

terests were on the electronic spectral studies to interpret the optical and other data.¹² The detailed molecular orbital treatments for square pyramidal oxovanadium(IV) complexes has been suggested that these complexes may have C_{4v} symmetry.¹³⁻¹⁶

As shown in Table 4, the calculated dipole moments for VO(acac)₂ complex in benzene solution, using equation (10), is in agreement with the experimental dipole moments. Small difference between the theoretical dipole moment and the observed value may however be due to the solvent effect on the dipole moments¹⁷ but the experimental value in dioxane solution is slightly higher than that of benzene solution. Table 4 also shows that the calculated dipole moments for adducts of bisacetylacetonato(oxo)vanadium(IV) with dioxane in dioxane solution is in agreement with the observed values. This calculated results may suggest that bisacetylacetonato(oxo)vanadium(IV) interact with oxygen-containing ligand to form adducts and the results of Table 4 may also suggest that this calculation method of the dipole moments for square pyramidal complexes is more superior than other approaches we have adopted in calculating the dipole moments for transition metal complexes as far as the calculation of the dipole moments of square pyramidal complexes is concerned. This work may be applied to calculate the dipole moments for square pyramidal complexes and may predict the geometric structure in inert or aprotic solvent solutions.

Acknowledgement. This work is supported, partly, by the Ministry of Education.

References

1. R.H. Holm and M.J. O'Connor, *Prog. Inorg. Chem.*, **14**, 241 (1977).
2. S. Sorriso, *Chem. Revs.*, **80**, 313 (1980).
3. T.S. Gilman, *J. Am. Chem. Soc.*, **88**, 1861 (1966).
4. C.G. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).
5. T. Ya, Mel'n Kova, Yu. V. Kolodyazhyi, A.K. Prokofier and O.A. Osipov, *Zh. Obs. Khim.*, **46**, 1812 (1976).
6. R.M. Golding and S. Ahn, *Bull. Korean Chem. Soc.*, **2**, 48 (1981).
7. K. Nakatomoto, Y. Morimoto and A.E. Martell, *J. Am. Chem. Soc.*, **83**, 1073 (1961).
8. J. Selbin, R.H. Monning and G. Cessac, *J. Am. Chem. Soc.*, **25**, 4533 (1963).
9. K. Dichmann, G. Hamer, S.C. Nyburg, and W.F. Reynolds, *Chem. Comm.*, 1295 (1970).
10. G. Berthier, *Adv. Quantum Chem.*, **8**, 183 (1974).
11. L. Dedock and H.B. Gray, "Chemical Structure and Bonding," Benjamin, California, 1980.
12. J. Selbin, *Chem. Revs.*, **65**, 105 (1965).
13. J. Selbin and L. Morpurgo, *J. Inorg. Nucl. Chem.*, **27**, 673 (1965).
14. J. Selbin, T.R. Ortoland and F.J. Smith, *Inorg. Chem.*, **2**, 1315 (1963).
15. G. Basu, W. Yeranov and R.L. Belford, *Inorg. Chem.*, **3**, 929 (1964).
16. T.R. Ortoland, J. Smith and S.P. McGlynn, *J. Chem. Phys.*, **41**, 2626 (1964).
17. S. Ahn, D.H. Kim and S.W. Oh, *Bull. Korean Chem. Soc.*, **5**, 3 (1984).

Phase Transition and Approximated Integral Equation for Radial Distribution Function

Byoung Jip Yoon

Department of Chemistry, Kangreung National University, Kangreung 210

Mu Shik Jhon

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Received July 5, 1985

A reduced condition for liquid-gas phase transition from the singularity of compressibility is derived using diagrammatic approach and is examined in the hard sphere system. The condition turns out that the Percus-Yevick and the Hyper-Netted-Chain approximation never conceive the idea of phase transition, and explains that the liquid-gas transition does not exist in hard sphere system. The solid-fluid transition is considered on the viewpoint of correlation function and diagrammatic analysis.

Introduction

Knowledge of the radial distribution function $g(r)$ is the essential prerequisite for a complete static description of homogeneous classical liquids whose molecules are taken to interact through effective two-body forces. The radial distribution function is expressed from the diagrammatic analysis¹ of density expansion with three unknowns, as is given

by

$$g(r) = e^{-\beta u(r)} \{1 + N(r)\} + e^{-\beta u(r)} Z(r) \quad (1-a)$$

$$Z(r) = e^{N(r) + E(r)} - \{1 + N(r)\} \quad (1-b)$$

where $N(r)$ is analyzed from the nodal group of which elements have at least one nodal point, $E(r)$ is from the cross-bridged group which has no nodal point, β is $1/kT$ and $u(r)$ is the pair potential. These functions also satisfy following equations

$$h(r) = N(r) + c(r) \quad (2-a)$$

$$h(r) = c(r) + \rho \int d\vec{r}' h(|\vec{r} - \vec{r}'|) c(r') \quad (2-b)$$

Eq.(2-b) is the Ornstein-Zernike(O-Z) equation² defining the direct correlation function $c(r)$ in terms of $h(r) = g(r) - 1$. Naturally from Eq.(2), the nodal group becomes a space-evolved indirect part of O-Z equation. It is helpful to rearrange the direct correlation function as follows,

$$c(r) = f(r) \{1 + N(r)\} + e^{-\beta u(r)} Z(r) \quad (3)$$

where $f(r)$ is the Mayer function i.e., $f(r) = e^{-\beta u(r)} - 1$. It is easily seen, in this arrangement, that the PY equation³⁻⁴ neglects all $Z(r)$, and the Hyper-Netted-Chain (HNC)⁵⁻⁶ equation does $E(r)$ only. Therefore,

$$Z_{PY}(r) = 0 \quad (4-a)$$

$$Z_{HNC}(r) = e^{-\beta u(r)} - \{1 + N(r)\} \quad (4-b)$$

The PY approximation generates the nodal group, $N(r)$, only which is solved analytically in case of hard-sphere potential. It is of interest, in case of the PY approximation, that the same term is neglected from both of exact $g(r)$ and $c(r)$. From this stand point, Croxton⁷⁻⁸ has proposed an extension of the PY theory which, he claimed, provides a theory of the solid-fluid transition for hard sphere system. He proposed, so called, "watermelon" integrals which are a particular choice of the diagrams of E group, but the adequate choice is difficult considering the cancellation of each other groups and the coefficients are not correct.⁹ However it is indicative. The approach might be worth pursuing and refining. It is shown, in this paper, that a reduced condition for liquid-gas phase transition is derived and that the PY or HNC approximations do not provide the phase transition theory. The solid-fluid phase transition is discussed in terms of correlation function and diagrammatic approach.

Theory

Condition of Liquid-Gas Phase Transition

Croxton⁸ thought that the analytical solution of exact $c(r)$ of hard core($r < \sigma$) is the solution of $c(r)$ of PY equation because of no contribution of the second term in Eq.(3) due to $e^{-\beta u(r)}$ factor, whether $Z(r)$ has any value in the region. This is incorrect, because PY equation-generated $N(r)$ is all the N group to the second power of density expansion, however, not all the N group of higher order than the second, i.e., because such terms of $N(r)$ are neglected in the PY equation,

$$\rho^2 \left(\text{diagram 1} + \text{diagram 2} + \text{diagram 3} + \text{diagram 4} \right) + \rho^4 (\dots) + \dots \quad (5)$$

that one part of nodal point is the term that is neglected in the PY approximation. Thus Eqs.(1-a) and (3) can be expressed as follows,

$$g(r) = e^{-\beta u(r)} \{1 + N_{PY}(r)\} + e^{-\beta u(r)} N'(r) + e^{-\beta u(r)} Z(r) \quad (6)$$

and

$$c(r) = f(r) \{1 + N_{PY}(r)\} + f(r) N'(r) + e^{-\beta u(r)} Z(r) \quad (7)$$

where $N'(r)$ is $N_{all}(r) - N_{PY}(r)$ and $N_{PY}(r)$ is the nodal group of solution of the PY equation and is neglected such terms in Eq.(5) (see the diagrams in ref.1). The second term of Eq.(7) shows clearly that the exact $c(r)$ is different from the PY $c(r)$ by the factor of $N'(r)$ for $r < \sigma$, even though the third term is

zero at $r < \sigma$.

Some thermodynamic properties have singular values at the phase transition. The compressibility is expressed in terms of direct correlation function as is given by

$$\beta \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{1}{1 - \rho \bar{c}(0)} \quad (8)$$

where $\bar{c}(0)$ is the Fourier transform of $c(r)$ when $k=0$ in the following equation,

$$\bar{c}(k) = \frac{4\pi}{k} \int_0^\infty r^2 c(r) \sin(kr) dr \quad (9)$$

And the O-Z equation in this form is

$$\bar{h}(k) = \bar{c}(k) + \rho \bar{c}(k) \bar{h}(k) \quad (10)$$

and thus

$$\bar{N}(k) = \rho \bar{c}(k) \bar{h}(k) \quad (11)$$

Thus the Fourier transform of N' is equal to

$$\bar{N}' = \rho \{ \bar{c}_{PY} + (f\bar{N}') + \bar{d} \} \bar{h}_{PY} + (e^{-\beta u(r)} N') + \bar{d} - \rho \bar{c}_{PY} \bar{h}_{PY} \quad (12)$$

where (k) is omitted for simplicity and \bar{d} is the Fourier transform of $e^{-\beta u(r)} Z(r)$. Here, the integration is separated into two terms for any function $A(r)$,

$$\bar{A}(k) = \bar{A}_0(k) + \bar{A}_1(k) \\ = \frac{4\pi}{k} \int_0^\sigma r^2 A(r) \sin(kr) dr + \frac{4\pi}{k} \int_\sigma^\infty r^2 A(r) \sin(kr) dr \quad (13)$$

where the subscript 0 denotes the first part and 1 denotes the second. Eq.(12) is then given by

$$\bar{N}'_0 + \bar{N}'_1 = \rho \{ \bar{c}_{PY} (\bar{N}'_1 + \bar{d}) - \bar{N}'_0 (\bar{h}_{PY} + \bar{N}'_1 + \bar{d}) + \bar{d} (\bar{h}_{PY} + \bar{N}'_1 + \bar{d}) \} \quad (14)$$

or

$$\bar{N}'_0 = \frac{\rho \{ \bar{c}_{PY} (\bar{N}'_1 + \bar{d}) + \bar{d} (\bar{h}_{PY} + \bar{N}'_1 + \bar{d}) \} - \bar{N}'_1}{1 + \rho (\bar{h}_{PY} + \bar{N}'_1 + \bar{d})} \quad (15)$$

And

$$c(r) = c_{PY}(r) + f(r) N'(r) + d(r) \quad (16)$$

thus the Fourier transform of $c(r)$ is given by,

$$\bar{c} = \bar{c}_{PY} - \bar{N}'_0 + \bar{d} \quad (17)$$

Substituting \bar{N}'_0 in Eq.(15) to Eq.(17).

$$\bar{c} = \bar{c}_{PY} - \frac{\rho \{ \bar{c}_{PY} (\bar{N}'_1 + \bar{d}) + \bar{d} (\bar{h}_{PY} + \bar{N}'_1 + \bar{d}) \} - \bar{N}'_1}{1 + \rho (\bar{h}_{PY} + \bar{N}'_1 + \bar{d})} + \bar{d} \quad (18)$$

which yields that

$$\bar{c} \{ 1 + \rho (\bar{h}_{PY} + \bar{N}'_1 + \bar{d}) \} = \bar{c}_{PY} + \rho \bar{c}_{PY} + \bar{d} + \bar{N}'_1 \quad (19)$$

The condition of liquid-gas phase transition is $\bar{c}(0) = \frac{1}{\rho}$

in Eq.(8), and therefore

$$\frac{1}{\rho} \{ 1 + \rho (\bar{h}_{PY}(0) + \bar{N}'_1(0) + \bar{d}(0)) \} = \bar{h}_{PY}(0) + \bar{d}(0) - \bar{N}'_1(0) \quad (20)$$

where the O-Z equation is used to cancel $\bar{c}_{PY}(0)$. After cancelling $\bar{h}_{PY}(0)$ and $\bar{d}(0)$ of both sides, it is obtained that

$$\bar{N}'_1(0) = -\frac{1}{2\rho} \quad (21)$$

i.e., the phase transition condition becomes

Table 1. The numerical representation of individual groups

| r $\rho=0.6$ | $h(r)$ | $N(r)$ | $h_{PY}=N_{PY}$ | $E(r)$ | $\frac{1}{2} \int_{\sigma}^{\infty} \frac{dZ}{dr}$ |
|--------------------|--------|--------|-----------------|--------|--|
| 1.00 | 1.613 | 1.362 | 1.460 | -.402 | -.250 |
| 1.05 | 1.259 | 1.088 | 1.186 | -.273 | -.213 |
| 1.10 | .956 | .859 | .942 | -.188 | -.178 |
| 1.15 | .707 | .657 | .726 | -.122 | -.147 |
| 1.20 | .505 | .480 | .538 | -.072 | -.121 |
| 1.25 | .342 | .327 | .377 | -.032 | -.102 |
| <hr/> | | | | | |
| r $\rho=0.08$ | $h(r)$ | $N(r)$ | $h_{PY}=N_{PY}$ | $E(r)$ | $\frac{1}{2} \int_{\sigma}^{\infty} \frac{dZ}{dr}$ |
| 1.00 | 3.026 | 2.306 | 2.581 | -.913 | -.544 |
| 1.05 | 2.056 | 1.706 | 1.947 | -.588 | -.409 |
| 1.10 | 1.337 | 1.186 | 1.407 | -.337 | -.318 |
| 1.15 | .839 | .784 | .957 | -.174 | -.259 |
| 1.20 | .493 | .456 | .592 | -.055 | -.215 |
| 1.25 | .243 | .193 | .304 | .025 | -.175 |
| 1.30 | .056 | -.001 | .082 | .004 | -.135 |
| 1.35 | -.083 | -.157 | -.080 | .007 | -.102 |
| 1.40 | -.182 | -.252 | -.193 | .005 | -.078 |
| 1.45 | -.248 | -.308 | -.265 | .002 | -.061 |

$$4\pi \int_{\sigma}^{\infty} r^2 N'(r) dr = -\frac{1}{2\rho} \quad (22)$$

The $N'(r)$ shown in Eq.(22) is the difference of the nodal group that is generated by PY approximation from the total $N(r)$ of exact RDF(see Eq.(5) for example). With this reduced condition, the function in which r is less than hard core diameter is no longer needed. This lessens the troublesome of thinking the physical meaning of direct correlation function in the region of $r < \sigma$.

This condition provides following arguments; (1) The PY approximation does not predict the phase transition because the reduced condition is found in their neglected groups nor the HNC approximation as well since the HNC equation also neglects some of $N'(r)$. (2) There is no liquid-gas phase transition for hard sphere system. The reasons are; the liquid-gas phase transition occurs at low density, and thus the right hand side of Eq.(22) is much large, however, the left hand side cannot have the large values, because the lowest power of $N'(r)$ is ρ^3 . It is known that the structure factors of dense liquid can be interpreted with a hard sphere model.¹⁰ But the simulation of hard sphere system is like the liquid state of high temperature over the critical point, namely, the fluid state (even though the hard sphere potential is temperature independent), or the liquid-gas equilibrium line is not exist in the phase diagram in case of hard sphere system.

Contribution of Individual Groups and Phase Transition

Of the two typical computer simulation (molecular dynamics(MD) and Monte Carlo(MC)) methods, the MC results¹¹ of hard sphere system are not valid since the value of $h(r)$ is lower than $h_{PY}(r)$, in case of $r = \sigma$. The exact $h(\sigma)$ must be larger than $h_{PY}(\sigma)$ because the neglected term $Z(\sigma)$ is always positive at the density less than unity, while the MD results satisfy this condition and the MD technique has been considered as an exact method.

Verlet and Weis¹² have proposed the correct RDF of hard sphere by adding the self-consistent empirical term to PY

result, and the computer program is available.¹³ They claimed that the RDF obtained in their way differs from the "exact" one (MD result) by at most 0.03. Henderson *et al.*¹⁴ obtained the exact direct correlation function with the Verlet and Weis' $h(r)$ and O-Z equation in Eq.(2) and suggested the empirical equation. The direct correlation function of $r < \sigma$ is the $Z(r)$ itself for hard sphere potential. The contributions of separated groups, *i.e.*, the two unknowns in Eq.(1) can be calculated from the $h(r)$ if the exact one is known. Table 1 shows what the values are like. An exact $h(r)$ is obtained using the program of ref.13, $N(r)$ is by solving Eq.(2) and then $E(r)$ is from Eq.(1). $h_{PY}(r)$ is the solution of the PY equation. There are several methods¹⁵ for the calculations by solving Eq.(2). $N'(r)$, the subtraction of the fourth column from the third in Table 1, is negative interestingly and it is speculated that the negative sign in Eq.(22) is from this fact. The last column is the lowest term of density expansion of E group and is calculated by integrating directly for the comparison to $E(r)$.

The characteristics of the two phase-transition (solid-liquid and liquid-gas) are different in their original natures. The solid-liquid (or more generally solid-fluid) transition is a matter of packing. In a solid phase, the particles are not free in their movements. The E group is important to complete the bridges between third particles, while N and $e^{N_{PY}}$ without considering E group have no confinement between the third particles whether they are overlapped or not. Another example of the phase transition is the sudden lowering of pressure with increasing density. In hard sphere system, the pressure is determined by the height of $h(\sigma)$. At the transition region, from fluid to solid, $h(\sigma)$ has to decrease rapidly. The neglected $Z(\sigma)$ has always a positive value and increases with density increase. But any of typical graphs do not conceive the idea of phase transition, because no diagram shows discontinuous behaviors at phase transition but all the diagrams are expected to be continuous, and thus the phase transition is a many body problem as is indicated in the Lee-Yang theory.¹⁶

The liquid-gas phase transition is different from that of solid-fluid, because Eq.(22) shows no expectation even though we calculate all of the diagrams with hard sphere potential. Thus it is natural to say that the liquid-gas phase transition occurs due to the attractive interactions. However, the repulsive forces dominate the quantitative behavior of the liquid structure factor.¹⁷

The direct correlation function of low density limit is the Mayer function itself. As a simplest form of attraction, we can see, in case of a square well potential, that the phase transition condition in Eq.(22) should be satisfy the following equa-

$$-\beta \epsilon = \ln \left\{ \left(\frac{3}{4\pi\rho} + 1 \right) / (a^3 - 1) \right\} \quad (23)$$

tion, in which the direct correlation function is approximated to the Mayer function in which ϵ and a are the respective depth and width of the potential. Thus the liquid state in equilibrium with the gaseous state has non-negligible attractive interactions to condense even at low density while the properties of liquid state have been simulated with repulsive forces only.

Conclusion

The diagrammatic approach shows the definite contributions of the approximated integral equations for RDF. It also turns out that the approximations known so far have no behaviors of phase transitions and that the liquid-gas phase

transition is a matter of attractive forces, while the liquid properties are dominantly affected by repulsive forces. The hard sphere system without attractive forces never distinguishes its liquid and gas states. It is worth pursuing to formulate an approximation of integral equation which provides a satisfactory phase transition by selecting some of nodal group and/or E group.

References

1. See for example, R. Balescu, "Equilibrium and Nonequilibrium Statistical Mechanics," (John Wiley and Sons, New York), 1975. T. Boublik, I. Nezbeda, and K. Hlavaty, "Statistical Thermodynamics of Simple Liquids and Their Mixtures," Elsevier, Sci. Publ. Co., New York, 1980.
2. L.S. Ornstein and F. Zernike, *Proc. Akad. Sci. Amsterdam*, **17**, 793 (1914).
3. J.K. Percus and H.J. Yevick, *Phys. Rev.* **110**, 1 (1958).
4. J.K. Percus, *Phys. Rev. Lett.* **8**, 462 (1962).
5. J.M.J. van Leeuwen, J. Groenvelde, and J. de Boer, *Physics* **25**, 792 (1959).
6. T. Morita and K. Hiroike, *Progr. Theoret. Phys.* (Kyoto) **23**, 1003 (1960); **25**, 537 (1961).
7. C.A. Croxton, "Introduction to Liquid State Physics", John Wiley and Sons, New York, p. 97, 1975.
8. C.A. Croxton, *J. Phys. C.* **7**, 3723 (1974).
9. J.A. Barker and D. Henderson, *Rev. Modern Phys.* **48**, 587 (1976).
10. N.W. Aschroft and J. Lekner, *Phys. Rev.* **145**, 83 (1966).
11. See for example, B.J. Alder, S.P. Frenkel and V.A. Lewinson, *J. Chem. Phys.* **23**, 417 (1955).
12. L. Verlet and J.-J. Weis, *Phys. Rev.* **A5**, 939 (1972).
13. D.A. McQuarrie, "Statistical Mechanics," 2nd Ed. (Happer and Row, New York) Appendix D, 1976.
14. D. Henderson and E.W. Grundke, *J. Chem. Phys.* **63**, 601 (1975).
15. See for example, A.A. Broyles, *J. Chem. Phys.* **35**, 493 (1961), R.J. Baxterr, *Australian J. Phys.* **21**, 563 (1968), and F. Mandel, R.J. Bearman and M.Y. Bearman, *J. Chem. Phys.* **52**, 3315 (1970).
16. K. Huang, "Statistical Mechanics," Wiley, New York, Chap. 15 (1963).
17. J.D. Weeks, D. Chandler, and H.C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).

Synthesis of Nucleophilic Adducts of Thiols (VII). Addition of Thioglycolic Acid to α -Cyano- β -phenylacrylic Acid Derivatives

Tae-Sung Huh* and Hee-Jong Lee

Department of Chemistry Song Sim College for Women, Bucheon 150-71

In-Sup Han

Department of Chemistry, Kangweon National University, Chuncheon 200

Tae-Rin Kim

Department of Chemistry, Korea University, Seoul 151, Received July 5, 1985

Reaction of α -cyano- β -phenylacrylic acid derivatives (I) with thioglycolic acid in the molar ratio of 1:2 in saturated sodium bicarbonate solution yielded 3-(4'-oxo-2'-thiazolin-2'-yl)-2-phenyl-4-oxotetrahydrothiophene derivatives (V). Thioglycolic acid was found to be added not only to carbon-carbon double bond but also to carbon-nitrogen triple bond and those adducts were cyclized to V.

Introduction

As a part of continuous investigation on the syntheses of thiol derivatives by nucleophilic addition, the reactions of thiol with β -nitrostyrene^{1,2} and ω,ω -diacetylstyrene³ have been reported recently. Much information has been appeared in the literature concerning the anticancer and antimicrobial activities of these thiol adducts.⁴⁻⁷

Elnagdi, *et al.*,⁸ prepared 3,3-dicyano-2-phenyl-4-oxotetrahydrothiophene and 2-(4-oxo-2-thiazolin-2-yl) cinnamionitrile by the addition of thioglycolic acid to benzyliden-malononitrile in refluxing pyridine. This paper presents our study of the addition of thioglycolic acid to α -cyano- β -

phenylacrylic acid derivatives.

Results and Discussion

When α -cyano- β -phenylacrylic acid (Ia) was treated with thioglycolic acid in the molar ratio of 1:2 in saturated sodium bicarbonate solution, a product of molecular formula $C_{11}H_{11}NS_2O_2$ was formed. The IR spectrum of the product revealed absorption band at 1780 cm^{-1} , which is attributable for C=O group in cyclic ketone. The mass spectrum shows the molecular ion of m/e 277. Intensity ratio of $M+2$ peak vs. M^+ peak is 11.43% : 100%, which represents the presence of two sulfur atoms (calculated for $C_{11}H_{11}NS_2O_2$: 10.25%).