On the heat capacity of liquids at high temperatures

S.M. Stishov

PII: S0378-4371(17)30221-2
DOI: http://dx.doi.org/10.1016/j.physa.2017.03.001
Reference: PHYSA 18067

To appear in: *Physica A*

Received date : 20 November 2016
Revised date : 26 December 2016

Please cite this article as: S.M. Stishov, On the heat capacity of liquids at high temperatures, *Physica A* (2017), http://dx.doi.org/10.1016/j.physa.2017.03.001

On the heat capacity of liquids at high temperatures

S.M. Stishov

Institute for High Pressure Physics of RAS, 108840, Troitsk, Russia

---

Abstract

Making use of a simple approximation for the evolution of the radial distribution function, we calculate the temperature dependence of the heat capacity C_v of Ar at constant density. C_v decreases with temperature roughly according to the law $\sim T^{-1/4}$, slowly approaching the hard sphere asymptotic value $C_v = \frac{3}{2}R$. However, the asymptotic value of C_v is not reachable at reasonable temperatures , but stays close to 1.6–1.7 R over a wide range of temperatures after passing a " magic " $2R$ value at about 300 K. Nevertheless these values have nothing to do with loss of vibrational degrees of freedom, but arise as a result of a temperature variation of the collision diameter σ.

Keywords: heat capacity, collision diameter, argon
PACS: 05.20.-y, 05.20.Jj, 05.70.-a

It has been known for a long time that C_v of many liquids almost equals that of solids at the melting point, decreases with temperature, and reaches a value of $\sim 2R$ (R-gas constant) [1, 2, 3, 4, 5, 6]. A similar trend was observed in model systems of particles interacting with an inverse power potential [7]. With time, a general belief was formed that C_v varies from $\sim 3R$ to $\sim 2R$ with temperature from the melting to the critical temperature. Ref. [8] provides an attractive, though probably wrong, explanation of this behaviour of C_v. It assumes that, in liquids at high temperatures, the transverse vibrational modes cease to exist, whereas the longitudinal mode still remains, resulting in $C_v = 1R + 1/2R + 1/2R = 2R$. Recently, it has been proposed that decreasing the heat capacity beyond the $2R$ value implies a transition to a truly gaseous state without any vibrational degrees of freedom. A corresponding line in the P-T space bordering a region with $C_v \geq 2R$ was named a Frenkel line in honor of the Russian theoretician Yaakov Frenkel [9, 10, 11].

However, the interpretation of the $2R$ value of a heat capacity as a result of loss of the transverse elastic response is not proved in either case. So it is appropriate to carry out an analysis of the situation based on a traditional approach to the thermodynamics of liquids and gases.

Lets write the energy of a classical system of particles in the form,

$$E = \frac{3}{2}RT + \frac{N^2}{2V}\int_0^\infty \Phi(r)g(r)4\pi r^2 dr \qquad (1)$$

where $\Phi(r)$ - pair interaction potential, $g(r)$ - radial distribution function, N - Avogadro number, R - gas constant.

Email address: `sergei@hppi.troitsk.ru` (S.M. Stishov)

Preprint submitted to Physica A *December 26, 2016*