

QUANTUM CONFINEMENT EFFECTS ON SEEBECK COEFFICIENT

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ABSTRACT

Seebeck coefficient is analytically derived for Fermi gas by considering quantum size effects to investigate the dependencies of Seebeck coefficient on domain size and quantum degeneracy. Under the relaxation time approximation, particle flux equation is expressed in terms of external potential, chemical potential and temperature gradient. The summations in the expression of particle flux are replaced by the Poisson summation formula to consider quantum size effects. Since the system size considered here is comparable to the thermal de Broglie wavelength, the contribution of zero correction term of the Poisson summation formula is included. In order to obtain an analytically solvable problem, rectangular domain geometry is considered. The results show that quantum size effects cause a significant improvement on Seebeck coefficient when the system size in one direction approach to thermal de Broglie wave length. This improvement is due to transition from bulk to quantum well behaviour. Variation of quantum size effects with quantum degeneracy, which is represented by dimensionless chemical potential, is also examined. It is seen that the chemical potential value for the maximum dimensionless Seebeck coefficient decreases with decreasing system size while the Seebeck coefficient increases.

INTRODUCTION

Since the low dimensional behaviours of the thermoelectric materials are different than the bulk ones, higher thermoelectric efficiencies can be achieved by using low dimensional structures like quantum wells, wires and dots [1-3]. The conversion efficiency of thermoelectric devices depends on the properties of the materials and determined by the well known figure of merit relation, $Z = S^2\sigma/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity. Since the all variables in the figure of merit relation are dependent, they adversely affect each other so that the figure of merit does not vary significantly for the bulk thermoelectric materials. However, in the literature, it is proposed that quantum confinement plays an important role to enhance the figure of merit by using low dimensional nanostructures [4-8].

In contrast to the macroscopic approaches, transport properties of materials become size and shape dependent when the domain size is comparable to the characteristic length scale of the problem. Therefore, size and shape of the system are considered as additional control parameters on transport properties of nanoscale devices [9, 10]. In sufficiently small structures, the wave character of particles significantly changes the transport properties by modifying probability density distribution, the smallest values of the momentum components and momentum spectrum of particles [9, 11]. Some contributions arise when the thermal de Broglie wavelength of particles are not negligible in comparison with the size of the domain. These contributions are called as quantum size effects (QSE) in general [9, 11].

In the calculations here, free electrons in the conduction band of conductors and semi-conductors are considered as an

ideal Fermi gas and Seebeck coefficient is analytically derived by considering QSE. Through the confinement, sizes of the domain are smaller than the mean free path of the particles but equal to or greater than the thermal de Broglie wave length. Therefore conventional definitions of particle flux and transport coefficients are used. Dependencies of Seebeck coefficient on domain size and quantum degeneracy are investigated. Particle flux equation is derived in terms of external potential, chemical potential and temperature gradients. Relaxation time approximation is used to obtain non-equilibrium distribution function. Furthermore, relaxation time is assumed to be equal to the inverse of the collision frequencies of the particles. The summations inside the particle flux expression are replaced by the Poisson summation formula to consider QSE. Since the system size in at least one direction is comparable to the thermal de Broglie wavelength, the contribution of zero correction term of the Poisson summation formula is included. On the other hand, discreteness correction term is neglected since all the sizes are equal to or larger than the thermal de Broglie wavelength of particles. In order to obtain an analytically solvable problem, rectangular domain geometry is considered.

DERIVATION OF PARTICLE FLUX AND SEEBECK COEFFICIENT

Transport domain is a rectangular structure with dimensions of L_x, L_y, L_z and the domain is strongly confined through the direction x . The particle flux in direction x is written as,

$$J_x^N = \sum_{ijk} v_{w,x} f \quad (1)$$

where $v_{w,x}$ is the x component of velocity of the carrier at quantum state w and f is non-equilibrium distribution function. The equilibrium distribution function for Fermi-Dirac statistics is given by,

$$f_0 = \frac{1}{V} \frac{1}{\exp\left[\frac{(\varepsilon_w - \mu)}{k_b T}\right] + 1} \quad (2)$$

where ε_w is the translational energy of the carriers, μ is the chemical potential, T is temperature, V is the domain volume, k_b is the Boltzmann's constant. Under the relaxation time approximation, the non-equilibrium distribution function in direction x can be determined as,

$$f = f_0 - \tau v_{w,x} \frac{\partial f_0}{\partial x} \quad (3)$$

where τ is the relaxation time which is expressed by using the particle-boundary mean free path (geometric mean free path, $L_g = V/2A$ where A is the surface area of the domain) and the particle velocity v as $\tau(v) = L_g/v$. Inserting Eq.(3) into Eq.(1), the particle flux in direction x for the particle-boundary collision dominated transport is derived as [9, 12],

$$J_x^N = \frac{L_g}{k_b T V} \left(\frac{2k_b T}{m} \right)^{1/2} (g_0 F_x^{\Phi T} + g_2 F_x^T) \quad (4)$$

where $F_x^{\Phi T} = F_x^\Phi - (\mu/k_b T) F_x^T$ and m is the mass of the carrier. Driving forces are defined by the gradients of the chemical and electrical (electrochemical) potentials and temperature as $F_x^\Phi = -(\partial\mu/\partial x + \partial\phi/\partial x)$, $F_x^T = -k_b(\partial T/\partial x)$ respectively. In Equation.(4), g function is a dimensionless quantity given by,

$$g_a = \sum_w \frac{m v_{w,x}^2 / 2k_b T}{(\varepsilon_w / k_b T)^{\frac{1-a}{2}}} \frac{\exp(B_w)}{[\exp(B_w) + 1]} \quad (5)$$

where $B_w = (\varepsilon_w - \mu)/k_b T$ [9, 12]. By using the parabolic dispersion relation, translational kinetic energy of the particles is easily written as,

$$\varepsilon_{ijk} = \frac{\hbar^2}{8m} \left[\left(\frac{i}{L_x} \right)^2 + \left(\frac{j}{L_y} \right)^2 + \left(\frac{k}{L_z} \right)^2 \right] \quad (6)$$

where $i, j, k = 1, 2, 3, \dots, \infty$. By using Eq.(6), $\varepsilon_w/k_b T$ is written as,

$$\frac{\varepsilon_w}{k_b T} = \frac{\varepsilon_{ijk}}{k_b T} = (\alpha_x i)^2 + (\alpha_y j)^2 + (\alpha_z k)^2 \quad (7)$$

where $\alpha_x = L_c/L_x$, $\alpha_y = L_c/L_y$, $\alpha_z = L_c/L_z$ and the length $L_c = \hbar/\sqrt{8mk_b T}$ is half of the most probable de Broglie wavelength of the particles.

In macroscale, sums may be replaced by integrals with a negligible error. However, since the system size approaches to thermal de Broglie wavelength at nanoscale this replacement causes a considerable error. Therefore, instead of replacing sum with an integral, Poisson summation formula is used to have more accurate result to calculate the sum in Eq.(5). For an even function, Poisson summation formula is written in the form of,

$$\sum_{i=1}^{\infty} f(i) = \int_0^{\infty} f(i) di - \frac{f(0)}{2} + 2 \sum_{s=1}^{\infty} \int_0^{\infty} f(i) \cos(2\pi s i) di \quad (8)$$

where the first term is the bulk term, the second term is the zero correction term which is important when the system size approach to the thermal de Broglie wavelength, and the third term is the discreteness correction term. Although it is possible to calculate sums exactly with Poisson summation formula, the third term of the Poisson summation formula is negligible compared with the others since the domain sizes here are always larger than the thermal de Broglie wavelength [9]. Inserting Eq.(7) into Eq.(5) and by using Poisson summation formula given in Eq.(8), g_a function is analytically obtained as,

$$g_a = -\frac{2\pi}{3\alpha_x \alpha_y \alpha_z} \Gamma\left(\frac{4+a}{2}\right) Li_{\frac{2+a}{2}} \left[1 - \frac{3(\alpha_x + \alpha_y + \alpha_z)}{4} \frac{\Gamma\left(\frac{3+a}{2}\right) Li_{\frac{1+a}{2}}}{\Gamma\left(\frac{4+a}{2}\right) Li_{\frac{2+a}{2}}} + \frac{3(\alpha_x \alpha_y + \alpha_y \alpha_z + \alpha_z \alpha_x)}{2\pi} \frac{\Gamma\left(\frac{2+a}{2}\right) Li_{\frac{a}{2}}}{\Gamma\left(\frac{4+a}{2}\right) Li_{\frac{2+a}{2}}} \right] \quad (9)$$

where Γ is Gamma function and Li_n is the Polylogarithm function with the degree of n and argument of $-\exp(\mu/k_b T)$. In Eq.(9), the first term is the bulk term which could be obtained by replacing sum with the integral and the other terms in the square bracket come from the second term of Poisson summation formula and arise due to wave character of particles. Inserting Eq.(9) into Eq.(4), size dependent particle flux is obtained. It is clear that the size dependency of particle flux appears for the confined directions only since the value of α is zero for other directions.

Seebeck coefficient is defined as the ratio of the electrochemical gradient to temperature gradient under zero particle flux condition and given by,

$$S = \frac{k_b}{q} \left(\frac{F_x^\Phi}{F_x^T} \right)_{J_N=0} \quad (10)$$

where q is the charge of the particle. By using Eqs.(9) and (10), Seebeck coefficient is obtained in term of g_a function as,

$$S = \frac{k_b}{q} \left(\frac{g_2}{g_0} - \Lambda \right) \quad (11)$$

where $\Lambda = \mu/k_b T$.

RESULTS

To show the deviations from the macroscopic picture, Seebeck coefficients derived with and without QSE (S and S_o) versus dimensionless chemical potential are plotted for a Fermi gas in Fig.1. Transport domain is confined only in x direction ($\alpha_y = \alpha_z \approx 0$, $\alpha_x = 1$).

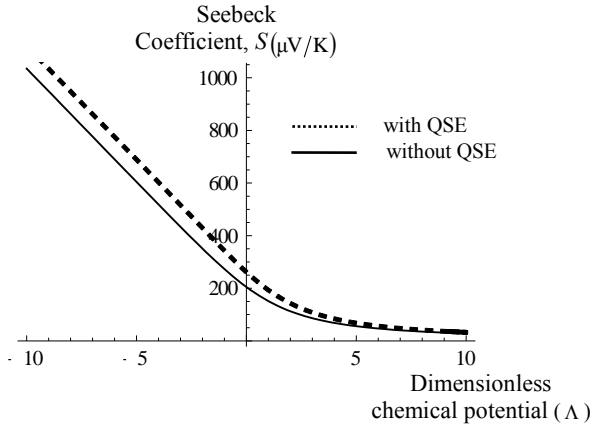


Fig.1: Variation of S and S_o with $\Lambda = \mu/k_bT$.

Fig.1 shows that increasing chemical potential (increasing degeneracy) decreases the contribution of the quantum size effects on Seebeck coefficient due to decreasing of mean de Broglie wave length. Therefore the difference between the curves becomes smaller for the higher values of Λ . The dimensionless form of the Seebeck coefficient is defined by dividing S to S_o and given by,

$$\tilde{S} = \frac{S}{S_o} \quad (12)$$

In Fig.2, \tilde{S} versus Λ is given for different values of domain size in x direction. The results show that QSE cause a significant improvement (as high as %30) on Seebeck coefficient when the system size approaches to thermal de Broglie wave length, ($\alpha_x \rightarrow 1$). Variation of quantum size effects with dimensionless chemical potential shows that there is a maximum value for \tilde{S} which increases with decreasing system size or increasing de Broglie wavelength.

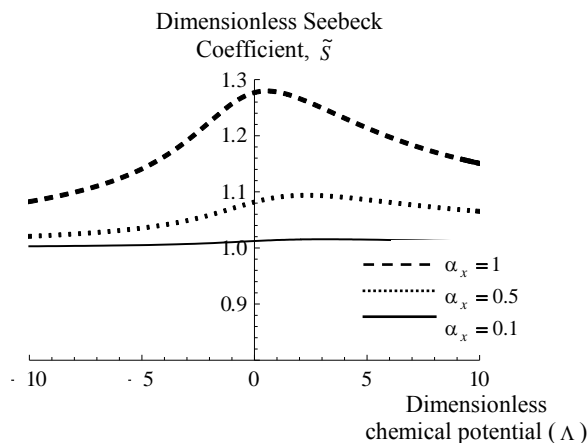


Fig.2: Variation of \tilde{S} with Λ for different values of α_x .

In Fig.3, variation of the maximum value of dimensionless Seebeck coefficient with dimensionless inverse scale factor in x direction is given. The effect of domain size on Seebeck coefficient is clearly seen. It is possible to improve Seebeck coefficient only by decreasing the domain size without making any change in the composition of the material. Therefore, size itself becomes a control parameter on material properties. This is due to the transition from bulk to quantum well behavior. Similarly, size itself play an important role during the transition from quantum well to quantum wire and from quantum wire to quantum dot behaviors.

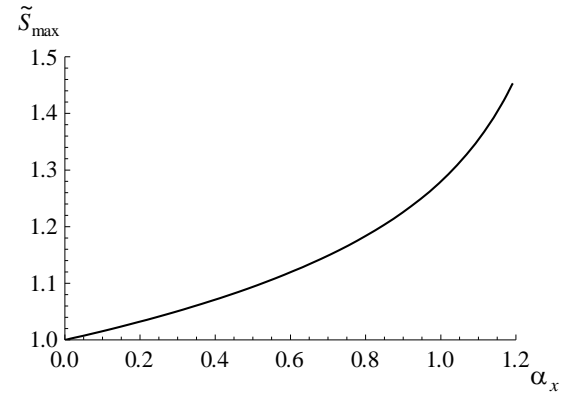


Fig.3: Variation of maximum dimensionless Seebeck coefficient with α_x for $\alpha_y = \alpha_z \approx 0$.

NOMENCLATURE

Symbol	Quantity	SI Unit
A	Surface area of the domain	m^2
f	Nonequilibrium distribution function	<i>dimensionless</i>
f_0	Equilibrium distribution function	<i>dimensionless</i>
F_x^Φ	Driving force due to electrochemical potential gradient	J / m
F_x^T	Driving force due to temperature gradient	J / m
h	Planck's constant	$J s$
i, j, k	Quantum numbers	<i>dimensionless</i>
k_b	Boltzman's constant	J / K
L_c	Half of the most probable de Broglie wave length	m
L_g	Geometric mean free path	m
Li	Polylogarithm function	<i>dimensionless</i>
L_x, L_y, L_z	Sizes of domain	m
m	Mass of particle	kg
q	Charge of particle	C
S	Seebeck coefficient	V / K
\tilde{S}	Dimensionless Seebeck coefficient	<i>dimensionless</i>
S_o	Seebeck coefficient without QSE	V / K
\tilde{S}_{max}	Dimensionless maximum Seebeck coefficient	<i>dimensionless</i>
T	Temperature	K

V	Volume	m^3
Z	Figure of merit	$1/K$
$\alpha_x, \alpha_y, \alpha_z$	Inverse scale factors	<i>dimensionless</i>
σ	Conductivity	$1/\Omega m$
Γ	Gamma function	<i>dimensionless</i>
ε_w	Translational energy	J
κ	Thermal conductivity	W/mK
Λ	Dimensionless chemical potential ($\mu/k_b T$)	<i>dimensionless</i>
μ	Chemical potential	J
τ	Relaxation time	s
φ	External potential	J

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