2}{k_B T} + \frac{\langle N^2 \rangle}{k_B T} = \frac{\langle \Delta N^2 \rangle}{k_B T}, \tag{2}
$$

so that

$$\langle \Delta N^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

Of course, this expression is an example of fluctuation-dissipation relation that one can derive directly from the general probability of fluctuation, see handout Eq.(10.21).

5. **Energy fluctuations**
   For a system of N free electrons the statistical weight, $\Omega(E)$, is proportional to $\exp[(NE/\epsilon_0)^{1/2}]$, where ϵ_0 is about 10^{-19} J. Calculate the heat capacity, C, of the system at room temperature. Show that the probability distribution of the energy of the system is approximately Gaussian and find the root mean square fractional energy fluctuation, $\sqrt{\langle \Delta E^2 \rangle / \langle E \rangle^2}$, for a system with $N = 10^{23}$ at room temperature.
   [Answer: $C = 2.8 \times 10^{-25}$ J K^{-1} per electron; $\sqrt{\langle \Delta E^2 \rangle / \langle E \rangle^2} = 4.5 \times 10^{-11}$.]

Solution: This is only one of several possible ways to derive the result... The statistical weight is

$$\Omega(E) \quad \propto \quad \exp(NE/\epsilon_0)^{1/2}, \quad \text{with} \quad S = k_B \ln \Omega,$$

and we effectively have $U = U(S, N)$, i.e. in correct variables. In this case we can evaluate the usual thermodynamic derivative

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{\partial}{\partial E} k_B \ln \Omega(E) = \frac{k_B}{2} \left(\frac{N}{\epsilon_0} \right)^{1/2} E^{-1/2},$$

and therefore

$$T = \frac{2}{k_B} \left(\frac{\epsilon_0 U}{N} \right)^{1/2},$$

where U in this expression is the average internal energy $\langle E \rangle$. The specific heat capacity C (per particle) is given by

$$
\begin{aligned}
C &= \frac{\partial}{\partial T} \frac{\langle E \rangle}{N} = \frac{\partial}{\partial T} \frac{T^2 k_B^2}{4\epsilon_0} = \frac{k_B^2 T}{2\epsilon_0} \\
&= 2.8 \times 10^{-25} \, \text{JK}^{-1}.
\end{aligned}
$$

The probability distribution of the internal energy is given by the Boltzmann distribution,

$$P(E) = \frac{1}{Z} \Omega(E) \, e^{-E/k_B T}.$$

It is often easier to work with $\ln P$,

$$\ln P(E) = -\frac{E}{k_B T} + \ln \Omega(E) + \text{constant}.$$

The maximum in $\ln P(E)$ occurs at the same value of E as the maximum in $P(E)$. Expand $\ln P(E)$ about its maximum value which occurs at $\langle E \rangle$, defining $\Delta E = E - \langle E \rangle$:

$$\ln P(E) = \ln P|_{\langle E \rangle} + \frac{\Delta E^2}{2} \left. \frac{\partial^2}{\partial E^2} \ln P \right|_{\langle E \rangle} + \dots,$$

because the term linear in ΔE must vanish. Hence at constant T,

$$\left. \frac{\partial \ln P}{\partial E} \right|_{\langle E \rangle} = -\frac{1}{k_B T} + \left. \frac{\partial \ln \Omega}{\partial E} \right|_{\langle E \rangle} = 0 \quad \text{so} \quad \left. \frac{\partial \ln \Omega}{\partial E} \right|_{\langle E \rangle} = \frac{1}{k_B T}$$

(in a sense, we have just re-defined the entropy). Note that $\Omega(E)$ is not a function of T, but the average energy $\langle E \rangle$ is. Solving for $\langle E \rangle$ we obtain

$$\langle E \rangle = \frac{k_B^2 T^2 N}{4\epsilon_0}.$$

The width of the distribution, $\langle \Delta E^2 \rangle$, can be obtained from

$$
\left. \frac{\partial^2 \ln P}{\partial E^2} \right|_{\langle E \rangle} = \left. \frac{\partial^2 \ln \Omega}{\partial E^2} \right|_{\langle E \rangle} = \left. \frac{\partial^2}{\partial E^2} \left(\frac{NE}{\epsilon_0} \right)^{1/2} \right|_{\langle E \rangle}
$$

$$
= -\frac{1}{4} \left(\frac{N}{\epsilon_0} \right)^{1/2} \langle E \rangle^{-3/2},
$$

and

$$
\langle \Delta E^2 \rangle = -\frac{1}{\left. \dfrac{\partial^2 \ln P}{\partial E^2} \right|_{\langle E \rangle}} = \frac{k_B^3 T^3 N}{2\epsilon_0}.
$$

Therefore

$$
\frac{\langle \Delta E^2 \rangle}{\langle E \rangle^2} = \frac{8\epsilon_0}{k_B T N} = 4.5 \times 10^{-11} \quad \text{at } T = 290 \text{ K.}
$$

The probability distribution of the energy of the system is therefore approximately a Gaussian of width $\langle \Delta E^2 \rangle$ and mean $\langle E \rangle$. This long-winded derivation is given to illustrate several points made in the lectures (see the end of handout section 11.2). If you want a simple shortcut, then see how Eq.(11.11) is derived in the handout.

6. **Critical fluctuations**
   Find the mean square fluctuation of magnetisation, $\langle \Delta M^2 \rangle$, as a function of temperature on both sides of the critical point T_c of the ferromagnetic phase transition, which can be described by the Landau free energy expansion

   $$
   F = a(T - T_c)M^2 + bM^4 \ .
   $$

   Solution: This is a simplest form of Landau model of 2nd order transition. Evaluating the derivative of free free energy, we find the solution for the equilibrium magnetisation $M^*(T)$

   $$
   \frac{\partial F}{\partial M} = 2M \left[a(T - T_c) + 2bM^2 \right] = 0 \quad \text{gives} \quad M^* = \pm \sqrt{\frac{a(T_c - t)}{2b}}
   $$

   The non-zero solution only exists below the critical point $T = T_c$.

   Now, speaking about fluctuations, we have the generic expression valid on both sides of the transition,

   $$
   \langle (\Delta M)^2 \rangle = \left. \frac{k_B T}{\left| \dfrac{\partial^2 F}{\partial M^2} \right|} \right|_{M = M_{\text{eq.}}}
   $$

   This gives different results above and below the phase transition:

   $$
   T > T_c : \quad \langle (\Delta M)^2 \rangle = \frac{k_B T}{2a(T - T_c)}
   $$

   $$
   T < T_c : \quad \langle (\Delta M)^2 \rangle = \frac{k_B T}{2a(T - T_c) + 12bM^{*2}} = \frac{k_B T}{4a(T_c - T)}
   $$

   This is an important result showing that the m.s. amplitude of the order parameter fluctuations (magnetisation in this case) diverges on approaching the critical point. However, there is a constant factor between the two expressions, making the fluctuations in the disordered phase always bigger than in the ordered phase. If you plot both curves against T, the result will look like the Greek letter λ, hence the name for this effect: "lambda-point".

7. **Anharmonic oscillator**

A system is governed by the anharmonic potential energy $E(x) = ax^2 + bx^4$, which makes evaluating the partition function and the thermodynamic equilibrium difficult. An approximate solution could be obtained using the 'Gaussian Variation Method' by considering a model harmonic energy $E_\alpha = \alpha x^2$ with the adjustable parameter α, and finding the best α that approximates the equilibrium properties of a system governed by $E(x)$. To follow this process, first show that the true free energy can be approximated as

$$F \approx \tilde{F} = -k_B T \ln Z_\alpha + \langle E(x) - E_\alpha(x) \rangle_\alpha \ ,$$

where $Z_\alpha = \int \exp(-\alpha x^2/k_B T) dx$, and the average is evaluated with the probability distribution $\rho_\alpha(x) = Z_\alpha^{-1} \exp(-\alpha x^2/k_B T)$.

Explain why $\tilde{F}$ is an upper bound for F, and use this to show that $\tilde{F}$ most closely approximates F for $\alpha = a + 6b\langle x^2 \rangle_\alpha$. Calculate and sketch the temperature dependence of α and $\langle x^2 \rangle_\alpha$ for $a > 0$.

Solution: First of all, let's write down the definitions and do the algebra. For the energy $E(x) = ax^2 + bx^4$, the equilibrium free energy is determined by its partition function: $F = -k_B T \ln \left[\int \exp(-(ax^2 + bx^4)/k_B T) dx \right]$. Let's add and subtract E_α in the exponent, and then Taylor-expand to the leading order in $(E - E_\alpha)$, which we assume is small:

$$F = -k_B T \ln \left[\int \exp(-[E(x) - E_\alpha]/k_B T) \exp(-E_\alpha]/k_B T) dx \right]$$

$$\approx -k_B T \ln \left[\int \exp(-E_\alpha/k_B T)(1 - [E(x) - E_\alpha]/k_B T + ...) dx \right]$$

$$= -k_B T \ln \left[\int \exp(-E_\alpha/k_B T) dx \right] - k_B T \ln \left[(1 - \frac{\int dx \exp(-E_\alpha/k_B T)[E(x) - E_\alpha]/k_B T}{\int \exp(-E_\alpha/k_B T) dx} \right]$$

$$\approx -k_B T \ln [Z_\alpha] + \langle E(x) - E_\alpha(x) \rangle_\alpha \ ,$$

as required (after another Taylor expansion of the logarithm).

Since all the integrals here are Gaussian, we can evaluate both terms:

$$\tilde{F} = -k_B T \ln \left[\sqrt{\frac{\pi k_B T}{\alpha}} \right] + (a - \alpha)\langle x^2 \rangle_\alpha + b\langle x^4 \rangle_\alpha$$

$$= -k_B T \ln \left[\sqrt{\frac{\pi k_B T}{\alpha}} \right] + (a - \alpha)\frac{k_B T}{2\alpha} + 3b\left(\frac{k_B T}{2\alpha}\right)^2 \ ,$$

where we used the variance of the Gaussian in the first term, and the Wick's theorem relation $\langle x^4 \rangle = 3\langle x^2 \rangle^2$, which can easily be shown for Gaussian distributions.

In equilibrium, the system adjusts its probability distribution $\rho(x)$ in such a way that the free energy of the microstate $E(x)$ is minimised. Calculating the average (or the most probably) $E - TS$ for a <u>different</u> probability distribution will produce a larger value than the true F. $\tilde{F}$ is such a case, namely the free energy for the anharmonic system is approximated by using the probability distribution for the harmonic system. This can at best be equal to F, but in reality one cannot exactly match the anharmonic $E(x)$ with a harmonic E_α, so $\tilde{F} > F$.

All we need to do now is to find α for which $\tilde{F}$ is minimal:

$$\frac{\partial \tilde{F}}{\partial \alpha} = 0 = \frac{k_B T}{2\alpha} - a\frac{k_B T}{2\alpha^2} - 3b\frac{(k_B T)^2}{2\alpha^3}$$

$$\text{or} \quad \alpha^2 - a\alpha - 3bk_BT = 0 \ ,$$

which you can alternatively write as: $\alpha = a + 6b\langle x^2\rangle_\alpha$. This already suggests that the system becomes less responsive at higher T, when the variance goes up and the system explores the anharmonic part of the potential more and more.

In detail, the solution of the quadratic gives $\alpha = a/2 + \sqrt{(a/2)^2 + 3bk_BT}$. For low T, α starts out as a, as expected for the system fluctuations to be confined at small x where E and E_α can coincide. At high T it rises $\alpha \propto \sqrt{T}$, as the system spends more time at large x-values, where the true potential rises more steeply and the model parameter α needs to reflect that by increasing its value. Conversely, the variance $\langle x^2\rangle$ starts off at low T as $\propto T$, as would be expected from the equipartition theorem, but with increasing T, when the response of the system becomes stiffer, the variance increases sublinearly.

8. **Brownian motion**
   Derive the Stokes-Einstein relationship for the diffusion constant of particles of radius R in a fluid of viscosity η

$$D = \frac{k_BT}{6\pi\eta R} \ .$$

In 1928 Pospisil observed the Brownian motion of soot particles of radius 0.4×10^{-7} m immersed in a water-glycerine solution of viscosity 2.78×10^{-3} kg m^{-1} s^{-1}, at a temperature of 292 K. The observed value of $\langle x^2\rangle$ was 3.3×10^{-12} m^2 in a 10-second interval. Use these data to determine an estimate for k_B and compare it with the modern value.

Solution: The first part of the question is straight bookwork, with details in the Handout Chapter 11, up to eq.(11.8)-(11.9). This requires knowledge of the Stokes' drag coefficient for a sphere, $\gamma = 6\pi\eta R$.

The second part of the question is calculation. In microscopic observations you only see a **plane** projection of a general 3D motion, so $\langle x^2\rangle = 4Dt$ should be used. With the given $\langle x^2\rangle = 3.3 \times 10^{-12}$m^2 and $t = 10$s, I obtain $D = 0.83 \times 10^{-13}$m^2/s, which then leads to the estimate of k_B which is smaller than the actual k_B, which is probably because the effective hydrodynamic radius R of the small Brownian particle is bigger than its physical size.

9. **Diffusion**
   Consider free Brownian particles diffusing along the axis $x \geq 0$, so that there is a reflecting wall at $x = 0$. Also there is a "sink" at $x = L$ where the particles can escape from the system, so that the probability at that point is $P(L,t) = 0$ at any time.

   If the diffusion constant is D, estimate how long on average it would take for all the particles to escape from the system.

Solution: This requires solving the free diffusion equation for $P(x,t)$ with the boundary conditions $P(x = L) = 0$ and $dP/dx(x = 0) = 0$. Separating variables, we have:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2} \quad \text{taking} \ \ P = T(t)X(x)$$
$$\dot{T} = -\lambda T \quad \text{and} \quad X'' + (\lambda/D)X = 0$$

The time dependence gives a simple exponential, $T(t) = e^{-\lambda t}$. The x-dependence is best described by the harmonic functions (since we see the oscillator equation), $X = A\sin\sqrt{\lambda/D}x + B\cos\sqrt{\lambda/D}x$. The reflecting wall at $x = 0$ means that $X'(0) = \sqrt{\lambda/D} \cdot A\cos 0 = 0$, that is, the constant $A = 0$. The particle "sink" at the end of our range

demands: $X(L) = B\cos\sqrt{\lambda/D}\,L = 0$. This gives the discrete values ("quantisation") of the parameter λ:

$$\sqrt{\frac{\lambda}{D}}L = \pi(n+1/2) \quad \text{so that} \quad P(x,t) = \sum_n B_n e^{-\frac{\pi^2 D}{L^2}(n+1/2)^2 t}\cos\frac{\pi x}{L}(n+1/2)$$

One could analyse this solution, and the evolution of particle distribution in this system, in much greater detail (especially if an initial condition $P(t = 0)$ would be given, of which B_n are the Fourier coefficients). To answer the question quickly, it is clear that the relevant time scale of particles escaping is $\tau = 4L^2/\pi^2 D$, which is the life time of the longest-surviving mode.