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Thermodynamics of a One-Dimensional Finite Quantum Well in Ideal Electron Gas

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Abstract. We present a theoretical study of the thermodynamics of a one-dimensional electron gas in the presence of a single attractive finite square-well. The bound-state spectrum of the well is obtained by solving the even and odd parity matching conditions for the wavefunctions, while the continuum of scattering states is treated using a phase-shift method to account for its contribution to the density of states. From this analysis we construct the well contribution to the grand thermodynamic potential, which in turn allows us to calculate excess thermodynamic quantities (per well) such as the entropy and heat capacity in the fixed-number ensemble. Our results show that the presence of the well induces qualitative changes in the thermodynamic behavior: in particular, we find a pronounced peak in the heat capacity as a function of temperature due to the presence of the well. This heat-capacity anomaly is a direct consequence of the bound states and their interplay with the temperature dependence of chemical potential.

Keywords: one–dimensional finite well; phase shift; one-dimensional thermodynamics; heat capacity

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1. Introduction

Impurities in low-dimensional quantum systems can have an outsized impact on the host material's properties. In one-dimensional (1D) electron gases, in particular, even a single impurity (a localized potential perturbation) can markedly affect transport and thermodynamic characteristics. An attractive impurity potential in 1D is capable of supporting several bound states and also modifies the phase of scattering states. These spectral changes due to the impurity will alter thermodynamic observables of the electron gas. Understanding impurity-induced thermodynamic changes is not only of fundamental interest in statistical physics but also relevant for interpreting experiments on quasi-1D conductors and analogous systems (such as cold atom gases in tight waveguides) where controlled impurity potentials can be introduced.

2. Calculating spectrum

We consider a single attractive square well of width a and depth V_0 embedded in an otherwise free 1D electron gas. In this section we solve the time-independent Schrödinger equation for this potential to obtain all energy eigenstates. We find the discrete bound-state energies and the phase shifts for continuum (scattering) states, which will be needed for the thermodynamic analysis.

The Hamiltonian of the system has the following form

$$H = \frac{p^2}{2m} + V(x) \tag{1}$$

with the potential energy

$$V(x) = \begin{cases} 0, & |x| > a/2 \\ -V_0, & |x| \le a/2 \end{cases} \tag{2}$$

The time independent Schrödinger equation $H\psi(x)=E\psi(x)$ has a discrete spectrum for $E<0$ (bound states), and continuous spectrum for $E>0$ (unbound states). As the Hamiltonian commutes with space inversion operator $I\psi(x)=\psi(-x)$ we can assign the eigenstates a parity (even or odd). The following notations are used in the calculations bellow

$$E_0=\frac{\hbar^2}{2ma^2}\qquad\qquad \text{Energy scale}$$

$$v=\frac{\sqrt{2mV_0}}{\hbar}\qquad\qquad \text{Wavenumber corresponding to the well}$$

For $E<0$, the solutions decay outside the well (bound states), while for $E>0$, we have scattering solutions characterized by phase shifts. We treat these two cases separately.

2.1 Bound states

Let $-V_0<E<0$ and $E=-\hbar^2\kappa^2/(2m)$. The Schrödinger equation transforms to

$$\begin{aligned}\psi''(x)-\kappa^2\psi(x)=0,&\quad |x|>a/2\\ \psi''(x)+(v^2-\kappa^2)\psi(x)=0,&\quad |x|\le a/2\end{aligned}\tag{3}$$

The even and odd wave functions have the form

$$\psi_e(x)=\begin{cases}Ae^{\kappa x}, & x<a/2\\ \cos\left(\sqrt{v^2-\kappa^2}\,x\right), & |x|\le a/2\\ Ae^{-\kappa x}, & x>a/2\end{cases}\qquad \psi_o(x)=\begin{cases}-Ae^{\kappa x}, & x<a/2\\ \mathrm{B}\sin\left(\sqrt{v^2-\kappa^2}\,x\right), & |x|\le a/2\\ Ae^{-\kappa x}, & x>a/2\end{cases}\tag{4}$$

Above we have already used the boundary condition at infinities $\psi(x\to\pm\infty)=0$. The equations on κ follow from the continuity of logarithmic derivative $\frac{d\psi/dx}{\psi}$ at the boundaries $x=\pm a/2$.

Let $x=\sqrt{(va)^2-(\kappa a)^2}/2$ and $y=\kappa a/2$. The equations on the energy levels take the form

$$\begin{aligned}&x\tan x=y,\quad \text{for even states}\\ &\mathrm{x}\cot x=-y,\quad \text{for odd states}\\ &\text{With constraint}\quad \mathrm{x}^2+y^2=(va/2)^2\end{aligned}\tag{5}$$

Solving the equations above numerically yields the spectrum of bound states. The number of even and odd bound states can be calculated analytically by formulas

$$\begin{aligned}N_{\text{bound}}^{\text{even}}&=1+\left\lfloor\frac{va}{2\pi}\right\rfloor\\ N_{\text{bound}}^{\text{odd}}&=\left\lfloor\frac{va}{2\pi}+\frac{1}{2}\right\rfloor\\ N_{\text{bound}}=N_{\text{bound}}^{\text{even}}+N_{\text{bound}}^{\text{odd}}&=1+\left\lfloor\frac{va}{\pi}\right\rfloor\end{aligned}\tag{6}$$

Note, that the only parameter affecting the discrete spectrum is the combination va.

2.2 Unbound states

Let $E = \hbar^2 k^2/(2m) > 0$. The Schrödinger equation transforms to

$$\begin{aligned} \psi''(x) + k^2\psi(x) = 0, \quad & |x| > a/2 \\ \psi''(x) + (v^2 + k^2)\psi(x) = 0, \quad & |x| \le a/2 \end{aligned} \tag{7}$$

Let $\beta(k) = \sqrt{k^2 + v^2}$. The even and odd wave functions have the form

$$\psi_e(x) = \begin{cases} A\cos(kx - \theta_e), & x < a/2 \\ \cos(\beta x) & |x| \le a/2 \\ A\cos(kx + \theta_e) & x > a/2 \end{cases} \quad \psi_o(x) = \begin{cases} A\sin(kx - \theta_o), & x < a/2 \\ \sin(\beta x) & |x| \le a/2 \\ A\sin(kx + \theta_o) & x > a/2 \end{cases} \tag{8}$$

The boundary conditions are the same - continuity of logarithmic derivative at the boundaries $x = \pm a/2$. The resulting phase shifts are

$$\begin{aligned} \theta_e(k) &= -\frac{ka}{2} + \arctan\left(\frac{\beta(k)}{k}\tan\left(\frac{\beta(k)a}{2}\right)\right) + \pi\left\lfloor \frac{\beta(k)a}{2\pi} + \frac{1}{2} \right\rfloor \\ \theta_o(k) &= -\frac{ka}{2} + \arctan\left(\frac{k}{\beta(k)}\tan\left(\frac{\beta(k)a}{2}\right)\right) + \pi\left\lfloor \frac{\beta(k)a}{2\pi} + \frac{1}{2} \right\rfloor \end{aligned} \tag{9}$$

The last terms containing floor function in the expressions above is present to ensure continuity of phase shifts as a function of the wavenumber k. Note that

$$\begin{aligned} \theta_e(k \to 0) - \theta_e(\infty) &= \pi\left\lfloor \frac{va}{2\pi} \right\rfloor + \frac{\pi}{2} = \pi N_{\text{bound}}^{\text{even}} - \frac{\pi}{2} \\ \theta_o(k \to 0) - \theta_o(\infty) &= \pi\left\lfloor \frac{va}{2\pi} + \frac{1}{2} \right\rfloor = \pi N_{\text{bound}}^{\text{odd}} \end{aligned} \tag{10}$$

in accordance to Levinson's theorem for 1D Schrödinger equation [1]. Also note that only the parameter va affects the phase shifts, which means that the whole spectrum is controlled only by this parameter.

2.3 Density of states via phase shifts

To calculate thermodynamic properties, we need the density of energy levels. We use the phase shift method to separate the density of states into the free-particle part and the well-induced part. To do so, we put our system in a box ranging from $x = -L$ to $x = L$ with zero boundary conditions.

$$\begin{aligned} kL + \theta_e = \pi N_e - \frac{\pi}{2} \quad &\to \quad N_e = k\frac{L}{\pi} + \frac{1}{2} + \frac{\theta_e}{\pi} \quad \to \quad \rho_e(E) = \frac{dN_e}{dE} = \frac{L}{\pi}\frac{dk}{dE} + \frac{1}{\pi}\frac{d\theta_e}{dE} \\ kL + \theta_o = \pi N_o \quad &\to \quad N_o = k\frac{L}{\pi} + \frac{\theta_o}{\pi} \quad \to \quad \rho_o(E) = \frac{dN_o}{dE} = \frac{L}{\pi}\frac{dk}{dE} + \frac{1}{\pi}\frac{d\theta_o}{dE} \end{aligned} \tag{11}$$

Total density of states $\rho(E) = \rho_e(E) + \rho_o(E)$ takes the form

$$\rho(E) = \frac{L}{\pi}\sqrt{\frac{2m}{\hbar^2 E}} + \frac{1}{\pi}\frac{d(\theta_e + \theta_o)}{dE} = \rho_0(E) + \rho_w(E); \qquad \rho_w = \frac{1}{\pi}\frac{d(\theta_e + \theta_o)}{dE} = \frac{1}{\pi}\frac{d\theta}{dE} \tag{12}$$

where $\rho_0(E)$ is the density of states of the host in the absence of the well, and $\rho_w(E)$ is the change caused by the well.

3. Thermodynamics

We assume an ideal gas with Fermi statistics. The grand potential is given by expression [2]

$$\Omega=-T\sum_k \ln\left(1+\exp\frac{\mu-\varepsilon_k}{T}\right) \tag{13}$$

For our system the grand potential takes the form $\Omega(T,\mu)=\Omega_0(T,\mu)+\Omega_w(T,\mu)$ with

$$\Omega_0=-T\int_0^\infty \rho_0(\varepsilon)\ln\left(1+\exp\frac{\mu-\varepsilon}{T}\right)d\varepsilon \tag{14}$$

$$\Omega_w=-T\sum_{n=1}^{N_{\text{bound}}}\ln\left(1+\exp\frac{\mu-\varepsilon_n}{T}\right)-\frac{1}{\pi}\int_0^\infty\frac{\theta(\varepsilon)}{1+\exp\dfrac{\varepsilon-\mu}{T}}d\varepsilon+\frac{T}{\pi}\theta(0)\ln\left(1+e^{\mu/T}\right) \tag{15}$$

where $\Omega_0(T,\mu)$ is the grand potential in the absence of the impurity. Above we have simplified the expression for the contribution of the well to the grand potential $\Omega_w(T,\mu)$ using integration by parts.

To calculate the heat capacitance for fixed number of particles, we need to perform Legendre transform from grand potential $\Omega(T,\mu)$ to free energy $F(T,N)$.

$$F_0(T,N)=\Omega_0\left(T,\mu_0(T,N)\right)+N\mu_0(T,N) \quad \text{where} \quad N=-\left.\frac{\partial\Omega_0}{\partial\mu}\right|_{T,\mu_0} \tag{16}$$

$$F(T,N)=\Omega_w\left(T,\mu(T,N)\right)+\Omega_0\left(T,\mu(T,N)\right)+N\mu(T,N) \quad \text{where} \quad N=-\left.\frac{\partial(\Omega_0+\Omega_w)}{\partial\mu}\right|_{T,\mu} \tag{17}$$

Let $\mu(T,N)=\mu_0(T,N)+\Delta\mu(T,N)$. The expansion of N in terms of $\Delta\mu$ is

$$N=-\left.\frac{\partial\Omega_0}{\partial\mu}\right|_{T,\mu_0}-\left.\frac{\partial^2\Omega_0}{\partial\mu^2}\right|_{T,\mu_0}\Delta\mu-\left.\frac{\partial\Omega_w}{\partial\mu}\right|_{T,\mu_0}+O\left(\Delta\mu^2\right) \tag{18}$$

The $O(1)$ coefficients must cancel out, which leads us to

$$\Delta\mu=-\left(\left.\frac{\partial\Omega_w}{\partial\mu}\right|_{T,\mu_0}\right)\Big/\left(\left.\frac{\partial^2\Omega_0}{\partial\mu^2}\right|_{T,\mu_0}\right)\propto\frac{1}{L}\to 0 \tag{19}$$

As we see, the shift of chemical potential $\Delta\mu$ caused by adding the well vanishes in the limit of big L. Expanding (17) by $\Delta\mu$ gives us the free energy of the well in the leading order

$$F_w(T,N)=\Omega_w\left(T,\mu_0(T,N)\right) \tag{20}$$

where $\mu_0(T,N)$ is given implicitly in terms of particle concentration $n=N/(2L)$ by expression

$$n=\frac{N}{2L}=-\frac{1}{2L}\frac{\partial\Omega_0}{\partial\mu}=\frac{1}{L}\int_0^\infty\frac{\rho_0(\varepsilon)}{1+\exp\dfrac{\varepsilon-\mu_0}{T}}d\varepsilon=\frac{1}{2\pi a\sqrt{E_0}}\int_0^\infty\frac{\varepsilon^{-1/2}}{1+\exp\dfrac{\varepsilon-\mu_0}{T}}d\varepsilon \tag{21}$$

The changes in entropy and heat capacity caused by the well for fixed N are

$$S_w(T)=-\frac{\partial F_w}{\partial T}=-\left.\left\{\frac{\partial\Omega_w}{\partial T}+\frac{\partial\Omega_w}{\partial\mu}\frac{d\mu_0}{dT}\right\}\right|_{T,\mu_0} \tag{22}$$

$$C_w^N(T)=-T\frac{\partial^2F_w}{\partial T^2}=-T\left.\left\{\frac{\partial^2\Omega_w}{\partial T^2}+2\frac{\partial^2\Omega_w}{\partial T\partial\mu}\frac{d\mu_0}{dT}+\frac{\partial^2\Omega_w}{\partial\mu^2}\left(\frac{d\mu_0}{dT}\right)^2+\frac{\partial\Omega_w}{\partial\mu}\frac{d^2\mu_0}{dT^2}\right\}\right|_{T,\mu_0} \tag{23}$$

4. Results

The parameters which define the behavior of our system are va (depth of the well), na (concentration of electrons) and E_0, which we will use as our energy scale.

On Fig. 1 we see the dependence of heat capacity from temperature for a well with $va = 7,\ na = 0.01$ and the contribution of each term in eq. (23) to it. We note, that the low temperature peak ($T / E_0 \approx 1.4 \cdot 10^{-4}$) is entirely due to the term containing $d^2\mu / dT^2$. The peak arises due to the maximum of the function $\mu(T)$ at $T \approx 0.94\mu(0)$ [3]. The exact position of the heat capacity peak is slightly shifted due to the term being multiplied by other functions of the temperature, but it is proportional to $\mu(0) = E_0(\pi na)^2$. For $T > \mu(0)$ the host gas may be considered non-degenerate.

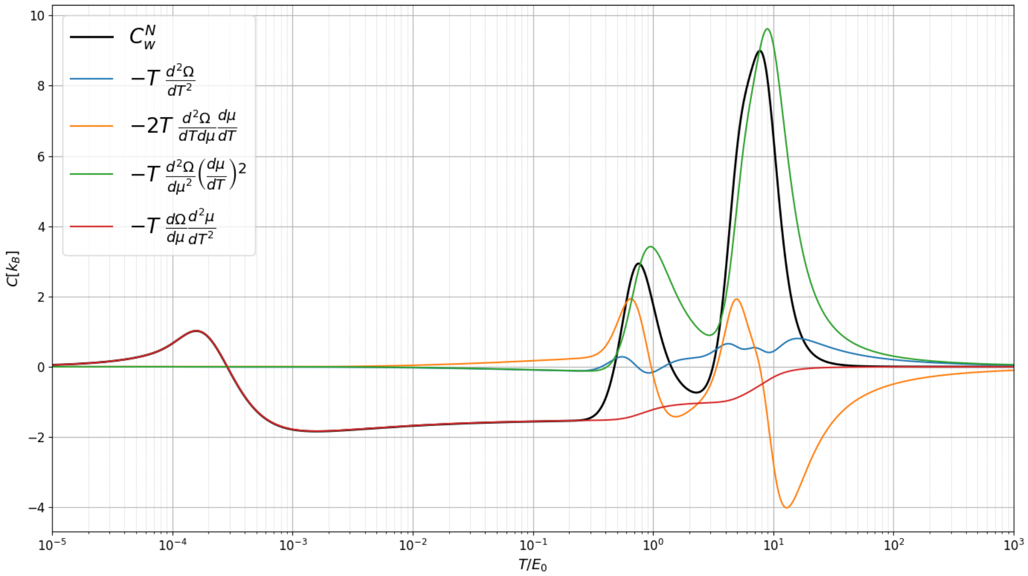


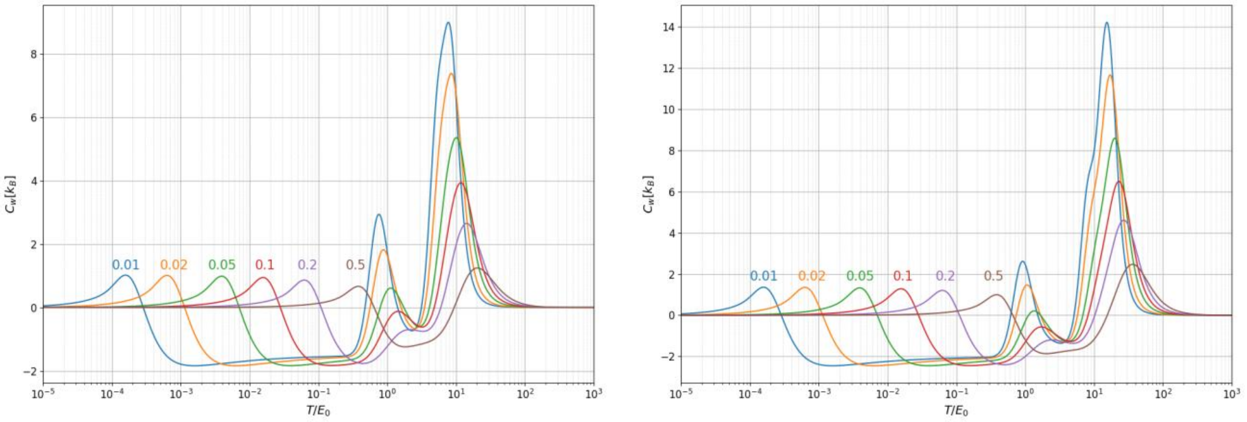
Figure 1: The contributions to heat capacity of each term in eq. (23).
The parameters of the well are $\mathrm{va} = 7, \mathrm{na} = 0.01$

The consequent peaks are mostly the result of the term containing $-d^2\Omega_w / d\mu^2$. As the temperature rises, the chemical potential becomes more negative. $N_w = -d\Omega_w / d\mu$ is the number of particles trapped by the well. If $T = 0$, N_w is the number of states with energy below μ_0, which means that as the chemical potential becomes more negative, N_w decreases with sharp integer steps as μ crosses the energies of the bound states. The derivative of those steps are seen as peaks of the function $-d^2\Omega_w / d\mu^2 = dN_w / d\mu$. If the temperature is finite, the peaks become less pronounced as the temperature increases, and might merge together.

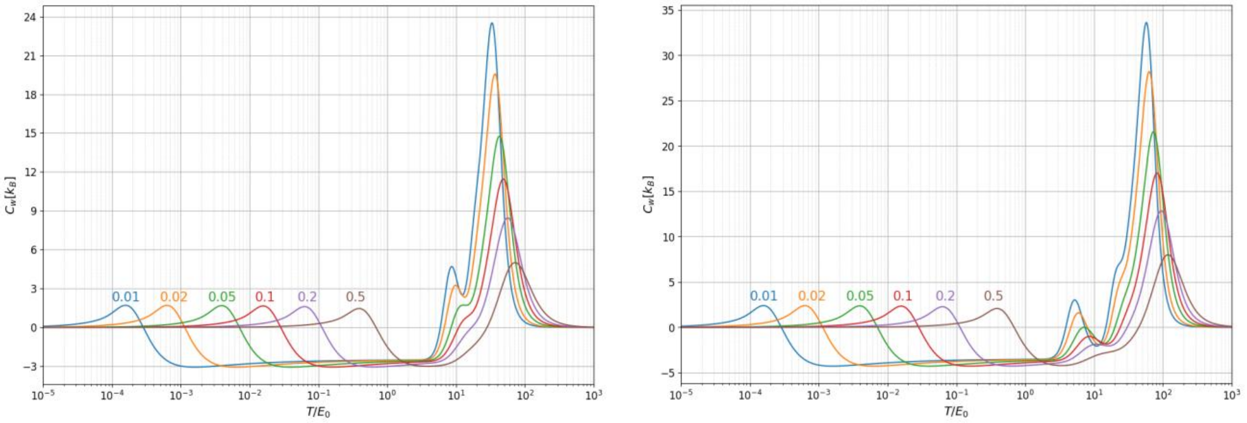
On Fig. 2 we can see the temperature dependences $C_w^N(T)$ for different values of va and na. It can be seen that as the concentration increases, the peaks shift to the right and become less pronounced. If we look at the dependence of the chemical potential from temperature in the non-degenerate approximation

$$\mu_0(T, na) = -T\,\ln\left(\frac{\sqrt{T}}{2na\sqrt{\pi E_0}}\right) \tag{24}$$

we see the following - the chemical potential is more negative for the lower values of na. This means, that for lower values of na the chemical potential crosses the energy values of bound states at lower temperatures, which leads to taller and more pronounced peaks, as the temperature doesn't smear the steps of the function $N_w(T, \mu)$ as much compared to higher values of na.



(a) $va = 7$ (b) $va = 10$



(c) $va = 15$ (d) $va = 20$

Figure 2: Calculated heat capacities C_w^N for 4 different values of $va = 7, 10, 15, 20$. The values of na are noted on the plots.

5. Conclusions

In conclusion, we have investigated the thermodynamics of a one-dimensional electron gas in the presence of a single attractive finite square-well. By exactly solving the quantum well problem for bound and scattering states and employing the phase-shift formulation of the density of states, we obtained the well-induced change in the grand potential of the system. This approach enabled us to calculate excess entropy and excess heat capacity attributable to the well, with careful attention to the fixed particle number constraint. The analysis confirms that even a single quantum well can produce a measurable thermodynamic effect: the additional localized energy levels and the altered continuum states lead to enhanced entropy at intermediate temperatures and, notably, a peak in the heat capacity as a function of temperature. Our results are quantitatively specific to the square-well potential, but they illustrate a general principle that applies to any localized impurity in a Fermi gas – namely, that new energy scales (such as a binding energy) introduced by the impurity will imprint themselves on thermodynamic curves.

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