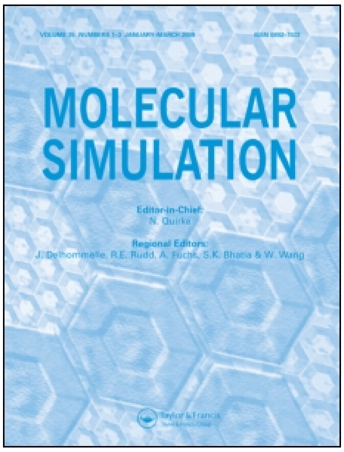

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Monte-Carlo Simulations of Centrifugal Gas Separation

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The use of a Monte–Carlo formalism in a centrifugal gas process separation simulation provides an efficient predictor of dew-pointing as a function of the imposed radial pressure gradient. Previously, this was done by simply calculating radial pressure and then resorting to a separate equation of state routine for evaluating whether condensation will occur or not. In our model, we incorporate the potential energy associated with rotation of a gas element into the simulation along with molecular interaction terms. This enables us to predict when sufficient nucleation has occurred that condensed material forms—an important limit for stable operation of a gas centrifuge.

Keywords: Gas centrifuge; Natural gas; Carbon dioxide; Hydrogen sulphide

INTRODUCTION

The utilisation of natural gas reserves is hindered by the requirement to remove contaminants. These "souring" contaminants are carbon dioxide and hydrogen sulphide. The standard technology for removing these contaminants is the solvent treater typified by the use of amines such as methyl diethanol amine [1]. These materials are environmentally undesirable. In operation the process is also energetically expensive and the energy cost of treating any gas stream with more than ca. 10% contaminants becomes prohibitive: at 10% contamination, nearly 10% of the clean gas value produced is used. At 50% contamination—a quite common figure in new fields—the energy cost rises to 75% of the clean gas produced, a clearly economically unacceptable figure.

The question then arises as to whether there are other separation processes that might be sufficiently economic. Examples of such processes include membrane and centrifugal separation processes [2,3]. For centrifugal separation, gas is spun up in a cylinder and this generates a radial pressure gradient with a reduction near the axis and elevated pressure near the cylinder wall [4]. There is generally the added advantage that the molecularly heavier contaminants are usually the easiest to condense. Thus any condensation (or formation of a dense supercritical fluid) will act in a synergistic fashion to the mass based separation in the centrifuge.

In the case that the components of the centrifuge can be modelled as an ideal gas, then it can be shown that the radial pressure distribution of component i as a function of radius R, in a centrifuge is given by [5]

$$p_i = \frac{A_i R^2}{e^{A_i R^2} - 1} p_{fi} e^{A_i R^2} \tag{1}$$

where p_{fi} is the centre point partial pressure of component i, and the coefficient of the exponential argument is given by a combination of molecular and centrifuge mechanical properties, viz.

$$A_i = \frac{M_i \omega^2}{2R_g T} \tag{2}$$

where M_i is the molar mass, ω is the angular velocity, R_g is the ideal gas constant, and T is the temperature.

For sub-critical systems, it is possible to compare the pressure calculated by Eq. (1) with the dew point pressure calculated by a suitable equation of state (e.g. Redlich–Kwong) in order to determine whether condensation has occurred. However, for systems close to critical, and for supercritical systems, this approach is profoundly unsatisfactory and molecular simulation provides a powerful alternative technique.

In this paper, we consider the centrifugal separation of hydrogen sulphide and methane, something

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which is of importance in removing the sulphur from streams of sour natural gas. In this case the normal situation applies in that the heavier component has stronger intermolecular forces than the lighter component.

We have also considered the separation of argon and ethane. Although of no direct industrial relevance, it provides an example of a simple case where the heavier component has weaker intermolecular forces than the lighter component. In this case the separation achieved is a trade-off between the two effects.

EQUILIBRIUM SIMULATION OF A CENTRIFUGE

Consider a multicomponent fluid spinning in a centrifuge with angular speed ω (Fig. 1). The centrifuge can be considered as being divided into a number of boxes of negligible size containing the fluid, each box being representative of the grand canonical ensemble.

The model presented here treats the centrifuge as being in equilibrium. This means that there is no net transport of material within the centrifuge. Clearly for a practical centrifuge system, there has got to be a flux of material and there will be a requirement to take into consideration the transport properties of the fluid. The model presented here can simulate the situation where the fluid remains close to equilibrium.

In an equilibrium situation, the chemical potential of a given component must be constant throughout the centrifuge. Likewise the temperature of the fluid is assumed constant.

The only non-standard feature of the simulation technique is that molecules in the simulation are given a potential energy associated with the rotation of the centrifuge (in addition to the intermolecular forces). This extra potential energy is given simply by the usual expression for centripetal potential energy:

$$V_{\text{cent}} = -\frac{1}{2} m R^2 \omega^2 \tag{3}$$

where m is the mass of a molecule, and R is the distance from the centre of the centrifuge.

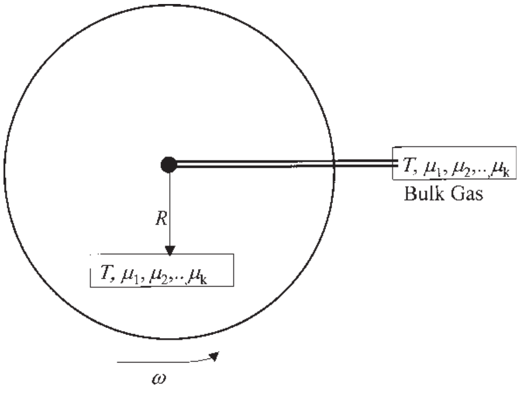


FIGURE 1 Conceptual model of centrifuge.

Each box is considered sufficiently small compared to the size of the centrifuge that R (and hence the centripetal potential energy for a given species) can be assumed to be constant. However, the boxes are sufficiently large that they are representative of the grand canonical ensemble.

It can be helpful to consider a box located at the centre of the centrifuge (where $V_{\text{cent}} = 0$) as being equivalent to a bulk fluid. It may be the case in a practical situation that the centre of the centrifuge is connected to a reservoir as is shown in Fig. 1.

Although it is possible in principle to simulate multi-component mixtures, this work is restricted to simulations of two component mixtures. Where a separation factor (or separative strength) S, is discussed and it is taken to be the ratio of mole fractions at radius R, to the ratio at zero radius. For the example of the H_2S/methane separation, this is given by

$$S = \frac{\left(\frac{[H_2S]}{[CH_4]}\right)_R}{\left(\frac{[H_2S]}{[CH_4]}\right)_f} \tag{4}$$

(Note that we assume a feed equivalent to conditions at the centre of the centrifuge.) The Grand Canonical Monte Carlo (GCMC) simulation technique for mixtures has been described previously [6]. The three usual types of GCMC trial [7,8] were included in the simulation, namely attempts to move particles in the system, attempts to create particles, and attempts to delete particles. To these are added a fourth type of trial—attempts to swap the identities of particles in the simulation. It is shown in reference [6] that although this type of trial is not strictly necessary for convergence of the Markov chain, it does lead to a large improvement in statistical accuracy. All four types of move are conducted with the same probability.

Each simulation was typically run for five million configurations and contained up to 600 particles.

INTERMOLECULAR FORCES

Dispersion forces between sites i and j at distance r apart were modelled with the Lennard–Jones potential:

$$U^{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{5}$$

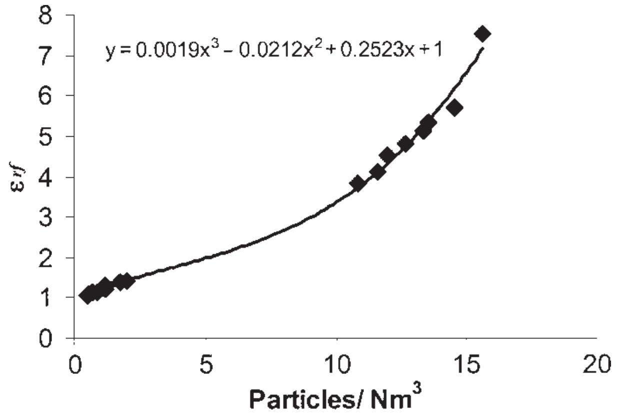


FIGURE 2 Variation of $\varepsilon_{\mathrm{RF}}$ with particle density taken from the calculations of Delhommelle *et al.* [10].

where the usual Lorrenz–Berthelot mixing rules are applied for cross interactions:

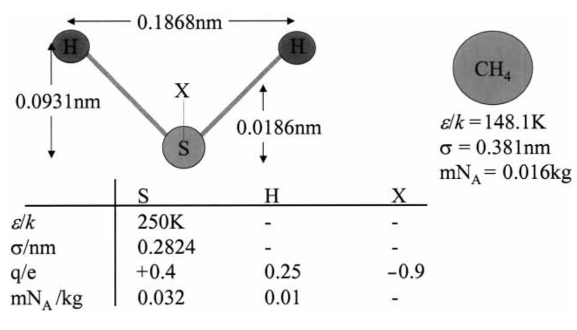
$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{6}$$

The Lennard–Jones interactions were cut off at 1.2 nm, and the standard long range correction applied to the attractive part of the potential [7].

Electrostatic interactions between sites *i* and *j* on hydrogen sulphide were calculated from the usual expression for a Coulombic interaction combined with a reaction field approximation of the long range forces [9]:

$$U^{\mathrm{elec}}(r_{ij}) = \sum_{i>j}\sum \frac{q_i q_j}{4\pi\varepsilon_0}\left[\frac{1}{r_{ij}} + \left(\frac{\varepsilon_{\mathrm{RF}} - 1}{2\varepsilon_{\mathrm{RF}} + 1}\right)\frac{r_{ij}^2}{r_{\mathrm{cut}}^3}\right] \tag{7}$$

where ε_0 is the permittivity of free space, $\varepsilon_{\mathrm{RF}}$ is the relative permittivity of the dielectric medium of the reaction field. The method requires the cavity to be electrically neutral, and so r_{cut} is the cut off radius of the centre of mass. The variation of $\varepsilon_{\mathrm{RF}}$ with particle density was taken from the calculations of Delhommelle *et al.* [10]. After re-plotting the data from Table V, and Figure 1 of Ref. [10] for both vapour and liquid H_2S at various pressures, it is seen that $\varepsilon_{\mathrm{RF}}$ is correlated with particle density (Fig. 2), regardeless of pressure or temperature.



	S	H	X
ε/k	250K	-	-
σ/nm	0.2824	-	-
q/e	+0.4	0.25	−0.9
mN$_A$/kg	0.032	0.01	-

FIGURE 3 Intermolecular potentials for H_2S and CH_4.

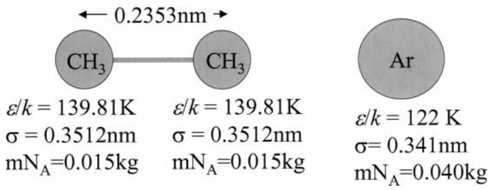


FIGURE 4 Intermolecular potentials for ethane and argon.

The molecular geometries and the Lennard–Jones and Coulombic parameters for the systems studied are shown in Figs. 3 and 4. The origins of the parameters are summarised in Table I.

CENTRIFUGAL SEPARATION OF METHANE AND HYDROGEN SULPHIDE

In this case the normal situation applies in that the heavier component has stronger intermolecular forces than the lighter component. This serves to increase the separation factor over what would be predicted by the ideal gas formulation of Eq. (1).

The results are presented in terms of separation factor versus ideal gas pressure, since this is a more familiar thermodynamic property than rotor radius, *R* and angular velocity *ω*. The ideal gas partial pressure of each component is directly related to these parameters (and to the centre point partial pressures) through Eq. (1). We have chosen 70,000 RPM as a representative angular velocity throughout this study, with values of *R* up to around 0.2 m. The pressure therefore increases monotonically with the distance *R* from the centre point of the centrifuge.

Figure 5 shows results for the condition where there is a centre point mole fraction of hydrogen sulphide of 10%, with a centre point pressure of 1 bar and a constant temperature of 298 K. Unsurprisingly, for low pressures, the simulated separation factor is identical to Eq. (1). At pressures above 20 bar, there is a deviation with condensation (dew pointing) around 34 bar. As a check on the calculation, we looked at the mole fractions of each component as a function of ideal gas pressure to see where dew pointing would be predicted by an equation of state.

TABLE I Origin of potential parameters

Particle	*Potential*	*Reference*
Hydrogen sulphide	Kristof and Liszi	[11]
Methane	Steele	[12]
Ethane	Fischer *et al.*	[13]
Argon	Hirschfelder *et al.*	[14]

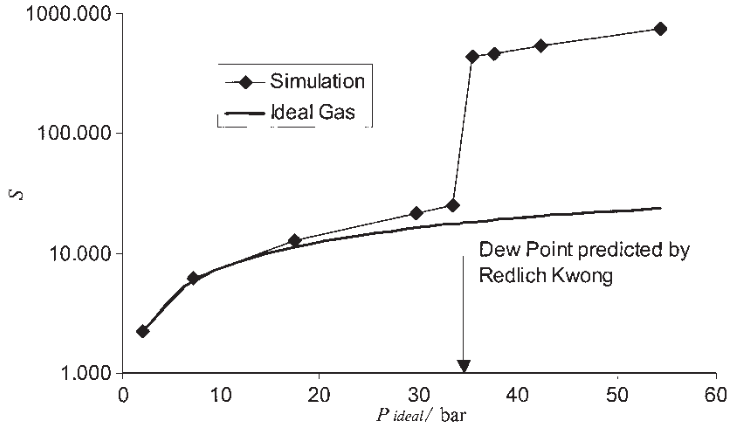


FIGURE 5 Separation factor of H_2S/CH_4 in a centrifuge. $T = 298\,K$, $P_f = 1bar$, $x_f[CH_4] = 0.9$.

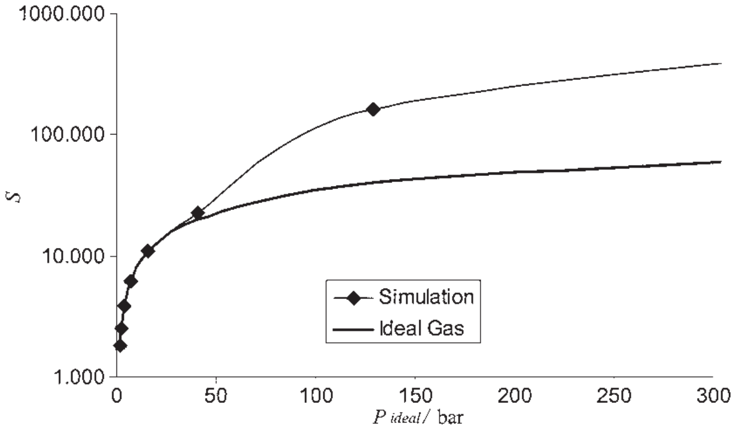


FIGURE 6 Separation factor of H_2S/CH_4 in a centrifuge. $T = 400\,K$, $P_f = 1bar$, $x_f[CH_4] = 0.9$.

We found that the simulation pressure at which phase change occurs is in excellent agreement with predictions from a Redlich–Kwong equation of state. This gives confidence in the validity of the technique.

It can be seen that prior to condensation there is a significant discrepancy between the simulated separation factor and the ideal gas prediction of Eq. (1) (bearing in mind that separation factor is plotted on a logarithmic scale). Although the combination of Eq. (1) and an equation of state can provide information about where condensation is expected in this case, it does not provide a good

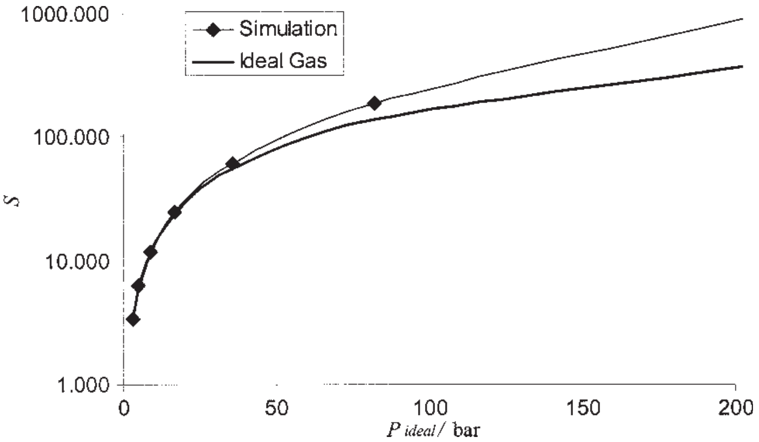


FIGURE 7 Separation factor of H_2S/CH_4 in a centrifuge. $\omega = 70,000\,RPM$, $T = 298\,K$, $P_f = 1bar$, $x_f[CH_4] = 0.9999$.

indication of the separation factor itself—the key information that is required. By contrast, the GCMC technique therefore provides an excellent predictive tool of the separation factors as well as any phase changes that may occur. (It should be noted that once the phase transition has occurred and the liquid is compressed, the actual pressure predicted from the simulation becomes much greater than the ideal gas pressure.)

Figure 6 shows results for a supercritical temperature (400 K), where obviously there is no phase transition, but the separation factor determined from the simulation can differ by an order of magnitude from the ideal gas version of Eq. (1). Figure 7 shows results at 298 K, but with only 100 ppm volume hydrogen sulphide. There is no phase transition but again a significant difference between the separation factors is observed at higher pressures. This behaviour at low concentration of H_2S is important because even this low level of contamination is still well above the safety limit mandated for cleaned gas prior to commercial distribution—1 ppm H_2S.

CENTRIFUGAL SEPARATION OF ARGON AND ETHANE

Although not particularly interesting from a commercial application viewpoint, a mixture such as argon (MW = 40) and ethane (MW = 30) is theoretically interesting, because the heavier component has weaker intermolecular forces than the lighter component. It can be seen in the 4 sets of conditions studied in Fig. 8, that at low pressures, Eq. (1) and the molecular simulation are in good agreement. However, stronger intermolecular forces in ethane cause the separation factor to be less than predicted. Depending on the temperature, the ethane may condense (see Fig. 8a) causing over prediction of the separation by many orders of magnitude.

Comparing Fig. 8a–c, it can be seen that (as would be expected) the higher the temperature, the closer the simulation results are to Eq. (1). When the pressure becomes very high, the simulation results actually predict separation factors higher than Eq. (1). This is because the repulsive part of the intermolecular forces becomes dominant.

Figure 8b and d show the same situation except that Fig. 8d has a higher centre line pressure. Both Eq. (1) and the simulation results are shifted to lower separation factors with the higher centre line pressure. Although of little practical relevance, it can be seen that such a system where the centripetal forces and the intermolecular forces compete for dominance can show a rich thermodynamic behaviour.

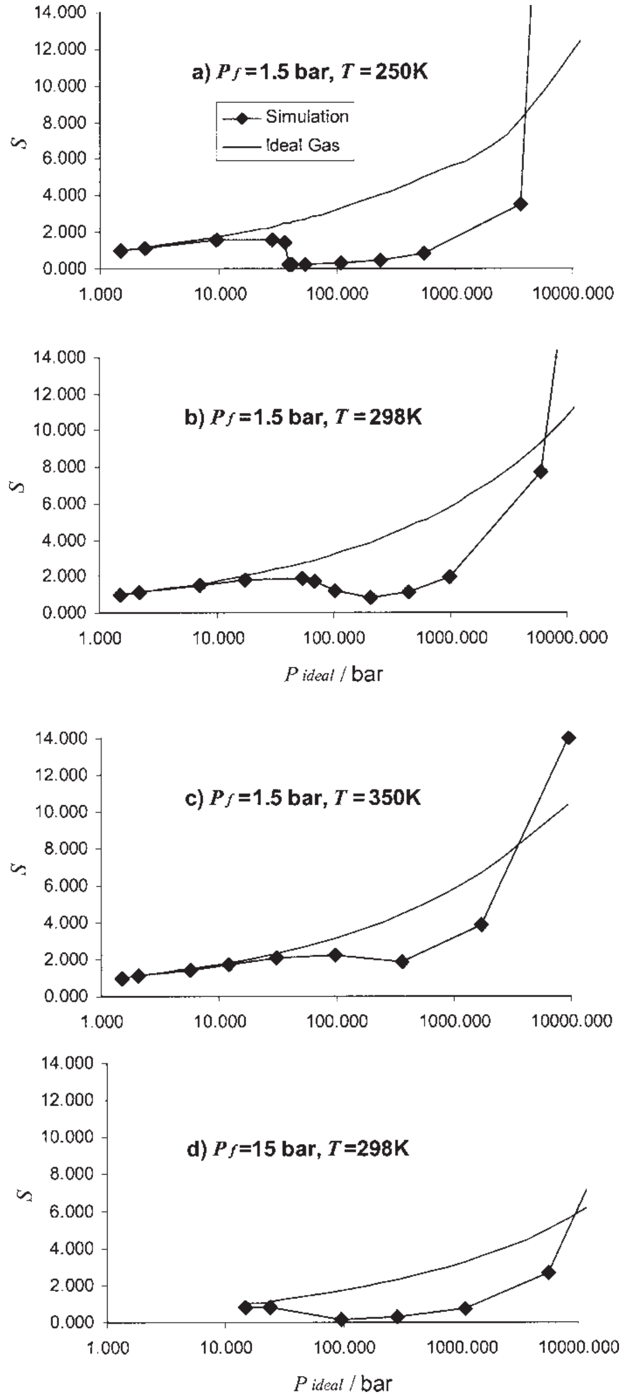


FIGURE 8 Separation factor of argon/ethane in a centrifuge. Equal bulk gas fugacities. If $S > 1$, the higher mass of argon is dominant. If $S < 1$, the stronger intermolecular forces in ethane are dominant.

CONCLUSIONS

We have shown that the technique of GCMC can be used successfully to model the equilibrium thermodynamic behaviour within a gas centrifuge.

The centrifugal separation of hydrogen sulphide from methane is of importance in removing the sulphur from streams of sour natural gas. In this case the typical situation applies in that the heavier component has stronger intermolecular forces than the lighter component and thereby augments the operation of the centrifuge, particularly where condensation (dew pointing) occurs. The GCMC simulation technique is a more effective way of predicting separation factors than the alternative combination of an ideal gas calculation combined with an equation of state to test for dew pointing.

We have also considered the separation of argon and ethane, which is an example of a simple case where the heavier component has weaker intermolecular forces than the lighter component. Our results suggest that such systems can show a rich thermodynamic behaviour.

The technique could easily be applied to gravitational forces on molecules. We wonder therefore whether it could be used to model the atmospheric chemistry and physics of planets with extremely strong gravitational fields.

Acknowledgements

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