In the foregoing discussion, we have used the definition

$$\epsilon^{\pm}(-\omega,\mathbf{k})=1-\sum_s \frac{\omega_s^2}{k^2}\sum_{n=-\infty}^{\infty}\int d^3v \frac{1}{(\mathbf{k}\cdot\mathbf{v})_n\pm(\omega\pm i\lambda)}\left(\mathbf{k}\cdot\frac{\partial F_s}{\partial \mathbf{v}}\right)_n,$$

where the superscripts ($\pm$) designate the sign in front of $i\lambda$ (as $\lambda\to 0$).

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Suppression at High Temperature of Effects Due to Statistics in the Second Virial Coefficient of a Real Gas*

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It is shown that the repulsive core present in realistic two-body potentials and in hard spheres leads to the rapid suppression of the effects of statistics in the second virial coefficient, except at very low temperatures. For hard spheres, an upper bound is obtained which goes down exponentially with temperature when the latter becomes large.

THE effects of quantum mechanics on the second virial coefficient may be formally separated into diffraction effects which obtain for a Boltzmann gas and exchange contributions associated with the Bose-Einstein or Fermi-Dirac character of the gas.[1] This separation arises very naturally in the formalism developed by Lee and Yang[2] and allows us to consider the virial as being the sum of a direct term

$$B_{\text{direct}}=-(N/2)\int d\mathbf{r}[2^{3/2}\lambda_T{}^3\langle\mathbf{r}|e^{-\beta H_{\text{rel}}}|\mathbf{r}\rangle-1],$$

which in the limit $h\to 0$ gives us the classical answer, and of an exchange term

$$B_{\text{exch}}=\mp(N/2)[1/(2S+1)]\int d\mathbf{r}2^{3/2}\lambda_T{}^3\langle\mathbf{r}|e^{-\beta H_{\text{rel}}}|-\mathbf{r}\rangle.$$

H_{rel} is the relative Hamiltonian, β^{-1} is Boltzmann's constant times the temperature, λ_T is the thermal wavelength defined as $h(2\pi mkt)^{-1/2}$, N is Avogadro's constant, S is the spin of the individual component, and the sign is negative for Bose-Einstein statistics and positive for Fermi-Dirac cases.

In the case of a perfect gas we have

$$B_{\text{exch}}=\mp N(\lambda_T{}^3/2^{5/2})[1/(2S+1)].$$

At high temperatures this value is customarily[1] used to represent the quantum-mechanical effects due to statistics of a gas such as helium, while a Wigner-Kirkwood expansion is used to evaluate the direct term.

The purpose of this note is to point out that, in fact, for a real gas the presence of a strong repulsive core entails a drastic suppression of the exchange effect at high temperature.[3] We first show this to be the case for

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[1] See J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954) with special reference to the article by J. deBoer and R. Byron Bird on the quantum theory and the equation of state.

[2] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).

[3] Lloyd D. Fosdick has, independently, reached similar conclusions (private communication).

hard spheres and then consider more realistic potentials.

Introducing a complete set of eigenfunctions of the energy ψ_n, we can write

$$\langle \mathbf{r} | e^{-\beta H_{\mathrm{rel}}} | -\mathbf{r} \rangle = \sum_n \psi_n(\mathbf{r}) \psi_n(-\mathbf{r}) e^{-\beta E_n}.$$

Setting the collision diameter of the hard spheres at $r=\sigma$, we see that the matrix element is zero for $r<\sigma$ since the wave functions are zero inside this region. Next we show that for any $\mathbf{r}$ the matrix element for free particles is an upper bound to the exchange matrix element for particles subject to repulsive forces only. This result is immediate once we write the Wiener integral expression[4] for the exchange matrix element

$$\langle \mathbf{r} | e^{-\beta H_{\mathrm{rel}}} | -\mathbf{r} \rangle = \int_{C_{\beta;2\mathbf{r}}} \exp\left\{ -\int_0^\beta d\tau\, V[\mathbf{X}(\tau) - \mathbf{r}] \right\} d_{\omega(\beta;2\mathbf{r})}\mathbf{X}, \quad (1)$$

which is less than or equal to

$$\langle \mathbf{r} | e^{-\beta T_{\mathrm{rel}}} | -\mathbf{r} \rangle = \int_{C_{\beta;2\mathbf{r}}} d_{\omega(\beta;2\mathbf{r})}\mathbf{X}, \quad (2)$$

since the exponential is less than 1. (T_{rel} is the relative kinetic energy.) In fact since paths passing through the sphere contribute for free particles and not for hard spheres the inequality obtains. Evaluating the exchange matrix element for the kinetic energy yields

$$\langle \mathbf{r} | e^{-\beta T_{\mathrm{rel}}} | -\mathbf{r} \rangle = (1/2^{3/2}\lambda_T^3) e^{-2\pi r^2/\lambda_T^2}. \quad (3)$$

We thus have

$$|B_{\mathrm{exch}}| < [2\pi N/(2S+1)] \times \int_\sigma^\infty dr\, r^2 \langle \mathbf{r} | e^{-\beta T_{\mathrm{rel}}} | -\mathbf{r} \rangle 2^{3/2}\lambda_T^3,$$

which equals

$$[2\pi N/(2S+1)] \int_\sigma^\infty dr\, r^2 e^{-2\pi r^2/\lambda_T^2}.$$

At low temperatures (λ_T large) this integral has for limiting value the free-particle result, while at high temperatures we obtain the asymptotic expansion

$$|B_{\mathrm{perf\ exchange}}| \times 2^{3/2}(\sigma/\lambda_T) \times e^{-2\pi(\sigma/\lambda_T)^2}[1 + (1/4\pi)(\lambda_T/\sigma)^2 + \cdots].$$

Since λ_T is proportional to $T^{-1/2}$, we see that our upper bound goes down exponentially with temperature. In fact, if we set the collision diameter at about 2 Å and choose a value for the mass suitable for helium, we find that the dependence is roughly $e^{-T/2}$. Note that this precludes an asymptotic expansion in powers of $1/T$.

Physically, we can understand this formal result by noting that the free-particle exchange matrix element (Eq. 3) is highly peaked about $r=0$ and appreciable only for r of the order of $\lambda_T/(2\pi)^{1/2}$ or less. In other words we see that the exchange is nontrivial only if the particles are allowed to come closer to each other than the thermal wavelength. If this is not possible, because of the presence of repulsive forces, the exchange is negligible. This is the case for hard spheres when the temperature is large enough so that the collision diameter σ is greater than λ_T. In the example mentioned above $(\sigma/\lambda_T) \sim 1$ when T is ~ 16°K. As the previous remark made on deriving the inequality (Eq. 1 $\leqslant$ Eq. 2) indicates, the matrix element outside the core will be smaller than the free-particle result and the consequent B_{exch} smaller for a given temperature than has been estimated. This point will not be considered further in this note.[5]

Turning our attention now to more realistic potentials, we note two differences. In the first place the intermolecular potentials have an attractive part. If ϵ represents the maximum well depth ($\epsilon/k \sim 10$°K for helium) then Eqs. (1) and (2) show that

$$e^{\beta\epsilon} \langle \mathbf{r} | e^{-\beta T_{\mathrm{rel}}} | -\mathbf{r} \rangle = e^{\beta\epsilon} (1/2^{3/2}\lambda_T^3) e^{-2\pi r^2/\lambda_T^2}$$

is an upper bound to the exchange matrix element for all $\mathbf{r}$. At high temperature $e^{\beta\epsilon} \to 1$ and we recover the free-particle result. Another difference is of course that though realistic potentials provide strong repulsive forces they lack the abrupt "all or nothing" character of hard spheres. Nevertheless, since the repulsion is so strong, the potential rising rapidly and reaching values many orders of magnitude larger than the maximum well depth, the wave functions are essentially zero for r's within the core and so will be the exchange element.

We thus see again that at high temperature where the thermal wavelength is much smaller than the core radius, the exchange contribution to the virial will be completely negligible.

[4] S. G. Brush, Rev. Mod. Phys. **33**, 79 (1961). Especially relevant is the discussion pertinent to and centered about Eq. (2.13); see also Eqs. (5.4) and (5.5).

[5] We hope to show in a subsequent paper that the leading term in the asymptotic form of the logarithm of B_{exch} is in fact proportional to $-\frac{1}{2}\pi^3(\sigma/\lambda_T)^2$.