

An Application of the Linear Isotherm Regularity (LIR)

Jianxiang Tian^{*,†,‡} and Yuanxing Gui[‡]

Department of Physics, Qufu Normal University, Qufu 273165, P. R. China, and Department of Physics, Dalian University of Technology, Dalian 116024, P. R. China

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The linear isotherm regularity (LIR) for dense fluids is used to derive another regularity which is the isotherm $[(\partial E/\partial v)_T/\rho RT]v^2$ as a linear function of ρ^2 , where E is the molar internal energy, $(\partial E/\partial v)_T$ is the internal pressure, and ρ is the molar density (inverse of the molar volume v). The analytical expressions for the parameters of the latter regularity are obtained in terms of LIR parameters and reported for argon.

Introduction

Liquids, dense fluids, and supercritical fluids are usually considered to be complicated on a molecular scale and difficult to predict their properties by thermodynamic method and statistical mechanics method due to the complex interactions between molecules. However, they experimentally show a number of simple regularities. To our knowledge, there are nine regularities. The first is the Tait–Murnaghan relation, known for over 100 years, in which the bulk modulus (reciprocal compressibility) of a liquid (or solid) is linear with pressure.¹ The second regularity is the linear relation between temperature and density at unit compression factor ($Z = Pv/RT \equiv 1$) which was discovered in 1906, then forgotten and rediscovered several times, and recently named the “Zeno line”.² The third one was reported in the behavior of the reduced bulk modulus, $B_r = (1/RT)(\partial P/\partial \rho)_T$ for liquids. Huang and his co-worker³ found that B_r vs molar volume isotherms intersect at a common point, called the common bulk modulus point. They checked the experimental existence of this point for more than 250 different liquids. The fourth is the regularity of that compression factor vs the molar density isotherms of a fluid intersect at a common point, called the “common compression point”.⁴ The fifth regularity was observed experimentally to be near the linearity of P vs T at constant density (isochors) over the entire range from the perfect gas to the dense fluid.^{5–6} The sixth regularity is again the behavior of the reduced bulk modulus, which is stated as $(B_r - 1)v^2$ and is linear in ρ^2 for all isotherms of dense fluids.⁷ The seventh regularity is that $(Z - 1)v^2$ is linear in ρ^2 for isotherms of dense fluids,⁸ called the linear isotherm regularity (LIR). The eighth regularity is that isotherm $[(\partial E/\partial v)_T/\rho RT]v^2$ is a linear function of ρ^2 . It was recently derived to be valid for both compressed liquids and dense supercritical fluids.⁹ The ninth regularity was observed for many substances (including water, methane, and *n*-butane) and stated as isotherms in an α (coefficient of thermal expansion) vs P diagram, over a large temperature range, passing through a common intersection point.^{10–12}

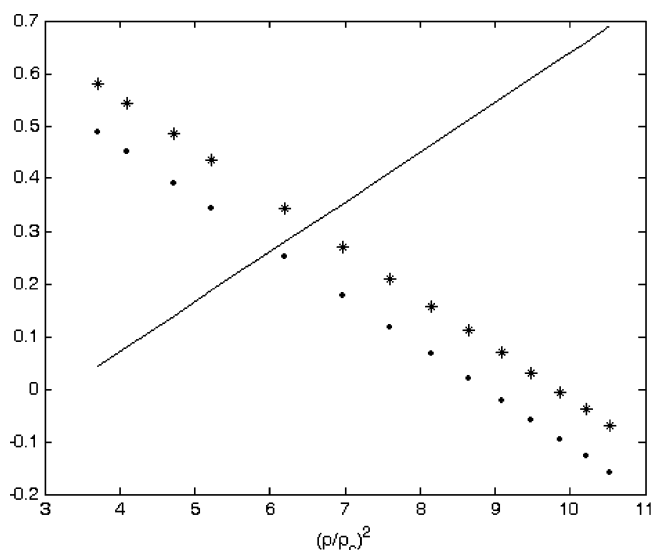


Figure 1. Two regularities for argon: straight line, typical isotherm of $(Z - 1)(\rho/\rho_c)^2$ vs $(\rho/\rho_c)^2$ at $T = 200$ K; dotted line, typical isotherm of $[(\partial E/\partial v)_T/(\rho RT)](\rho/\rho_c)^2$ vs $(\rho/\rho_c)^2$ at $T = 200$ K, derived by LIR; star line, typical isotherm of $[(\partial E/\partial v)_T/(\rho RT)](\rho/\rho_c)^2$ vs $(\rho/\rho_c)^2$ at $T = 200$ K, reported in ref 9 and calculated with the speed of sound.

The regularities from the first to the sixth have been derived from the LIR.⁷ The purpose of this paper is to derive the eighth regularity using the LIR. The LIR has been tested to be valid for 13 fluids, including nonpolar, polar, hydrogen-bonded, and quantum fluids.⁸ It holds experimentally for densities greater than the Boyle density and for temperatures below about twice the Boyle temperature. The upper density limit is less certain but seems to be the freezing line of compressed liquids and at least about twice the Boyle density for supercritical fluids. Additionally, the LIR has been found to be valid for binary mixtures as well¹³ and used to predict the gradual transition from metallic to nonmetallic successfully.¹⁴ In the following section, we will derive the eighth regularity using the LIR. The parameters of these two regularities are calculated experimentally for argon, and their relations are expressed.

* To whom correspondence should be addressed. E-mail: jianxiangtian@yahoo.com.cn. Tel.: 0086-411-84706203.

[†] Qufu Normal University.

[‡] Dalian University of Technology.

TABLE 1: Intercept A and Slope B of Equation of State $(Z - 1)(\rho_c/\rho)^2 = A + B(\rho/\rho_c)^2$; A_1 in eq 2; Intercept A_3 and Slope B_3 of Equation of State $[(\partial E/\partial v)_T/(\rho RT)](\rho_c/\rho)^2 = A_3 + B_3(\rho/\rho_c)^2$, Derived by LIR; the Pressure Range (ΔP) of the Data^a

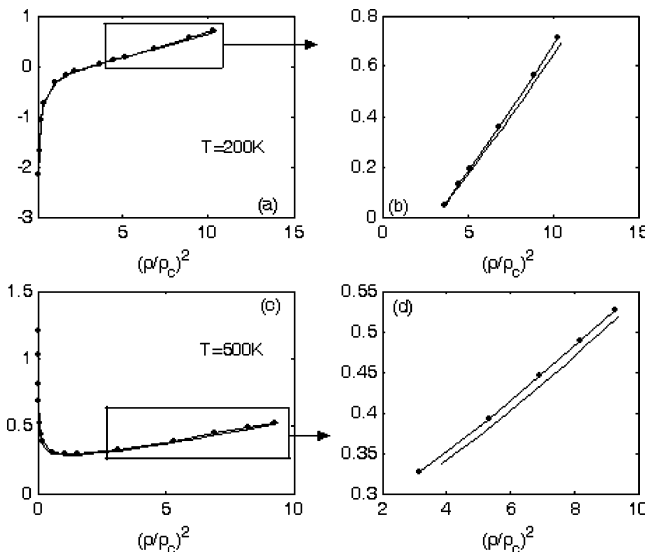
T/K	A	$-B$	$A_1\rho_c^2/RT$	A_3	B_3	A_3^b	B_3^b	$\Delta P/\text{MPa}$
200	-0.308 0	-0.09 48	0.8390	0.8390	-0.0948	0.9 34 3	-0.09 53	50–60 0
300	-0.012 2	-0.06 27	0.5593	0.5593	-0.0627	0.5 76 3	-0.06 89	100–1 000
400	0.1269	-0.04 48	0.4195	0.4195	-0.0448	0.3 86 6	-0.05 36	200–1 000
500	0.2052	-0.03 31	0.3356	0.3356	-0.0331	0.2 81 4	-0.04 47	250–1 000
600	0.2538	-0.02 49	0.2797	0.2797	-0.0249	0.2 14 5	-0.03 86	300–1 000
700	0.2910	-0.01 81	0.2397	0.2397	-0.0181	0.1 70 9	-0.03 45	300–1 000

^a All of the above data for argon (see ref 15). ^b Intercept A_3 and slope B_3 obtained by the evaluation of the thermal pressure using the speed of sound.⁹

TABLE 2: Ranges Where LIR and the Eighth Regularity Hold^a

T/K	T/T_B	$\Delta P/\text{KPa}$	$\Delta(\rho/\rho_B)$	$\Delta(\rho/\rho_c)$	R^2
200	0.4897	150–600	0.9021–1.8033	1.6238–3.2460	0.9999
300	0.7345	60–1000	0.8029–1.8687	1.4453–3.3637	0.9999
400	0.9793	60–1000	0.6084–1.7803	1.0952–3.2045	0.9999
500	1.2241	150–1000	0.8684–1.7046	1.5631–3.0683	0.9999
600	1.4690	350–1000	1.1499–1.6379	2.0698–2.9482	0.9999
700	1.7138	450–1000	1.1917–1.5778	2.1450–2.8400	0.9999
800	1.9586	550–1000	1.2244–1.5229	2.2038–2.7412	0.9999
900	2.2035	700–1000	1.2889–1.4722	2.3200–2.6500	0.9999
1000	2.4483	800–1000	1.3079–1.4251	2.3543–2.5652	0.9999

^a Data for argon (see ref 15).

**Figure 2.** LIR $(Z - 1)(\rho_c/\rho)^2$ vs $(\rho/\rho_c)^2$ for argon: solid line, ref 15; (\bullet - \bullet), ref 16.

Theory

The LIR is written in its original form as⁸

$$(Z - 1)v^2 = A + B\rho^2 \quad (1a)$$

or

$$(Z - 1)/\rho^2 = A + B\rho^2 \quad (1b)$$

Through the use of a simple model, the temperature dependence of A and B parameters are obtained as

$$A = A_2 - A_1/(RT) \quad (2)$$

and

$$B = B_1/(RT) \quad (3)$$

where the constants A_1 and B_1 are related to the intermolecular attraction and repulsion, respectively, and the constant A_2 is related to the nonideal contribution of thermal pressure.

If we substitute $P/(\rho RT)$ for Z , then eq 1b may be written as

$$P = RT\rho + ART\rho^3 + BRT\rho^5 \quad (4)$$

By the use of the definition of internal pressure

$$\left(\frac{\partial E}{\partial v}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] = \left[T\left(\frac{\partial P}{\partial T}\right)_\rho - P\right] \quad (5)$$

and combining eqs 4 and 5, we obtain

$$(\partial E/\partial v)_T = A'RT^2\rho^3 + B'RT^2\rho^5 \quad (6)$$

with

$$A' = dA/dT \quad (7)$$

$$B' = dB/dT \quad (8)$$

Now the eighth regularity is derived as

$$(\partial E/\partial v)_T/(\rho^3 RT) = A_3 + B_3\rho^2 \quad (9a)$$

or in its original form as⁹

$$[(\partial E/\partial v)_T/(\rho RT)]v^2 = A_3 + B_3\rho^2 \quad (9b)$$

with $A_3 = A'T$ and $B_3 = B'T$. Using eqs 2 and 3, we obtain

$$A_3 = A_1/(RT) \quad (10)$$

$$B_3 = -B_1/(RT) = -B \quad (11)$$

Now, we see the parameters of the LIR are related to the parameters of the eighth regularity. All of these parameters for argon are calculated experimentally and summarized in Table 1. These two regularities are shown in Figure 1.

Discussions and Conclusions

In this paper, we derived the regularity of the isotherm $[(\partial E/\partial v)_T/(\rho RT)]v^2$ (or written as $[(\partial E/\partial v)_T/(\rho RT)]/\rho^2$) as a linear function of ρ^2 using LIR and give the relations of their parameters. The two regularities are checked for argon.

The regularity of the isotherm $[(\partial E/\partial v)_T/(\rho RT)]v^2$ as a linear function of ρ^2 has been derived for dense fluids based on the Lennard-Jones potential function and using speed of sound results given in ref 9. There, the speed of sound was used to calculate the thermal pressure $T(\partial P/\partial T)_\rho$. The calculated and experimental values of thermal pressure are found to present a close agreement with each other. Then, the internal pressure can be calculated easily by eq 5. In this paper, this regularity is derived by LIR. The difference between these two methods is

shown in Figure 1 (the dotted line and the star line) and Table 1. Although the two methods derive the same regularity for dense fluids, the intercept and slope they predict at the same temperature are different. At $T = 300$ K, a tiny difference of $|0.5593 - 0.5763|$ of intercept A_3 and difference of $|0.0627 - 0.0689|$ of slope B_3 are shown. The difference increases with temperature up to $T = 700$ K along with the relative error. Figure 1 tells us that the internal pressure $(\partial E/\partial v)_T$ derived by LIR is smaller than the one obtained by the use of speed of sound at constant density in isotherm $T = 200$ K. But for constant density in isotherm $T \in [300 \text{ K}, 700 \text{ K}]$, the contrary case appears. This comparison can also be obtained easily through Table 2.

LIR has been found to be valid experimentally for densities greater than the Boyle density and for temperatures below about twice the Boyle temperature. The upper density limit is less certain but seems to be the freezing line of compressed liquids and at least about twice the Boyle density for supercritical fluids.⁸ In our work, we find the LIR holds in a larger temperature range and density range. The valid ranges where LIR holds in different isotherms are summarized in Table 2. In Table 2, the coefficient of determination R^2 , which is simply the square of the correlation coefficient, is shown up to 0.9999 in the pressure range we select wittingly. We found that the LIR also holds experimentally for densities less than the Boyle density when $T = 200\text{--}400$ K. For example, Figure 2 shows that the LIR holds well at $T = 200$ K and $T/T_B = 0.4897$ in this case. In Table 2, $\rho/\rho_c \approx 1.8$ experimentally⁸ and $T_B/T_C = 2.711$ experimentally,¹⁷ for argon, are used.

It is known that many physical and chemical properties such as the nine regularities here depend strongly on the interaction energy among particles. Normally, the pairwise interaction potential only changes with separation. But the attempt to explain the ninth regularity denotes that the interaction potential should have a term depending on pressure (or volume).¹¹ The work of the prediction of the temperature and density dependencies of the parameters of the average effective pair potential using LIR EOS has found experimentally that the parameter σ , the separation at which the potential is zero, increases with temperature while the depth of the potential well, ϵ , decreases with temperature.¹⁸ We do think a more deep explanation at

the molecular level for regularities of fluids is an interesting and meaningful work in the future. The fact that all the regularities (excluding the ninth until now) are related to LIR similarly implies a simple and unequivocal explanation. The work is in process.

The LIR has been extended to dense mixtures successfully.¹⁹ In the future, we would like to know whether the eighth regularity behaves its extension for dense mixtures or not and whether it is possible to derive the ninth regularity by LIR or not. These are our current works.

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Supporting Information Available: Experimental data for argon. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Macdonald, J. R. *Rev. Mod. Phys.* **1969**, *40*, 316.
- (2) Xu, J.; Herschbach, D. R. *J. Phys. Chem.* **1992**, *96*, 2307.
- (3) Huang, Y.-H.; O'Connell, J. P. *Fluid Phase Equilib.* **1987**, *37*, 75.
- (4) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*, 2nd printing; Wiley: New York, 1964; pp 296–8.
- (5) Deiters, U. K. *Chem. Eng. Sci.* **1981**, *36*, 1139.
- (6) Song, Y.; Mason, E. A. *J. Chem. Phys.* **1989**, *91*, 7840.
- (7) Najafi, B.; Parsafar, G.; Alavi, S. *J. Phys. Chem.* **1995**, *99*, 9248.
- (8) Parsafar, G. A.; Mason, E. A. *J. Phys. Chem.* **1993**, *97*, 9048.
- (9) Moeini, V. *J. Phys. Chem.* **2006**, *110*, 3271.
- (10) Leon, T. M.; Philippe, P.; Alain, S. *J. Chem. Phys.* **1981**, *75*, 3064.
- (11) Randzio, S. L. *Phys. Lett. A* **1986**, *117*, 473.
- (12) Deiters, U. K.; De Reuck, K. M. *Pure Appl. Chem.* **1997**, *69*, 1237.
- (13) Farzi, N.; Parsafar, G. A. *J. Phys. Chem. B* **1997**, *101*, 8578.
- (14) Keshavarzi, E.; Parsafar, G. A. *J. Phys. Chem. B* **1999**, *103*, 6584.
- (15) Stewart, R. B.; Jacobsen, R. T. *J. Phys. Chem. Ref. Data* **1989**, *18*, 639.
- (16) Tegeler, Ch.; Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1999**, *28*, 779.
- (17) Ihm, G.; Song, Y.; Mason, E. A. *J. Chem. Phys.* **1991**, *94*, 3839.
- (18) Parsafar, G. A.; Kermanpour, F.; Najafi, B. *J. Phys. Chem. B* **1999**, *103*, 7287.
- (19) Parsafar, G.; Mason, E. A. *J. Phys. Chem.* **1994**, *98*, 1962.