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Quantum Effects on Gas Diffusion at the Nano Scale*

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Abstract: The thermodynamic and transport properties of gases confined at the nano scale are considerably different than those at the macro scale. At the nano scale, quantum size effects (QSE) become important and changes the behavior of gases. In this study, the diffusion coefficients of monatomic Fermi and Bose gases are analytically derived by considering QSE. The influences of QSE and quantum degeneracy on the diffusion coefficients are examined separately to analyze these effects individually. The variations of the ratio of diffusion coefficients of He3 and He4 gases with the concentration of He3 are analyzed for both low and high density conditions.

Keywords: *Quantum size effects; nano scale diffusion; quantum potential.*

1. Introduction

There has been a great deal of interest in understanding the electric, optic, thermodynamic and transport properties of nano scale systems in recent years. In these systems, size induced quantum confinement plays an important role affecting electron transport in thin films (Trivedi & Ashcroft, 1988) and metallic nano wires (Liu, Chien & Searson, 1998; Arora, 1981; Barati & Sadeghi, 2001), the transport properties of gases and water in carbon nano tubes (Jakobtorweihen, Keil & Smith, 2006; Skoulidas, Ackerman, Johnson & Sholl, 2002; Striole, 2006), the density distributions of ideal gases (Sisman, Ozturk & Firat, 2007), the optical properties of small metals (Oleshko 2008; Wood & Ashcroft, 1982), the thermodynamic properties of gases confined in nano structures (Firat & Sisman, 2009) and the transport properties of gases in nano channels (Ozturk & Sisman, 2009).

At the nano scale, the wave character of particles becomes important and modifies some fundamental quantities such as the probability density, the momentum components and the momentum spectrum of the particles. Quantum size effects (QSE) arise due to these modifications. Furthermore, in statistical mechanics, the infinite volume approximation is often used and infinite sums are replaced by integrals. However, when the size of the domain is scaled down to the nanometer, the thermal de Broglie wavelength of particles becomes comparable with the dimensions of the domain. In this case, infinite sums cannot be replaced by integrals and some more precise formulas, like Poisson's formula, must be used. In this case, results show that the shape and size of the domain affect the transport and thermodynamics properties of the system. Finite size effects on the thermodynamic properties of ideal Maxwellian and quantum gases have been examined in the literature (Sisman 2004; Dai & Xie, 2004, Molina, 1996; Pathria, 1998).

The classical and quantum mechanical descriptions use the particle and wave character of matter, respectively. There are some differences between these two viewpoints and the classical results differ considerably from those obtained by using quantum mechanics at the nano scale. From the classical viewpoint, the probability density of particles confined in a domain is constant. From the quantum mechanical viewpoint, however, the probability density is not homogeneous even at thermodynamic equilibrium and particle density goes to zero near the boundaries if the boundaries are impenetrable. In other words, due to the wave character of matter, the particle feels the boundaries when the distance between the particle and the boundary is on the order of the thermal de Broglie wave length. This behavior can also be modeled by introducing an effective quantum potential which keeps the particle away from the boundaries (Ozturk & Sisman, 2009). In the absence of an external potential field, chemical and effective quantum potentials together affect the particle distribution. In the inner part of the domain, the effective quantum potential is negligible even though it is very high near the boundaries. The inhomogeneous density region near the boundaries has been called a quantum boundary layer (Sisman, Ozturk & Firat, 2007) whose thickness has been found independent of the domain shape for an ideal Maxwellian gas (Firat & Sisman, 2009).

In this study, the diffusion coefficients of monatomic Fermi and Bose gases in a rectangular transport domain are analytically derived by considering QSE. To solve the problem analytically, mixtures of ideal monatomic gases with different concentrations of He3 and He4 confined in large containers connected with a rectangular nano channel is considered. In the transport direction, the nano channel is assumed to be much longer than the thermal de Broglie wave length and the mean free path of the gas particles. Thus, QSE can be neglected only in the transport direction. The diffusion process inside the channel is supposed to be carried out at constant temperature and pressure. The particle flux due to the density gradient at constant temperature and pressure is derived for Fermi and Bose gases by considering QSE. It is shown how the shape and size of the transport domain affect the diffusion process at the nano scale and how this behavior can in particular be used to enhance the isotropic enrichment for light elements.

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2. Derivation of diffusion coefficient

The equilibrium distribution function of Fermi and Bose gases can be written in a closed form as

$$f_0^s = \frac{\left|\psi_w(\mathbf{x})\right|^2}{\exp\left[\left(\varepsilon_w - \mu^s\right)/k_\mathrm{b}T\right] \pm 1} \tag{1}$$

where ε_w and ψ_w are the energy eigenvalue and the wave eigenfunction of a particle in quantum state *w*, respectively, μ^s is the chemical potential of species s (*s*=He4, He3), k_b is Boltzmann's constant, T is the temperature and the upper (lower) sign is used for a Fermi (Bose) gas. By considering the rectangular geometry and infinite potential representation for the boundaries, eigenvalues and wavefunctions are obtained by solving the Schrödinger equation. Therefore, ε_w/k_bT in Eq.(1) is written as

$$\frac{\varepsilon_w}{k_bT} = \frac{\varepsilon_{ijk}}{k_bT} = \left(\alpha_1 i\right)^2 + \left(\alpha_2 j\right)^2 + \left(\alpha_3 k\right)^2 \tag{2}$$

where $\alpha_1 = L_c/L_1$, $\alpha_2 = L_c/L_2$, $\alpha_3 = L_c/L_3$, the length $L_c = h\Big/\sqrt{8m^s k_bT}$ is one half of the most probable de Broglie wavelength of the particles, *h* is Planck's constant, m^s is the rest mass of a gas particle of specie s , and L_1, L_2 and L_3 are the sizes of the rectangular domain. By introducing an effective quantum potential, the quantum mechanical probability density, $\left|\psi(x)\right|^2$, is replaced by the classical probability density $1/V$. Thus the equilibrium distribution function is expressed as

$$f_0^s = \frac{1}{V}\frac{1}{\exp\left[\left(\varepsilon_w - \mu_q^s\right)/k_\mathrm{b}T\right] \pm 1} \tag{3}$$

where $\mu_q^s = \mu^s - \varphi^s$ and φ^s is the effective quantum potential (Ozturk & Sisman, 2009). Under the relaxation time approximation for the steady state case, the particle flux in direction 1 is given by

$$J_1^s = -\sum \tau v_1^2 \frac{\partial f_0^s}{\partial x_1} \tag{4}$$

where v_1 is the velocity of the particle in direction 1 and τ is the relaxation time. Since the sizes of the domain in the transverse directions are much smaller than the mean free path of the particles, the relaxation time is determined by $\tau = L_g/v$ where L_g is the geometric mean free path of the particles defined in terms of the volume *V* and surface area *A*, i.e., $L_g = 2V/A$. If Eq. (2) and Eq. (3) are used in Eq. (4) and the summation in Eq. (4) is calculated with the Poisson summation formula, the diffusive particle flux is derived as

$$J_1^s = -\frac{4L_g n}{3}\frac{k_bT}{\sqrt{2\pi m^s k_bT}}\left(\frac{Li_1}{Li_{1/2}}\right)_s \times \left[\frac{1 - \frac{3\sqrt{\pi}}{8}\left(\alpha_2 + \alpha_3\right)\frac{Li_{1/2}}{Li_1}}{\frac{1}{\sqrt{\pi}}\left(\alpha_2 + \alpha_3\right)\frac{Li_0}{Li_{1/2}}}\right]_s \frac{\partial c^s}{\partial x_1} \tag{5}$$

where c^s is the concentration of the species *s* defined by $c^s = n_s/n$, n_s and n are the species and total number density of particles, respectively, and Li is the polylogarithm function with an exponential argument $\mp\exp\left(\mu_q^s/k_bT\right)$. The details of the non-equilibrium distribution function in terms of driving forces are given in reference (Ozturk & Sisman, 2009). It should be noted that $\sum_s c^s = 1$ and the chemical potentials of He3 and He4 can be expressed in terms of the He3 concentration c^{He3} and the total density *n*, $\mu_q^{He3}\left(c^{He3}, n\right)$ and $\mu_q^{He4}\left(1 - c^{He3}, n\right)$. By using Eq.(5), the normalized diffusion coefficient of species *s* is written as

$$D_s = \frac{1}{\sqrt{m^s}}\left(\frac{Li_1}{Li_{1/2}}\right)_s \left[\frac{1 - \frac{3\sqrt{\pi}}{8}\left(\alpha_2 + \alpha_3\right)\frac{Li_{1/2}}{Li_1}}{1 - \frac{1}{\sqrt{\pi}}\left(\alpha_2 + \alpha_3\right)\frac{Li_0}{Li_{1/2}}}\right]_s \tag{6}$$

The normalization is done by dividing the diffusion coefficient by

$$\frac{4L_g n}{3}\frac{k_bT}{\sqrt{2\pi k_bT}} .$$

Here, the mixture consists of He3 and He4 gases which obey Fermi-Dirac and Bose-Einstein statistics, respectively. If the first and second brackets of Eq. (6) are represented by QD and SE , respectively, the dimensionless ratio of the diffusion coefficients of He3 to He4 is obtained as

$$\hat{D} = \frac{D_{He3}}{D_{He4}} = \sqrt{\frac{m_{He4}}{m_{He3}}}\frac{QD_{He3}}{QD_{He4}}\frac{SE_{He3}}{SE_{He4}} \tag{7}$$

Eq.(7) can be rewritten as

$$\hat{D} = \frac{D_{He3}}{D_{He4}} = \hat{D}_{cl}\hat{D}_{QD}\hat{D}_{SE} \tag{8}$$

where $\hat{D}_{cl} = \sqrt{m_{He4}/m_{He3}}$, $\hat{D}_{QD} = QD_{He3}/QD_{He4}$ and $\hat{D}_{SE} = SE_{He3}/SE_{He4}$. Therefore, $\hat{D}_{cl}$, $\hat{D}_{QD}$ and $\hat{D}_{SE}$ represent the influences of mass, degeneracy and size effects on diffusion, respectively. Before examining the variation of $\hat{D}_{QD}$ and $\hat{D}_{SE}$ versus c^{He3} and *n*, it is better to define the dimensionless total number density of particles as $\tilde{n} = n/n_q$ where n_q is the quantum density given by $n_q = 1/\lambda_{th}^3$ and $\lambda_{th} = 2L_c/\sqrt{\pi}$. During the calculations, the relation between the alpha values of He3 and He4 is used and is given by

$$\alpha_i^{He4} = \sqrt{m_{He3}/m_{He4}}\ \alpha_i^{He3};\ i=1,2,3.. \tag{9}$$

3. Results

Figure 1 shows the variation of the influence of weak quantum degeneracy on the diffusion coefficients ratio at low density conditions ($\tilde{n} = 0.1$) where Maxwellian statistics is valid. It seems that the diffusion coefficient of He3 increases more than that of He4 with increasing values of c^{He3} . Chemical potential of He3 increases with increasing He3 concentration and this causes a linear increment of $\hat{D}_{QD}$ since $\hat{D}_{QD}$ linearly depend on density at Maxwellian limit. The opposite behaviour is seen in Figure 2 for high density conditions ($\tilde{n} = 2$). Diffusion ability of He3 atoms decreases with increasing degeneracy. Therefore, $\hat{D}_{QD}$ is getting smaller values for higher He3 concentrations. It is seen that the variation of $\hat{D}_{QD}$ with c^{He3} becomes stronger for higher values of the total density.

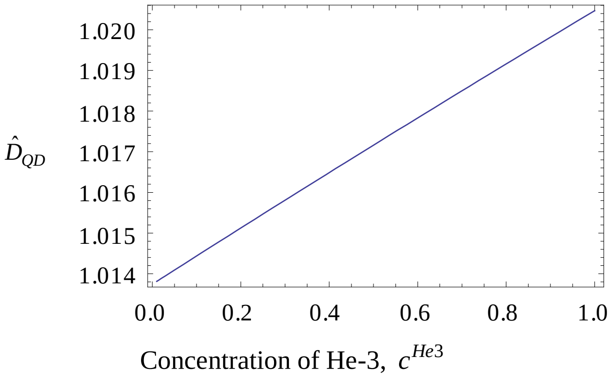

Figure 1. Variation of $\hat{D}_{QD}$ *vs* c^{He3} *for* $\tilde{n} = 0.1$.

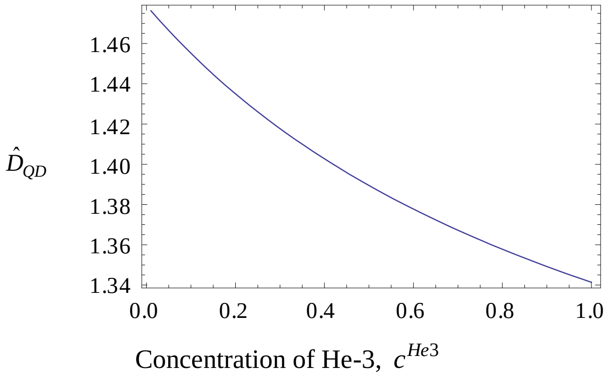

Figure 2. Variation of $\hat{D}_{QD}$ *vs* c^{He3} *for* $\tilde{n} = 2$.

The influence of QSE on the diffusion coefficient ratio at low density conditions ($\tilde{n} = 0.1$) is shown in Figure 3 for $\alpha = \alpha_2^{He3} = \alpha_3^{He3} = 0.2$. It is seen that the ratio is nearly constant, at 0.99. On the other hand, in Figure 4, the variation of $\hat{D}_{SE}$ for high density conditions ($\tilde{n} = 2$) is much greater than that in Figure 3. The de Broglie wave length decreases with increasing c^{He3} due to Fermi degeneration and the influence of QSE on the diffusion coefficient ratio decreases. Therefore $\hat{D}_{SE}$ goes to unity with increasing c^{He3} .

In the Maxwell limit, the ratio of the polylogarithm functions in Eq. (6) goes to unity. Substituting Eq. (9) into Eq.(6) and using $m_{He3}/m_{He4} = 3/4$, $\hat{D}_{QD}$ and $\hat{D}_{SE}$ simplify to $\hat{D}_{QD} = 1$ and

$$\hat{D}_{SE} = \frac{1 - \alpha^{He3}\left(\frac{3\sqrt{\pi}}{4} + \frac{\sqrt{3}}{\sqrt{\pi}}\right)}{1 - \alpha^{He3}\left(\frac{2}{\sqrt{\pi}} + \frac{3\sqrt{3}\pi}{8}\right)} \tag{10}$$

where $\alpha_2^{He3} = \alpha_3^{He3} = \alpha^{He3}$ is used for simplicity. For $\alpha^{He3} = 0.2$, $\hat{D}_{SE} = 0.9901$ which agrees with Figure 3.

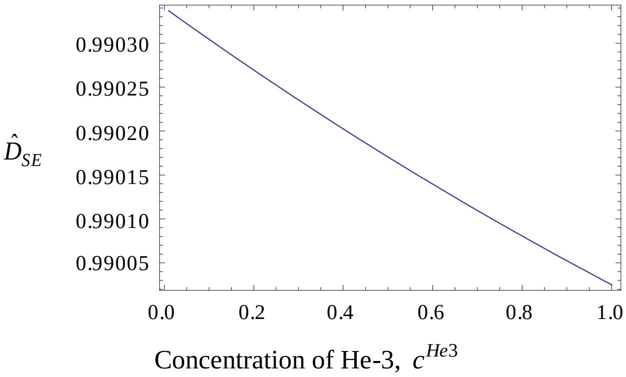

Figure 3. Variation of $\hat{D}_{SE}$ *vs to* c^{He3} *for* $\tilde{n} = 0.1$ and $\alpha = \alpha_2^{He3} = \alpha_3^{He3} = 0.2$.

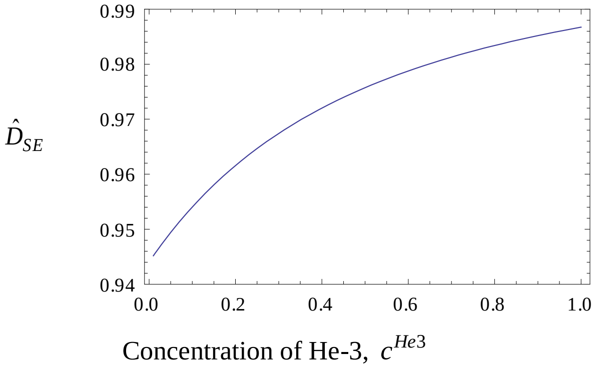

Figure 4. Variation of $\hat{D}_{SE}$ *vs to* c^{He3} *for* $\tilde{n} = 2$ and $\alpha = \alpha_2^{He3} = \alpha_3^{He3} = 0.2$.

4. Conclusion

Figure 3 and Figure 4 show that $\hat{D}_{SE}$ is different than unity especially for high density condition. It means that the diffusion coefficients of He3 and He4 are different due to QSE. QSE depends on the de Broglie wave length which is inversely proportional to the square root of particle mass. Therefore, QSE in the diffusion process can be used for the isotropic enrichment of especially light elements and supplements the classical method based on the mass dependency of diffusion coefficients. Furthermore, Figure 1 and Figure 2 show that the diffusion coefficients of He3 and He4 are different also due to quantum degeneracy. This difference becomes higher especially when the total density is high and He3 concentration is low. Therefore, the influence of quantum degeneracy on the diffusion process can also be used for isotropic enrichment. The quantum degeneracy effect on diffusion provides a more effective way for the separation of isotopes.

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Nomenclature

A	area
c^s	concentration of species s
$\hat{D}$	dimensionless ratio of the diffusion coefficient of He3 and He4
D_s	normalized diffusion coefficient for species s
f_0^s	equilibrium distribution function for species s
h	Planck's constant
i, j, k	integer numbers run from one to infinity
J^s	particle flux for species s
k_b	Boltzmann's constant
L_i	size of the rectangular domain in direction i
L_c	one half of the most probable de Broglie wavelength
L_g	geometric mean free path
Li	polylogarithm function
m^s	rest mass of a gas particle of species s
n	total number density of particles
n_s	number density of particles for species s
n_q	quantum density
T	temperature
v	velocity
V	volume

Greek symbols

α	L_c/L
ε_w	energy eigenvalue in quantum state w
λ_{th}	thermal de Broglie wavelength
τ	relaxation time
μ^s	chemical potential for species s
φ^s	effective quantum potential for species s
ψ_w	wave eigenfunction in quantum state w

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