

# Development of osmotic repulsive potential using lattice fluid model on ligand capped metallic nanoparticles in gas expanded liquid system

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**Abstract**—Not only obtaining nano-sized particles, but controlling mono-dispersed nanoparticles has been regarded as one of the important techniques to employ nano-engineering in many disciplines. To fractionate the nanoparticles synthesized, the gas expanded liquid system (GXLs) has proven to be very useful and effective. Many researchers considered the total interaction energy model comprised as a summation of van der Waals attractive potential, the elastic repulsive potential, and the osmotic repulsive potential as a promising thermodynamic model. In previous models, osmotic contribution was modeled based on the rigid lattice model. Consequently, it was impossible to consider the effect of pressure on GXL operation because osmotic repulsive potential based on rigid lattice model intrinsically could not reflect the pressure influence. We applied a lattice fluid model in the presence of holes to derive better osmotic repulsive potential. Thus, the effect of pressure on nanoparticle synthesis in GXL process has been successfully investigated. A nanoparticle size predicted using this improved model is in a better agreement to that obtained experimentally.

Keywords: Gas Expanded Liquid (GXL), Nanoparticle, Lattice Fluid (LF), Steric Stabilization

## INTRODUCTION

A gas-expanded liquid (GXL) has received a great deal of attention as a green medium to apply in many areas: reaction [1], extraction [2], polymer processing [3], and nanometer-sized particle synthesis [4]. Saunders and Roberts [5] reviewed the development of highly tunable CO<sub>2</sub> gas-expanded liquid systems to process nanoparticles in a sustainable and efficient manner. In particular, a CO<sub>2</sub> expanded liquid makes a process relying on toxic organic solvents more environmentally friendly. In parallel with advances on the experimental front, several modeling accomplishments have recently been achieved.

Thermodynamic models based on total interaction energy were developed for the size selective fractionation process using the thermodynamic properties of CO<sub>2</sub> or ethylene gas expanded liquids to predict the maximum particle size that can be dispersed as a function of CO<sub>2</sub> pressure. Previously, studies have been done to predict the particle size that can be stabilized at given conditions in conventional liquid solvents [6], supercritical ethane [7], compressed propane [8] and supercritical CO<sub>2</sub> [7,9] and supercritical ethylene [10]. Shah et al. [9] initiated this soft sphere modeling approach, where stabilization of nanoparticles in a given solvent depends on the balance between the van der Waals attractive forces with steric repulsive forces. Shah et al. [9] and several researchers [7,10,11] have employed a total interaction energy model to correlate the solvent-ligand interaction with the maximum size of a ligand stabilized nanoparticle that can be dispersed within a given solvent

system.

Some models that included interactions between the whole ligand and solvent molecules took into account volume fraction based total energy of molecules [7,11]. Other models attempted to consider only a certain fraction of the ligand surface effectively interacts with solvent molecules and showed reliable results compared to volume fraction model [10].

However, there was a major drawback to this modeling work pristinely based on rigid lattice model which cannot consider the effects of pressure on the GXL process. So, in this study we suggested a new model based on lattice fluid model to encompass the effects of pressure on the nanometer-sized particle fractionation system.

## THEORY

Shah et al. [9] used total interaction energy model to depict the stability of dispersions of the gold nanoparticles. The total interaction energy,  $\Phi_{total}$ , is given by

$$\Phi_{total} = \Phi_{vdW} + \Phi_{elas} + \Phi_{osm} \quad (1)$$

where  $\Phi_{vdW}$  is the van der Waals attractive potential;  $\Phi_{elas}$  is the elastic repulsive potential; and  $\Phi_{osm}$  is the osmotic repulsive potential.

The van der Waals attractive potential is approximated by

$$\Phi_{vdW} = -\frac{A_{131}}{6} \left[ \frac{2a^2}{d^2 - 4a^2} + \frac{2a^2}{d^2} + \ln \left( \frac{d^2 - 4a^2}{d^2} \right) \right] \quad (2)$$

where,  $A_{131}$  is the Hamaker constant;  $a$ , the radius of the particles; and  $d$ , the center-to-center separation distance between particles. To incorporate the ethylene/hexane GXL system, Eq. (3) was used to calculate the Hamaker constant for the mixed solvent sys-

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tem [11].

$$A_{131} \approx [\sqrt{A_{11}} - (\tilde{\phi}_3 \sqrt{A_{(33)}} + \tilde{\phi}_3'' \sqrt{A_{(33)}''})]^2 \quad (3)$$

where  $A_{11}$  represents the Hamaker constant of metal particles,  $3'$  represents either  $\text{CO}_2$  or ethylene depending on the solvent applied and  $3''$  represents the hexane.

So,  $\tilde{\phi}_3$  is the ethylene volume fraction in the solvent mixture excluding the ligand, and  $\tilde{\phi}_3''$  is the volume fraction of the hexane in the GXL solvent excluding the ligand. The Hamaker constants used in this study were  $3.1 \times 10^{-19}$  J for silver [10] and  $3.5 \times 10^{-19}$  J for gold [9]. The Hamaker constant of each solvent, namely,  $\text{CO}_2$  and ethylene, was calculated by using dielectric constants and refractive indexes [9].

The elastic repulsive potential is given by

$$\Phi_{\text{elas}} = \frac{2\pi k_B T l^2 \phi \rho_l}{M_l} \left\{ \frac{h}{l} \ln \left[ \frac{h}{l} \left( \frac{3-h/l}{2} \right)^2 \right] - 6 \ln \left[ \frac{3-h/l}{2} \right] + 3 \left( 1 - \frac{h}{l} \right) \right\} \quad (4)$$

$h < l$

where,  $h = d - 2R$ . Here,  $h$  is the separation distance between the surfaces of the particles;  $\rho_l$  is the density of the ligand;  $l$  is the effective ligand length;  $\phi$ , the volume fraction of ligand;  $M_l$ , the molecular weight of ligand, respectively.

### 1. The Derivation of Osmotic Repulsive Potential Using Lattice Fluid Model

It was impossible to reflect the effect of pressure on the total interaction energy only by applying either volume fraction model or surface fraction model. So, it is strongly desired to derive a new model to examine the pressure effect on the mono-dispersed nanoparticle fractionation system.

In the mixing with the change of volume, Gibbs free energy of mixing is the sum of combinatorial free energy and residual free energy shown as Eq. (5).

$$\Delta G_M = \Delta G^c + \Delta G^r \quad (5)$$

Surface fraction model (SFM) [10] and previous model [11] have the same expression in combinatorial free energy, but residual free energy term is different because SFM is represented by surface area fraction. LF model also has the same form as SFM, but a hole is added to a system as one component.

#### 1-1. The Combinatorial Gibbs Free Energy Term

According to Guggenheim's statistics, combinatorial Gibbs free energy term for random lattice-with-hole model may be written as [12-15]

$$\Delta G^c_1 = k_B T \left[ \delta N_0 \ln \phi_0 + \sum_{j=1}^N \delta N_j \ln \phi_j - \frac{z}{2} \delta N_q \ln \left[ 1 + \left( \frac{q_M}{r_M} - 1 \right) (1 - \phi_0) \right] \right] \quad (6)$$

$$\Delta G^c_2 = k_B T \left[ \delta N_0 \ln \phi_0 + \sum_{j=1}^N \delta N_j \ln \phi_j - \frac{z}{2} \delta N_q \ln \left[ 1 + \left( \frac{q_M}{r_M} - 1 \right) (1 - \phi_0) \right] \right] \quad (7)$$

$$\Delta G^c = \Delta G^c_1 + \Delta G^c_2 - \sum_{j=1}^N \delta G_j^c \quad (8)$$

where,  $k_B$  is Boltzmann constant;  $N$ , total number of molecules;  $\phi_j$ , segment fraction of component  $j$  in mixture; subscript 0 means hole;  $N_q = N_0 + \sum_{j=1}^N q_j N_j$ ;  $q_j$ , surface fraction parameter of component  $j$ ;  $r_j$ , segment number of component  $j$ ;  $z=10$ , coordination number;  $\delta G_j^c$ , configurational entropy of pure component  $j$ ;  $r_M = \sum_{j=1}^N r_j$ ;  $q_M = \sum_{j=1}^N q_j$ .

Assuming that there are no holes in polymer molecules and  $\delta N_p \rightarrow 0$  then, the number of molecules,  $\delta N_k$  and  $\delta N_0$  of component  $k$  and holes in the system are given by

$$\delta N_k = x_k \delta N_s = \frac{x_k (1 - \phi_p)}{\tilde{v}_M} \delta V \quad (9)$$

$$\delta N_0 = \frac{\phi_0}{v_H} \delta V \quad (10)$$

where  $N_s$ ,  $N_k$  are total number of solvent molecules and number of component  $k$  respectively;  $x_k$ , mole fraction of component  $k$  excluding polymer;  $v_H = 9.75 \text{ cm}^3/\text{mol}$ , molar volume of hole;  $\tilde{v}_M$ , molar volume of mixture excluding polymer;  $\phi_p$ , segment fraction of polymer;  $V$ , total volume of mixture.

$$\begin{aligned} \Delta G^c_1 &\cong k_B T \sum_{k=1}^{N_s} \left[ \frac{v_k - v_k^*}{v_H} \ln \phi_0 + \ln \phi_k \right] \delta N_k \\ &= k_B T \sum_{k=1}^{N_s} \left[ \frac{v_k - v_k^*}{v_H} \ln \phi_0 + \ln \phi_k \right] \frac{(1 - \phi_p)}{\tilde{v}_M} \delta V \end{aligned} \quad (11)$$

where,  $v_k$  and  $v_k^*$  molar volume and hard sphere molar volume of component  $k$ , respectively.

$$\begin{aligned} \Delta G^c_2 &\cong - \frac{z k_B T}{2} \sum_{k=1}^{N_s} x_k \left[ \frac{v_k - v_k^*}{v_H} + q_k \right] \\ &\quad \ln [1 + (s_M - 1)(1 - \phi_0)] \frac{(1 - \phi_p)}{\tilde{v}_M} \delta V \end{aligned} \quad (12)$$

The volume fraction,  $\phi_k$  of component  $k$  in the system is given by

$$\phi_k = \tilde{\phi}_k (1 - \phi_p) \quad (13)$$

where  $\tilde{\phi}_k$  is segment fraction of component  $k$  excluding polymer

Expressions for the logarithmic terms in  $\Delta G^c_1$  and  $\Delta G^c_2$  in the Taylor's series expansion at the limit of  $\phi_p$  approaching 0 yields the following expression:

$$\ln \phi_k = \text{constant} - \phi_p - \frac{\phi_p^2}{2} + \dots \quad (14)$$

$$\ln [1 + (s_M - 1)(1 - \phi_0)] \cong \text{constant} + 2 + \Phi \phi_p - [\Phi \phi_p]^2 + \dots \quad (15)$$

$$\text{where, } \Phi = \frac{(s_M - 1) \tilde{\phi}_0}{1 + (s_M - 1) \tilde{\phi}_s}.$$

Substituting Eqs. (13), (14) and (15) into Eqs. (11) and (12) and arranging second-order terms for  $\phi_p$  yields the following expression for the combinatorial Gibbs free energy. All terms except second-order terms for  $\phi_p$  vanish on taking the difference required by Eq. (29), evaluation of  $\Delta G_R$ , the mixing free energy change for the approach of two sterically stabilized particles from infinite separation to a separation  $d$ .

$$\Delta G^c_1 \cong \frac{k_B T}{2 \tilde{v}_M} \sum_{k=1}^{N_s} x_k \left[ \frac{v_k - v_k^*}{v_H} + 1 \right] \phi_p^2 \delta V = \frac{k_B T}{\tilde{v}_M} g_1^c \phi_p^2 \delta V \quad (16)$$

$$\Delta g_1^c = \frac{1}{2} \sum_{k=1}^{N_i} x_k \left[ \frac{v_k - v_k^*}{v_H} + 1 \right] \quad (17)$$

$$\begin{aligned} \delta(\Delta G^c)_2 &\cong -\frac{z k_B T}{2 \bar{v}_M} \sum_{k=1}^{N_i} x_k \left[ \frac{v_k - v_k^*}{v_H} + q_k \right] \Phi (1 + \Phi) \phi_p^2 \delta V \\ &= -\frac{k_B T}{\bar{v}_M} g_2^c \phi_p^2 \delta V \end{aligned} \quad (18)$$

$$\Delta g_2^c = -\frac{z}{2} \sum_{k=1}^{N_i} x_k \left[ \frac{v_k - v_k^*}{v_H} + \frac{q_k}{v_H} \right] \Phi (1 + \Phi) \quad (19)$$

### 1-2. The Residual Gibbs Free Energy Term

In a three-dimensional lattice of the coordination number  $z$  molecules of component  $j$  occupy  $r_j$  sites and interact with neighboring segment of molecules with surface area,  $q_j$ . For molecules which are not cyclic the following relation is assumed.

$$z q_j = z r_j - 2 r_j + 2 \quad (20)$$

The residual Gibbs free energy, which is the free energy arising from contact dissimilarities, is given by the following expression [12-15]:

$$\delta(\Delta G^R) = -\frac{z}{2} [\delta N_q \sum_j^s \sum_{k>j} \theta_j \theta_k \varepsilon_{jk} - \sum_{j=1}^s \delta N_{qj} \varepsilon_{jj} \theta_j^2] \quad (21)$$

where  $\theta_k$  the surface fraction of component  $k$ ;  $\theta_p$  the surface fraction of pure component  $j$ ;  $\Delta \varepsilon_{jk}$  interchange energy parameter;  $\varepsilon_{jp}$  interaction energy parameter of pure component  $j$ , respectively.

Assuming  $\delta N_p \rightarrow 0$  and substituting Eqs. (9) and (10) into Eq. (21) yields the following equation.

$$\delta(\Delta G^R) = -\frac{z}{2} [\gamma - q_M \phi_p] [\sum_j^N \sum_{k>j} \theta_j \theta_k \Delta \varepsilon_{jk}] \frac{\delta V}{\bar{v}_M} \quad (22)$$

$$\gamma = \frac{\bar{v}_M - \bar{v}_M^*}{v_H} + q_M \quad (23)$$

where  $\Delta \varepsilon_{jk}$  is interchange energy;  $\Delta \varepsilon_{jk} = \varepsilon_{jj} + \varepsilon_{kk} - 2 \varepsilon_{jk}$ ;  $q_M = \sum_{j=1}^N x_j q_j$ ;  $\theta_k$  surface fraction of component  $k$  and  $\theta_p$  surface fraction of polymer component.

$\theta_k$  and  $\theta_p$  in the Taylor's series expansion at the limit of  $\theta_p$  approaching 0 yield the following expressions:

$$\theta_k = \alpha_k + \beta_k \phi_p + \dots \quad (24)$$

$$\theta_p = \frac{s_p}{\tilde{\phi}_0 + \sum_{k=1}^{N_s} s_k \tilde{\phi}_k} \phi_p + \dots = \gamma \phi_p + \dots \quad (25)$$

$$\text{where } \alpha_k = \frac{s_k \tilde{\phi}_k}{\tilde{\phi}_0 + \sum_{k=1}^{N_s} s_k \tilde{\phi}_k} \text{ and } \beta_k = \frac{-s_k s_p \tilde{\phi}_k}{(\tilde{\phi}_0 + \sum_{k=1}^{N_s} s_k \tilde{\phi}_k)^2}.$$

Substituting Eqs. (24) and (25) into Eq. (22) and arranging second-order terms for  $\phi_p$  yields the following expression for the residual Gibbs free energy.

$$\delta(\Delta G^R) = -\frac{1}{\bar{v}_M} \Delta g^R \phi_p^2 \delta V \quad (26)$$

$$\begin{aligned} \text{where, } \Delta g^R &= \frac{z}{2} (\gamma - q_M \phi_p) [\sum_j^s \sum_{k>j} (\alpha_k \beta_j + \alpha_j \beta_k - \beta_j \beta_k) \Delta \varepsilon_{jk} \\ &\quad + \gamma \sum_{k>j}^s \beta_k \Delta \varepsilon_{kp}] \end{aligned} \quad (27)$$

According to Napper [16], it is assumed that the free energy of

attachment of the polymer chains is independent of the separation distance,  $d$ , of the plates, and the repulsive potential energy,  $\Delta G_R$  is

$$\Delta G_R = \Delta G_{M_d} - \Delta G_{M_e} \quad (28)$$

Assuming that  $\{x_j\}$  and  $\{\tilde{\phi}_k\}$  are independent of the distance of the separation, substituting  $\phi_p = v_H \rho_p(d)$  into Eqs. (12) and (15) yields

$$\Delta G_R = \frac{k_B T v_H^2 \phi_p^2}{\bar{v}_M} \left[ \Delta g_1^c + \Delta g_2^c - \frac{\Delta g^R}{k_B T} \right] \left[ \int_V \rho_p^2(d) \delta V - \int_V \rho_p^2(\infty) \delta V \right] \quad (29)$$

where,  $\rho_p(d)$  is the number density of the polymer

Assuming constant segment density and that the particles are equivalent spheres, we can obtain the expression of the osmotic interaction energy by applying Derjaguin approximation.

First, for the interpenetration domain integrating Eq. (29) gives the following result.

$$\Phi_{osm} = \frac{4 \pi a R T \rho_l}{\bar{v}_M M_l} \phi_p^2 \left[ \Delta g_1^c + \Delta g_2^c - \frac{\Delta g^R}{R T} \right] \left( l - \frac{h}{2} \right)^2 \quad l < h < 2l \quad (30)$$

And for the interpenetration plus compression domain integrating Eq. (29) gives the following result.

$$\Phi_{osm} = \frac{4 \pi a R T}{\bar{v}_M} \phi_p^2 \left[ \Delta g_1^c + \Delta g_2^c - \frac{\Delta g^R}{k_B T} \right] l^2 \left( 3 \ln \left( \frac{l}{h} \right) + 2 \left( \frac{h}{l} \right) - 1.5 \right) \quad h < l \quad (31)$$

## RESULTS AND DISCUSSION

### 1. Parameters

The particle size calculation using this model for CO<sub>2</sub> or ethylene expanded liquid system was performed with coordination number,  $z=10$ , and molar volume of hole,  $v_H=9.75$  cm<sup>3</sup>/mol and ligand surface coverage is assumed 75%. Pure component parameters, volume parameters,  $v_i^*$ , and energy parameters,  $\varepsilon_{ij}$  were used the results of You et al. [13] and were listed in Table 1. And physical properties for several solvents were also listed Table 2.

Geometric mean value for the interaction parameter between component  $i$  and  $j$  was assumed.

**Table 1. Pure parameters for several components**

	$v^*$ (cm <sup>3</sup> /mol) <sup>a</sup>	$\varepsilon_{ij}/R$ (K) <sup>a</sup>	$r_p$ segment number	$q_p$ surface parameter
CO <sub>2</sub>	36.2	86.1	3.7	3.2
Ethylene	46.9	74.2	4.8	4.1
Hexane	111.6	97.4	11.4	9.4
Dodecane	201.5	102.7	20.7	16.7

<sup>a</sup>The results of You et al. [12] at 303.15 K

**Table 2. Physical properties of CO<sub>2</sub>, ethylene, and hexane at 303.15 K and 3.45 MPa**

Compound	$v_L$ (cm <sup>3</sup> /mol)	$\delta$ (MPa/cm <sup>3</sup> ) <sup>1/2</sup>	Dielectric constant	Refractive index
CO <sub>2</sub>	65.5	12.3	1.483	1.185
Ethylene	74.5	12.9	1.572 [18]	1.257
Hexane	132	14.9	1.890 [24]	1.372

$$\varepsilon_{ij} = (1 - l_{ij}) \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (32)$$

where  $l_{ij}$  is binary interaction parameter and all binary interaction parameters in this calculation were set to 0.

## 2. Modeling Results

White and Kitchens [17] reported that the length of ligand in GXL system depends on CO<sub>2</sub> fraction (pressure). The ligand length decreases with an increase in the antisolvent CO<sub>2</sub> or ethylene concentration (pressure) due to the weaker solvent mixture being less able to solvate the ligand tails. In other words, the total ligand length is extended but only part of it is interacting with the solvent because only a portion of the ligand length is coming in contact with the solvent.

It must be considered the pressure dependence on the van der Waals interaction term and the osmotic repulsion term to calculate particle size exactly in the GXL nanoparticle fractionation system. But the effect of pressure on ligand length is not well known, so it is difficult to quantitatively reflect the effects in the theory.

First, we wanted to investigate the pressure dependence of LF based osmotic repulsion term on particle size in GXL system, and the results of the present model and the previous model calculated with a ligand length matched with experimental data at one

pressure are shown in Fig. 1-4. In this calculation, the largest nanoparticles at the given set of conditions can be determined by equat-

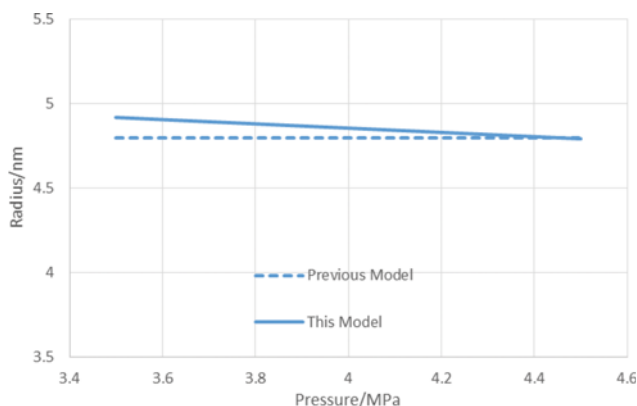


Fig. 1. Comparison of pressure dependence between the previous model and the present model for the CO<sub>2</sub> expanded liquid system containing Ag nanoparticles at 303.15 K.

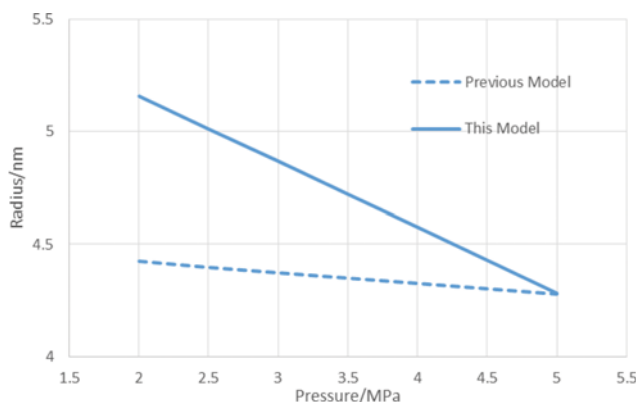


Fig. 2. Comparison of pressure dependence between the previous model and the present model for the CO<sub>2</sub> expanded liquid system containing Au nanoparticles at 303.15 K.

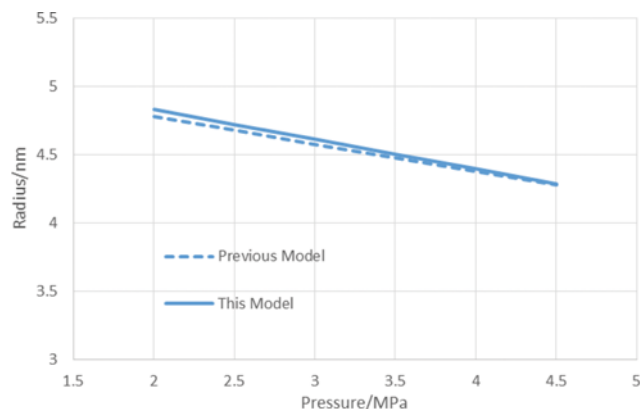


Fig. 3. Comparison of pressure dependence between the previous model and the present model for the Ethylene expanded liquid system containing Ag nanoparticles at 303.15 K.

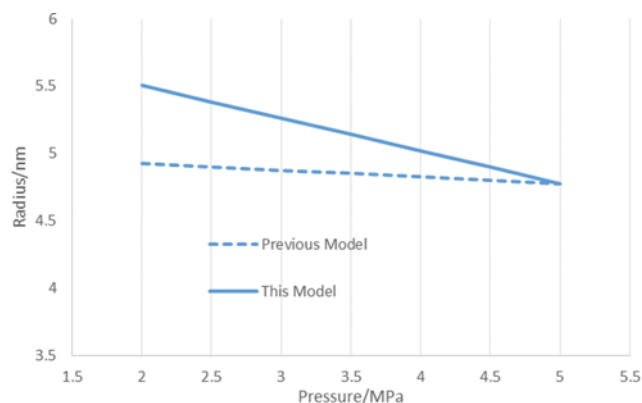


Fig. 4. Comparison of pressure dependence between the previous model and the present model for the ethylene expanded liquid system containing Au nanoparticles.

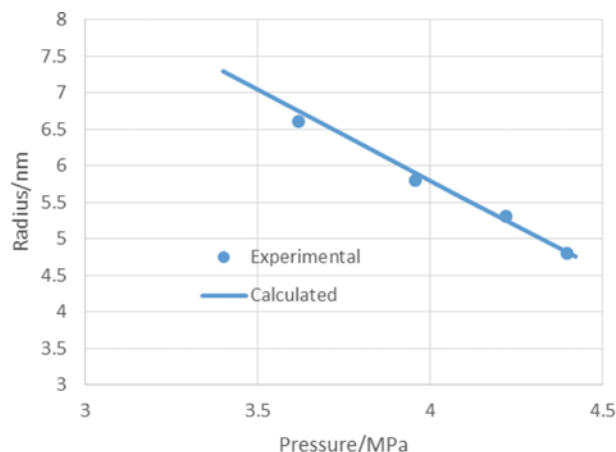


Fig. 5. The particle size as a function of pressure calculated as pressure-dependent ligand length,  $l/\text{nm} = -5.5314 \cdot P/\text{Mpa} + 36.527$  for the CO<sub>2</sub> expanded liquid system containing Ag nanoparticles at 303.15 K.

ing the minimum of the total interaction energy curve with  $-3/2k_B T$  and solving for the corresponding nanoparticle diameter.

Fig. 1 and Fig. 3 show the results for the GXL system containing silver nanoparticles, and there is little difference between the previous model and the present model. But Fig. 2 and Fig. 4 show the results for the GXL system containing gold nanoparticles; it can be seen that the previous model and the present model are different according to the pressure, and the present model shows the pressure dependency well.

In theory, the two terms that are affected by pressure in particle size calculations are vdW attraction term and the osmotic repulsion term.

Therefore, the pressure dependence in the particle size calculation can be thought of as the ligand length effect and the osmotic repulsion effect. In the case of the GXL system containing Ag nanoparticles, the main factor of the pressure dependence is mainly the ligand length effect, that is, it is mainly in the attraction term. There is no difference between the previous model and the present model in which the osmotic repulsion term using lattice-with-hole is modified.

On the contrary, in the case of the GXL system containing gold nanoparticles, the effect of the osmotic repulsion term due to the pressure is relatively large, and the calculation results of the previous model and the present model are different.

Therefore, it can be confirmed that the present model considers the influence of pressure on repulsion, which is one of the two major influences of pressure affecting particle size, in the current model.

Since both the previous and present model cannot consider the effect of the ligand length depending on the pressure, calculation results using pressure-independent ligand lengths show errors with experimental data. The particle size calculation results using pressure dependent ligand length for the GXL fractionation process are shown in Fig. 6-8. The experimental values are well expressed when the pressure-dependent ligand length is used, and this empiri-

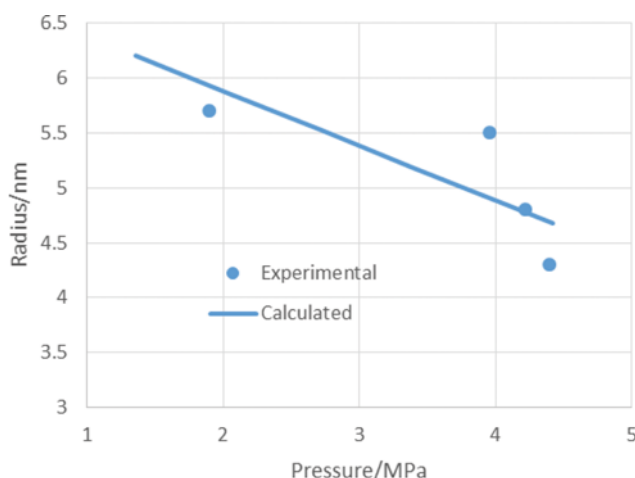


Fig. 6. The particle size as a function of pressure calculated as pressure-dependent ligand length,  $l/nm = -0.3147 \cdot P/\text{Mpa} + 14.414$  for the  $\text{CO}_2$  expanded liquid system containing Au nanoparticles at 303.15 K.

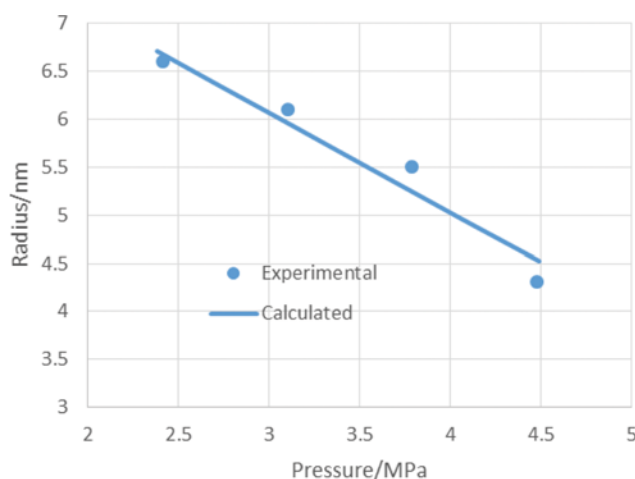


Fig. 7. The particle size as a function of pressure calculated as pressure-dependent ligand length,  $l/nm = -1.8955P/\text{MPa} + 20.389$  for the ethylene expanded liquid system containing Ag nanoparticles at 303.15 K.

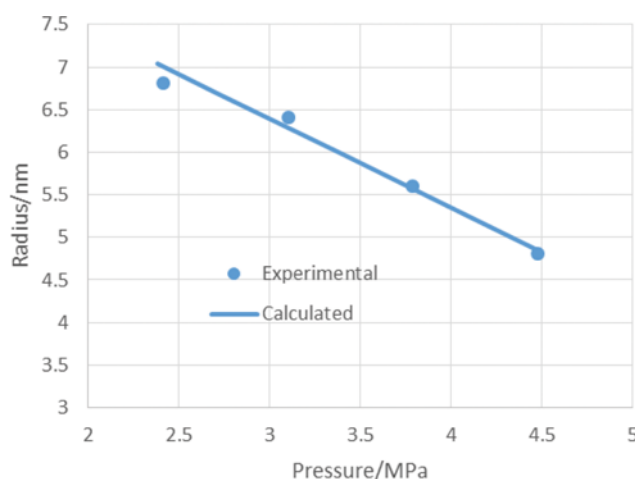


Fig. 8. The particle size as a function of pressure calculated as pressure-dependent ligand length,  $l/nm = -2.0833P/\text{Mpa} + 22.862$  for the ethylene expanded liquid system containing Au nanoparticles at 303.15 K.

cal relationship about ligand length is applicable to the process design.

## CONCLUSION

The synthesis of metal nanoparticles using GXLs has become popular because of its convenience on fractionation to obtain mono-dispersed particles. Although this experimental technique seems to be promising on generating uniform nanoparticle size, it has been less studied to predict the size of nanoparticles theoretically. Both volume fraction model and surface fraction model have failed in terms of inclusion of the pressure effect on the nanoparticle synthesis. A new osmotic repulsive energy equation was derived by applying random lattice fluid model to investigate the effect of pressure on nanometer-sized particles in GXL operation. It appears to be an improved osmotic repulsive potential is quite promising

in determining the nanoparticles in GXL process. However, there is still a room for improvement in the modeling by incorporating the status of ligand on the surface of the nanoparticles.

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