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THE RELATIVISTIC COVARIANCE OF ONNES EQUATION*

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On the assumption that Onnes equations meet the requirements of the relativistic covariance, virial coefficients as functions of temperature are derived by using the transformations between thermodynamic variables provided by the vector theory of relativistic thermodynamics, and result in agreement with those obtained from cluster expansions in statistics. This breaks, to some extent, the traditional ideas that the thermodynamic theory is not able to derive equations of state at all and presents a possibly simple and new way of finding theoretically the equation of state.

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In the theory of relativistic thermodynamics, either Planck-Einstein's thermodynamics (P-E theory),[1,2] or the vector theory of relativistic thermodynamics (VTRT),[3] equations of state for ideal gases are relativistic covariant. In the P-E theory, for instance, the entropy and pressure are scalars, while both the temperature and volume have the same transformation, that is

$$S = S_0, P = P_0, T = T_0\sqrt{1-v^2}, V = V_0\sqrt{1-v^2}. \tag{1}$$

Accordingly, the equation of state for ideal gases (for 1 mol of gas)

$PV = RT \rightarrow P_0(V_0\sqrt{1-v^2}) = R(T_0\sqrt{1-v^2}) \rightarrow P_0V_0 = RT_0$, where R is the universal gas constant, which should be a scalar.

In the VTRT, however, transformations of the corresponding variables are as follows:

$$S = S_0, P = \gamma^2 P_0, T = \gamma T_0 \text{ and } V = \gamma^{-1}V_0 \tag{2}$$

where

$$\gamma = \begin{cases} (1-v^2)^{-1/2} & \text{in the Minkowski space-time} \\ (-g_{tt})^{-1/2} & \text{rest in the Riemann space-time} \end{cases}$$

Thus, we too have $PV = RT \rightarrow (\gamma^2 P_0)(\gamma^{-1}V_0) = R(\gamma T_0) \rightarrow P_0V_0 = RT_0$.

The above-mentioned facts lead us to the following basic assumption: general equations of state such as Onnes equation and others are relativistically covariant. The equation of state for ideal gases is a special example of the covariance of the general equations. Under the assumption, for a system described by P, V and T, it can be seen from Eq.(2) that the following equation of state meets the requirements for covariance,

$$P = \alpha_0 T^n V^{n-2}, \tag{3}$$

if n can be taken to be any real numbers, where α_0 is a scalar. That is,

$$\begin{aligned} P &= \alpha_0 T^n V^{n-2} \rightarrow (\gamma^2 P_0) \\ &= \alpha_0(\gamma T_0)^n \cdot (\gamma^{-1}V_0)^{n-2} \rightarrow P_0 = \alpha_0 T_0^n V_0^{n-2}. \end{aligned}$$

It is clear that if n=1, Eq.(3) will become the equation of state for real gases. In general, a linear combination of Eq.(3) still satisfy the covariance, i.e.

$$P = \alpha_0 T^n V^{n-2} + \beta_0 T^m V^{m-2} + \gamma_0 T^q V^{q-2} + \cdots, \tag{4}$$

where β_0 and γ_0 are scalars, m and q are real nmbers different from each other and n.

As is well known, there are two equivalent forms for Onnes equation:

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots\right) \tag{5}$$

and

$$P = \frac{RT}{V}(1 + B'P + C'P^2 + D'P^3 + \cdots), \tag{6}$$

where B (or B'), C(or C') and D (or D') are the second, third and fourth virial coefficients, which are related by the following expressions

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2} \text{ and } D' = \frac{D - 3BC + 2B^3}{(RT)^3}. \tag{7}$$

As for virial coeffcients, they are known in classic thermodynamics only to be functions of temperature, but detailed forms are yet unable to be given. Now we are able to find conversely their relationships with temperature on the basic assumption that Onnes equation

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must satisfy the covariance. Without losing generality, we take as an example the Onnes equation with the highest fourth virial coefficent for discussion. In order for Eq.(5) to be covariant, it can be easily seen that all terms in parentheses on the right side of Eq.(5) are scalars. In the first place, to ensure that $\frac{B}{V}$ is a scalar, there should be

$$B = q_1 b + \frac{B_1}{RT} \text{ or } \frac{B}{V} = q_1\left(\frac{b}{V}\right) + \frac{B_1}{V(RT)}, \tag{8}$$

where b has the dimensions of volume, so that b transforms as the volume in the space-time coordinate transformation, q_1 is a pure number, and B_1 is a scalar. Similarly, to make $\frac{C}{V^2}$ and $\frac{D}{V^3}$ scalar, we must have

$$\frac{C}{V^2} = q_2\left(\frac{b}{V}\right)^2 + \frac{bC_1}{V^2(RT)} + \frac{C_2}{V^2(RT)^2}, \tag{9}$$

and

$$\frac{D}{V^3} = q_3\left(\frac{b}{V}\right)^3 + \frac{b^2D_1}{V^3(RT)} + \frac{bD_2}{V^3(RT)^2} + \frac{D_3}{V^3(RT)^3}, \tag{10}$$

where q_2 and q_3 are pure numbers, C_1, C_2, D_1, D_2 and D_3 are scalars. It is easy to see that Eqs.(8)–(10) are unique and complete in form to ensure that $\frac{B}{V}$, $\frac{C}{V^2}$ and $\frac{D}{V^3}$ are scalars. Thus Eq.(5) can be reduced to

$$\begin{aligned} P =& \frac{RT}{V}\left[1 + q_1\left(\frac{b}{V} + \frac{B_1}{VRT}\right)\right. \\ &+ \left(q_2\frac{b^2}{V^2} + \frac{bC_1}{V^2(RT)} + \frac{C_2}{V^2(RT)^2}\right) \\ &\left.+ \left(q_3\frac{b^3}{V^3} + \frac{b^2D_1}{V^3(RT)^2} + \frac{bD_2}{V^3(RT)^2} + \frac{D^3}{V^3(RT)^3}\right)\right] \end{aligned}$$

or

$$\begin{aligned} P =& \frac{RT}{V}\left[\left(1 + q_1\frac{b}{V} + q_2\frac{b^2}{V^2} + q_3\frac{b^3}{V^3}\right)\right. \\ &+ \left(1 + q_1\frac{b}{V} + q_2\frac{b^2}{V^2}\right)\frac{B_0}{VRT} \\ &\left.+ \left(1 + q_1\frac{b}{V}\right)\frac{C_0}{V^2(RT)} + \frac{D_0}{V^3(RT)^3}\right], \end{aligned} \tag{11}$$

where $B_0 = B_1 + \frac{C_1}{q_1} + \frac{D_1}{q_2}$, $C_0 = C_2 + \frac{D_2}{q_1}$, $D_0 = D_3$.

The second virial coefficient can be obtained from Eq.(11)

$$B = q_1 b + \frac{B_0}{RT}, \tag{12}$$

the third virial coefficient

$$C = q_2 b^2 + q_1\frac{bB_0}{RT} + \frac{C_0}{(RT)^2}, \tag{13}$$

and the fourth virial coefficent

$$B = q_3 b^3 + q_2\frac{b^2B_0}{RT} + q_1\frac{bC_0}{(RT)^2} + \frac{D_0}{(RT)^3}. \tag{14}$$

Equations (12)–(14) are just the detailed virial coefficients as functions of temperature obtained from the relativistic covariance. The main results in finding virial coefficients in statistical mechanics by means of cluster expansions are as follows[4,5]:

Start from the general expression for the equation of state given by Mayer-Ursell, i.e.

$$P = \frac{RT}{V}\sum_{i=1}^{\infty} a_1(T)\left(\frac{\lambda^3}{V}\right)^{l-1}, \tag{15}$$

where $\lambda = (h/2\pi kmT)^{1/2}$ is the thermal wavelength. If $l = 4$, Eq.(15) can be rewritten as

$$P = \frac{RT}{V}\left[a_1 + a_2\frac{\lambda^3}{V} + a_3\frac{\lambda^6}{V^2} + a_4\frac{\lambda^9}{V^3}\right], \tag{16}$$

where a_1=1, $a_2 = -\frac{2\pi}{\lambda^3}\int_0^{\infty}(e^{-u(r)/KT} - 1)r^2\mathrm{d}r$.

If the Lennard-Jones potential is chosen for the interaction potential of particles, that is, $u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$, we can obtain

$$a_2 \approx \frac{2\pi r_0^3}{3\lambda^3}\left(1 - \frac{u_0}{kT}\right), \tag{17}$$

which can be expressed as $a_2 = \frac{b}{\lambda^3}\left(1 + \frac{U_0}{RT}\right)$, while $a_3 = \frac{5}{8}a_2^2$, and $a_4 = 0.28695a_2^3$. In comparison of Eq.(16) with Eq.(5) we have the second virial coefficient

$$B = a_2\lambda^3 = b\left(1 + \frac{U_0}{RT}\right), \tag{18}$$

the third virial coefficient

$$C = a_3\lambda^6 = \frac{5}{8}b^2\left(1 + \frac{2U_0}{RT} + \frac{U_0^2}{(RT)^2}\right), \tag{19}$$

and the fourth virial coefficient

$$D = a_4\lambda^9 = 0.28695b^3\left(1 + \frac{3U_0}{RT} + \frac{3U_0^2}{(RT)^2} + \frac{U_0^3}{(RT)^3}\right). \tag{20}$$

Comparing Eqs.(18)–(20) with Eqs.(12)–(14) shows that so far as the relationship of virial coefficients with temperature is concerned the two groups of equation are consistent with each other. We are of course not able to expect that the thermodynamic theory would provide all the values of the constants in the virial coefficients and microscopic meanings of b, even if in

statistical mechanics the determination of these constants depends on the basic assumption of $u(r)$. In addition, from Eq.(7) and Eqs.(12)–(14), we can obtain

$$\left.\begin{aligned} B' = \frac{q_1 b}{RT} + \frac{B_0}{(RT)^2}, \quad C' = \frac{q_1 b B_0}{(RT)^3} + \frac{C_0 - B_0^2}{(RT)^4}, \\ D' = \frac{q_2 b^2 B_0}{(RT)^4} + \frac{q_1 b(3B_0 - 2C_0)}{(RT)^5} + \frac{2B_0 - 3B_0 C_0 + D_0}{(RT)^6}. \end{aligned}\right\} \tag{21}$$

Substituting Eq.(21) into Eq.(6) verifies that Eq.(6) meets the need for the relativistic covariance. Finally, if $\frac{b}{V} \ll 1$ in the square brackets on the right-hand side is much less than unity, then the terms higher than $\frac{1}{V^2}$ can be neglected, Eq.(11) can be reduced to

$$P = \frac{RT}{V}\left[1 + q_1\frac{b}{V} + \frac{B_0}{VRT}\right] = \frac{RT}{V}\left(1 + q_1\frac{b}{V}\right) + \frac{B_0}{V^2},$$

that is, $P \approx \dfrac{RT}{V(1 - q_1\frac{b}{V})} + \dfrac{B_0}{V^2}$ or $\left(P - \dfrac{B_0}{V^2}\right)(V - q_1 b) = RT$. If we let $q_1 = 1$ and $B_0 = -a$, we have got Van der Waals equation $\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$, which is naturally covariant.

On the assumption that equations of state are invariant in form in the group of coordinate transfrmation, we can derive the detailed functions of the virial coefficients consistent with the results given in statistical mechanics. This point breaks to some extent the traditional ideas that the thermodynamic theory is unable to derive equations of state, thereby it is possible theoretically to provide a new and straightforward way of finding equations of state.

REFERENCES

[1] R. K. Patheia, Statistical Mechanics, Reprinte Planck, M, Zur Dynamik Bewegter Systeme, S. d. Kgl Preuss. Akad, d. Wiss (1907) P542

[2] A. Einstein, *Jahrbuch der Radioaktivitat und Elektronik*, **4**(1907), 411.

[3] Liu Zewen, *Science in China* (Series A) **37**(1994), 970.

[4] J. E. Mayer, *et al. J. Chem. Phys.*, **5**(1937), 74.

[5] R. K. Patheia, Statistical Mechanics, *Reprinted With Corrections* (1997) Chap. 9