THE THERMODYNAMIC PROPERTIES OF SIMPLE FLUIDS DESCRIBED BY LEBOWITZ VARIABLES*

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With the help of the Lebowitz variables $\lambda = T^{*\frac{n}{m}-1}$ and $\bar{\varrho} = \varrho\sigma^3 T^{*-\frac{3}{m}}$ the "experimental" data on some thermodynamic properties of simple fluids are discussed. In the limit as $\lambda \to 0$, some $X(\lambda, \bar{\varrho}) \to +\infty$ or $-\infty$, but there is the limiting curve having the property $[\lambda^k X(\lambda, \bar{\varrho})]$ and is finite for all $\bar{\varrho}$. Some thermodynamic properties are plotted in Lebowitz variables.

Lebowitz [1] introduced the variables $\lambda = T^{*\frac{n}{m}-1}$ and $\bar{\varrho} = \varrho\sigma^3 T^{*-\frac{3}{m}}$ and showed that for a system of classical particles interacting via a Lennard-Jones potential

$$\varphi(r) = c(m, n)\varepsilon\left[\left(\frac{\sigma}{r}\right)^m - \left(\frac{\sigma}{r}\right)^n\right], \tag{1}$$

where $c(m, n) = \dfrac{m}{m-n}\left(\dfrac{m}{n}\right)^{\frac{n}{m-n}}$, the thermodynamic properties are analytic functions of these variables in a certain neighbourhood of the point ($\lambda = 0$, $\bar{\varrho} = 0$). This enables one to expand the thermodynamic properties in a power series in λ and $\bar{\varrho}$. For $\lambda \to 0$ a system interacting via a Lennard-Jones (m—n) potential approaches the soft sphere system interacting via the repulsive part of a Lennard-Jones ($m-n$) potential. Malesiński [2] introduced the repulsive configurational internal energy U_r and the attractive configurational energy U_a defined by

$$U_r = \langle \phi_r(\mathbf{r}^N)\rangle = \tfrac{1}{2}N(N-1)\frac{\int \varphi_r(r_{12})\exp[-\beta\phi(\mathbf{r}^N)]d\mathbf{r}^N}{\int \exp[-\beta\phi(\mathbf{r}^N)]d\mathbf{r}^N} \tag{2}$$

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and

$$U_a = \langle \phi_a(\boldsymbol{r}^N) \rangle = \tfrac{1}{2} N(N-1) \frac{\int \varphi_a(r_{12}) \exp[-\beta\phi(\boldsymbol{r}^N)] d\boldsymbol{r}^N}{\int \exp[-\beta\phi(\boldsymbol{r}^N)] d\boldsymbol{r}^N}. \tag{3}$$

We will find these quantities useful when discussing the behaviour of the thermodynamic properties of a Lennard-Jones fluid with Lebowitz variables.

Let us introduce the reduced position vector $\boldsymbol{R} = \varrho \boldsymbol{r}$ and Lebowitz variables into the nondimensional quantities $\beta U_r/N \equiv \beta u_r$ and $\beta U_a/N \equiv \beta u_a$. Then for the Lennard-Jones potential

$$\beta u_r = \tfrac{1}{2}(N-1)c \frac{\int \left(\frac{\bar{\varrho}^{1/3}}{R_{12}}\right)^m \exp\left\{-c \sum_{i<j} \left[\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m - \lambda \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^n\right]\right\} d\boldsymbol{R}^N}{\int \exp\left\{-c \sum_{i<j} \left[\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m - \lambda \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^n\right]\right\} d\boldsymbol{R}^N} \tag{4}$$

and

$$\beta u_a = -\tfrac{1}{2}(N-1)c\lambda \frac{\int \left(\frac{\bar{\varrho}^{1/3}}{R_{12}}\right)^n \exp\left\{-c \sum_{i<j} \left[\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m - \lambda \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^n\right]\right\} d\boldsymbol{R}^N}{\int \exp\left\{-c \sum_{i<j} \left[\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m - \lambda \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^n\right]\right\} d\boldsymbol{R}^N}. \tag{5}$$

In the limit as $\lambda \to 0$, the quantity βu_r approaches

$$\lim_{\lambda \to 0} (\beta u_r) = \tfrac{1}{2}(N-1)c \frac{\int \left(\frac{\bar{\varrho}^{1/3}}{R_{12}}\right)^m \exp\left[-c \sum_{i<j} \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m\right] d\boldsymbol{R}^N}{\int \exp\left[-c \sum_{i<j} \left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m\right] d\boldsymbol{R}^N} = \beta u_r^s, \tag{6}$$

where $\beta u_r^s = \beta U_r^s/N$ is dependent only on $\bar{\varrho}$ and u_r^s is the true configurational internal energy of a soft sphere system. In Fig. 1 the values of βu_r are plotted as functions of $\bar{\varrho}$ for the Lennard-Jones (12–6) potential for different values of λ. The curves approach each other. As λ decreases the βu_r curves are pushed down and the limiting curve — that is, when $\lambda = 0$ — is the lowest of the βu_r curves. In the previous paper [3] the isotherms u_r were plotted as functions of $\varrho\sigma^3$. From those results and the above result we may see that for $\lambda \to 0$ the u_r curves for a given constant value of $\bar{\varrho}$ will approach infinity.

The quantity βu_a for $\lambda \to 0$ approaches zero as expected. One can easily see that there exists another limit different from zero, namely

$$\lim_{\lambda\to 0}\left(\frac{\beta u_a}{\lambda}\right) = -\tfrac{1}{2}(N-1)c\,\frac{\int\left(\frac{\bar{\varrho}^{1/3}}{R_{12}}\right)^n \exp\left[-c\sum_{i<j}\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m\right]dR^N}{\int \exp\left[-c\sum_{i<j}\left(\frac{\bar{\varrho}^{1/3}}{R_{ij}}\right)^m\right]dR^N} = \beta^{\frac{n}{m}} u_a^s, \tag{7}$$

where $\beta^{\frac{n}{m}} u_a^s = \beta^{\frac{n}{m}} U_a^s/N$ is dependent only on $\bar{\varrho}$. U_a^s would be the attractive configurational internal energy calculated with a soft sphere radial distribution function. In Fig. 2 the values

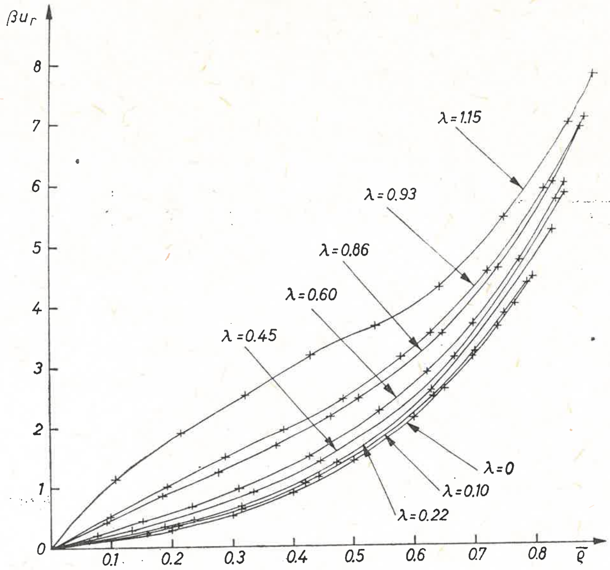

Fig. 1. βu_r versus $\bar{\varrho}$ for λ = const

of $\beta u_a/\lambda$ are plotted as functions of $\bar{\varrho}$ for the Lennard-Jones (12–6) potential for different values of λ. As λ decreases the curves are moved up and the limiting curve for $\lambda = 0$ is the highest $\beta u_a/\lambda$ curve. In the previous paper [3] the isotherms u_a were plotted as functions of $\varrho\sigma^3$. From those results and the above result we may see that for $\lambda \to 0$, u_a for a given value of $\bar{\varrho}$ will tend to minus infinity, u_r to plus infinity and their sum $u_r + u_a$ to plus infinity.

The sum of βu_r and βu_a are plotted in Fig. 3. These curves are less close than those in Fig. 1 and moreover

$$\lim_{\lambda\to 0} (\beta u) = \beta u_r^s, \tag{8}$$

i. e. the limit is the same as for βu_r, because $\lim_{\lambda\to 0} \beta u_a = 0$. As λ decreases the curves βu are moved upwards and the limiting curve for $\lambda = 0$ is the highest βu curve.

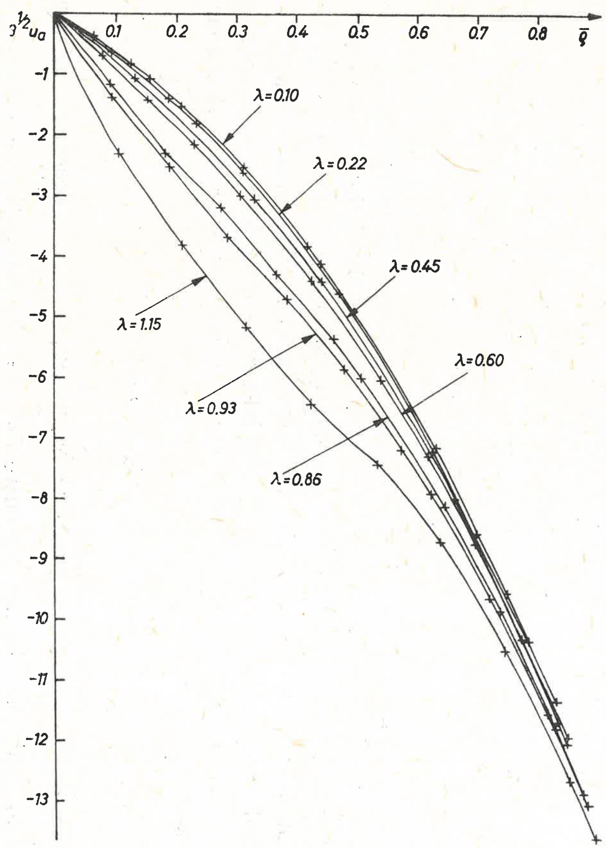

Fig. 2. $\beta^{1/2}u_a$ versus $\bar{\varrho}$ for λ = const

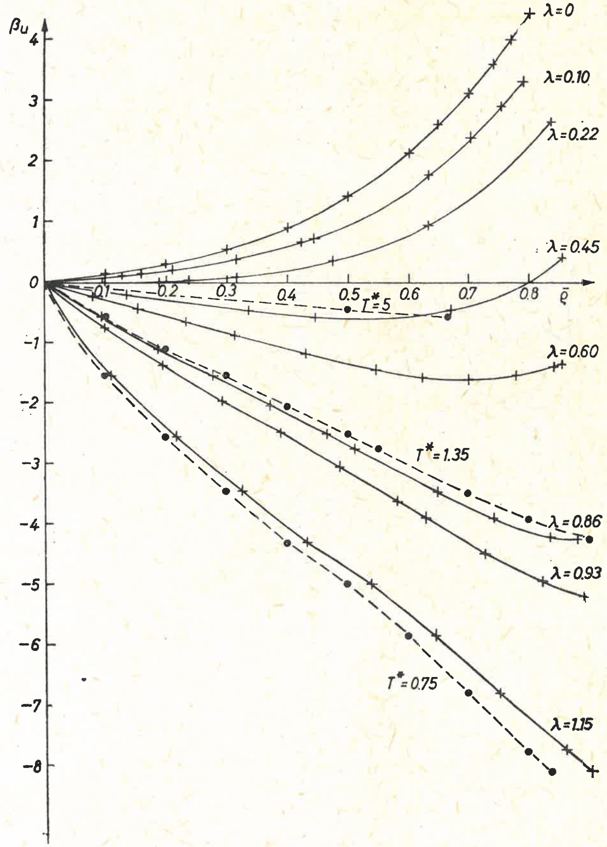

Fig. 3. βu versus $\bar{\varrho}$ for λ = const (solid curves) and versus ϱ for T^* = const (dashed curves)

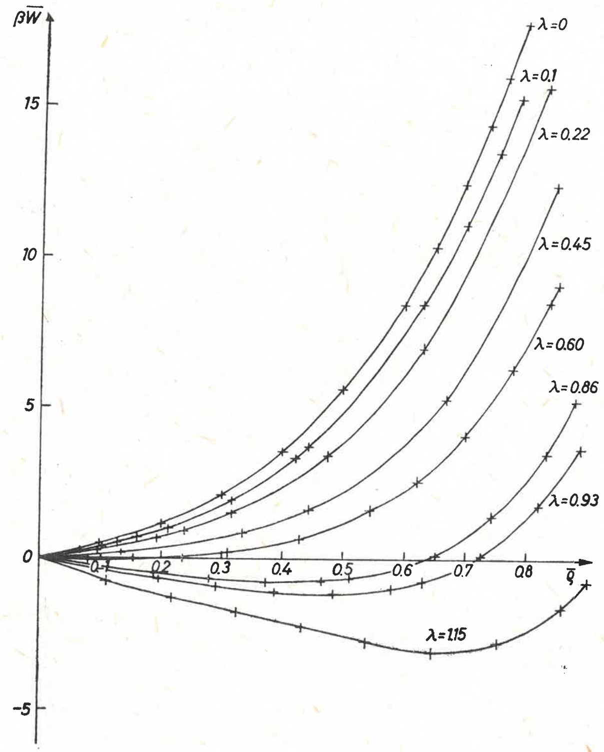

Fig. 4. $\beta\langle W\rangle$ versus $\bar{\varrho}$ for λ = const

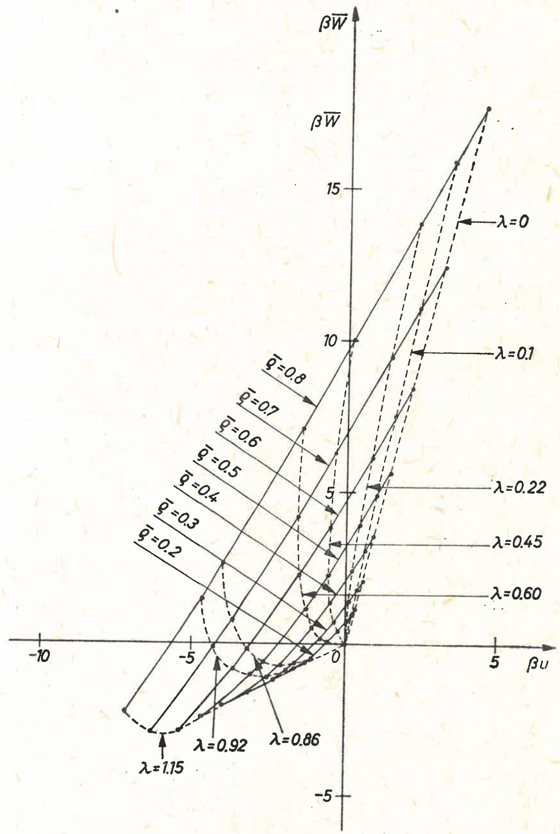

Fig. 5. $\beta\langle W\rangle$ versus βu for $\bar{\varrho}$ = const

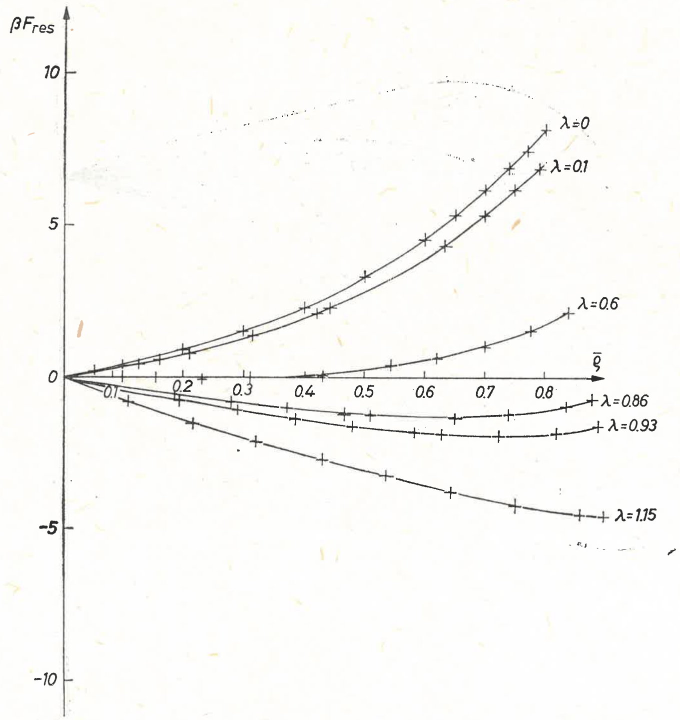

Fig. 6. βF_{res} versus $\bar{\varrho}$ for λ = const

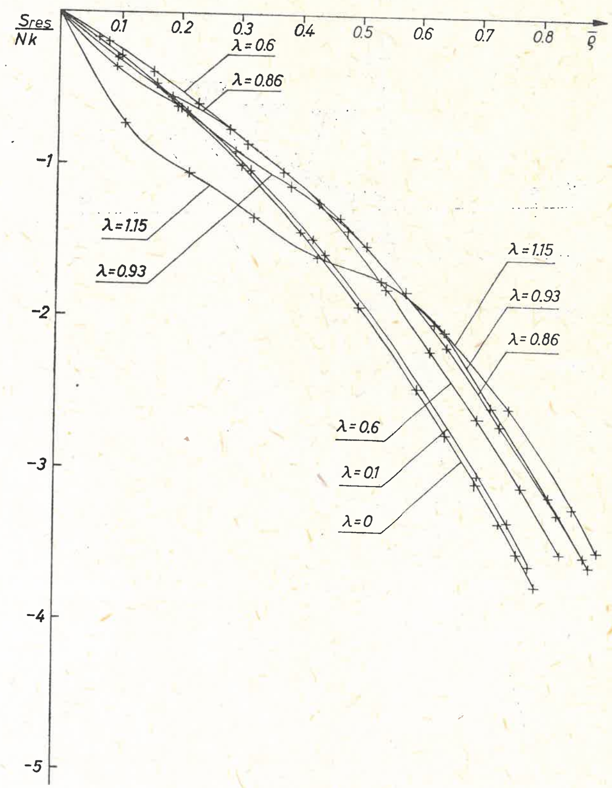

Fig. 7. S_{res} versus $\bar{\varrho}$ for λ = const

In Lebowitz variables the average value of the virial is equal to

$$\langle W\rangle \equiv p\frac{V}{N}-kT = \frac{m}{3}u_r+\frac{n}{3}u_a. \tag{9}$$

The quantity $\beta\langle W\rangle$ has the following limit

$$\lim_{\lambda\to 0}(\beta\langle W\rangle) = \lim_{\lambda\to 0}(z-1) = \frac{m}{3}\beta u_r^s, \tag{10}$$

where z is the compressibility factor. In Fig. 4 the curves of $\beta\langle W\rangle$ are plotted as functions of $\bar{\varrho}$ for λ = const. As λ decreases the values of $\beta\langle W\rangle$ are moved up and the limiting curve for $\lambda = 0$ is the highest $\beta\langle W\rangle$ curve.

In one of our papers [4] we discussed correlations of the configurational internal energy and average virial. In Fig. 5 $\beta\langle W\rangle$ curves are plotted against βu for $\bar{\varrho}$ = const obtained by graphical interpolation of "experimental" data for the (12–6) potential presented in Fig. 3 and in Fig. 4. For large $\bar{\varrho}$ we obtained a linear dependence of $\beta\langle W\rangle$ on βu. Moreover, the curves λ = const for $\lambda \to 0$ approach a straight line with slope tg $\alpha = m/3$; here $m/3 = 4$.

For $\lambda \to 0$ the residual Helmholtz free energy F_{res} divided by kT, βF_{res}, has, in Lebowitz variables, the limiting curve which may be seen in Fig. 6. The limiting curve is the highest βF_{res} curve. This result can be predicted if we take into account the relation

$$\beta F_{res} = \int_0^{\bar{\varrho}}\left(\frac{m}{3}\beta U_r+\frac{n}{3}\beta U_a\right)\frac{d\bar{\varrho}}{\bar{\varrho}}. \tag{11}$$

In Fig. 7 the S_{res}, obtained from relation

$$S_{res} = \beta U - \beta F_{res}, \tag{12}$$

are plotted. These curves also have the limiting curve for $\lambda \to 0$ but are intersecting themselves and for low temperatures cross the limiting curve. For large $\bar{\varrho}$ with an increase of temperature the curves go lower. That behaviour is not characteristic of typical T, ϱ variables. In the last variables the "experimental" curves of S_{res} are not crossing themselves and S_{res} is increasing function of temperature.

All graphs for $T^* = 0.75$, 1.15, 1.35 and 2.74 were obtained on the basis of the Verlet and Weis data [5]. For $T^* = 5$, 20 and 100 the curves were plotted from the Hansen data [6]. For $T^* = \infty$ i. e. for $\lambda = 0$ all curves were plotted from the data of Hoover et al. [7].

The graphs presented here may be compared with the graphs of our earlier paper [3] where nondimensional variables $\varrho\sigma^3$ and $T^* = kT/\varepsilon$ were used. Qualitatively, the shape of the isotherms (T^* = const) is the same; only the scale of ϱ is expanded or contracted. This is illustrated for three isotherms in Fig. 3. The limiting curves for $\lambda = 0$ are seen only in the Lebowitz coordinates.

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