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FREE ENERGY OF AN ASSEMBLY OF NONSPHERICAL MOLECULES WITH A HARD CORE

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The free energy of an assembly of slightly nonspherical molecules with a hard core is expressed as the sum of the free energy of a system of equivalent hard spheres plus correction terms related to eccentricity. An estimate of these terms is made for ellipsoidal molecules.

The contribution of noncentral interactions to the thermodynamic properties of fluids has been formulated by several authors either as a perturbation expansion in reciprocal powers of temperature, starting from an assembly of spherical molecules,[1] or by introducing an effective temperature-dependent potential with central symmetry.[2] Such treatments are actually limited to weak noncentral forces.

The kind of systems discussed here is completely different: We consider molecules interacting through a hard-core anisotropic potential, i.e., strong noncentral forces. When the anisotropy is small the free energy of such a system may be expressed by means of properties of an assembly of hard spheres.

Consider the configurational integral of N hard spheres of diameter D_0:

$$Q_0=\int d\vec{r}^N \prod_{ij} \eta(r_{ij}-D_0),$$

where r_{ij} is the distance between molecules i, j and $\eta(x)$ equals 0 for $x<0$ and 1 for $x>0$. For an assembly of axially symmetric molecules interacting through a hard-core potential we similarly have

$$Q=\int d\vec{r}^N d\vec{\omega}^N \prod_{ij}\eta(r_{ij}-D_{ij}),$$

where $D_{ij}=D(\vec{\omega}_i,\vec{\omega}_j)$ is the shortest distance of approach of two molecules with orientations $\vec{\omega}_i$, $\vec{\omega}_j$. We next write

$$D(\vec{\omega},\vec{\omega}')=D_0[1+\gamma(\vec{\omega},\vec{\omega}')]$$

with γ defined in such a way that its a priori average $\langle\gamma\rangle$ over all orientations is zero; we subsequently call D_0 the diameter of the equivalent hard sphere. Expanding $\ln Q$ in terms of γ we obtain $\ln[(4\pi)^N Q_0]$ as zeroth term. In first order we have

$$\delta \ln Q=-\tfrac{1}{2}\langle\gamma\rangle D_0[N(N-1)/Q_0] \times\int d\vec{r}^N \delta(r_{12}-D_0)\prod_{ij}{}'\eta(r_{ij}-D_0)$$

which vanishes as $\langle\gamma\rangle=0$. The second-order term is equal to

$$\delta^2 \ln Q=D_0^2[N(N-1)/Q_0]\{\tfrac{1}{2}\langle\gamma^2\rangle\int d\vec{r}^N\delta'(r_{12}-D_0)\prod_{ij}{}'\eta(r_{ij}-D_0) +(N-2)\int d\vec{r}^N\langle\gamma_{12}\gamma_{13}\rangle\delta(r_{12}-D_0)\delta(r_{13}-D_0)\prod_{ij}{}'\eta(r_{ij}-D_0)\}, \qquad (1)$$

where $\langle\gamma_{12}\gamma_{13}\rangle$ depends on the angle u between r_{12} and r_{13}. Following Pople[1] we expand γ in spherical harmonics:

$$\gamma(\vec{\omega},\vec{\omega}')=\sum_l\sum_{l'}\sum_m \gamma_{ll'|m|}S_{lm}(\theta,\varphi)S_{l'm}(\theta',\varphi'),$$

$$S_{lm}(\theta,\varphi)=\left[(2l+1)\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}P_l^{|m|}(\cos\theta)e^{im\varphi}$$

with $l, l' \geq 0$, $|m| \leq \min(l, l')$, $\gamma_{000}=0$, and $\gamma_{ll'|m|}$ real. θ, φ and θ', φ' specify the orientations of the axes of the two molecules with respect to the line joining their centers. This gives

$$\langle\gamma^2\rangle=\sum_l\sum_{l'}\sum_m \gamma_{ll'|m|}^2, \quad \langle\gamma_{12}\gamma_{13}\rangle=\sum_l \gamma_{l00}^2 P_l^0(\cos u). \tag{2}$$

Noticing finally that (1) is expressible in terms of the pair and triplet distribution functions of hard spheres $f_2(r)$ and $f_3(r_{12}, r_{13}, r_{23})$, we find that the Helmholtz free energy of the system is equal to that of a system of equivalent hard spheres at the same density ρ, plus a correction per molecule,

$$\Delta f/kT=\tfrac{1}{4}\langle\gamma^2\rangle 4\pi\rho D_0^2\left[\frac{d}{dr}r^2 f_2(r)\right]_{r=D_0}$$
$$-\tfrac{1}{4}\sum_l \gamma_{l00}^2(2\pi\rho D_0^3)^2\int_{\frac{1}{3}\pi}^{\pi}P_l^0(\cos u)f_3(D_0, D_0, 2D_0\sin\tfrac{1}{2}u)\sin u\,du \tag{3}$$

to the second order in γ. (The same correction holds for the Gibbs free energy at fixed pressure.)

At low density only the first term of Eq. (3) is relevant and $\Delta f/kT \simeq 2\pi\rho D_0^3\langle\gamma^2\rangle$. At high density both terms of Eq. (3) are expected to be significant. For a dense fluid of hard spheres ($0.5<\rho<0.9$) $r^2f_2(r)$ is a decreasing function near $r=D_0$ and the first term of Eq. (3) is negative. In the solid region ($1.0<\rho<\sqrt{2}$), however, $r^2f_2(r)$ ultimately increases with r near $r=D_0$, when the close packing is approached,[3] and the first term of Eq. (3) is positive. The behavior of the second term of Eq. (3) is hard to anticipate because it depends on the detailed form of $\gamma(\vec{\omega}, \vec{\omega}')$.

As an illustration consider prolate ellipsoids with principal axes a and b ($a>b$). For a sufficiently small anisotropy $\epsilon=(a-b)/b$, the only significant coefficients $\gamma_{ll'|m|}$ are $\gamma_{200}=\gamma_{020}=\epsilon/3\sqrt{5}+O(\epsilon^2)$. The relation between D_0 and the volume v of such an ellipsoidal molecule is

$$\pi D_0^3/6=v[1+(2/15)\epsilon^2+O(\epsilon^4)].$$

In the low-density limit our formulation agrees with the results of Isihara for the second virial coefficient.[4] At higher densities Δf was evaluated numerically from data on f_2 and f_3 obtained by applying the Monte Carlo method to a system of 108 hard spheres.[5] For $\rho=0.77\,254$ (fluid), $0.83\,685$ (fluid), and 1.0000 (solid) we obtained, respectively,

$$\Delta f/kT\epsilon^2$$
$$=-1.37\pm0.01+1.58\pm0.02=0.21\pm0.03 \quad \text{(f)}$$
$$=-2.14\pm0.03+2.52\pm0.05=0.38\pm0.08 \quad \text{(f)}$$
$$=-0.03\pm0.02+4.59\pm0.07=4.56\pm0.09 \quad \text{(s)}.$$

Δf is positive in each case but very small in the fluid region because of a large compensation between the two terms of (3): For $\epsilon=0.1$, $\Delta f/kT \simeq 0.002$ and 0.004, respectively. In this case the equivalent fluid of hard spheres with diameter D_0 seems an excellent approximation. In the solid region, however, $\Delta f/kT$ is much more important (0.046 for $\epsilon=0.1$) and should be retained.

The present note is but a preliminary one: Other types of regid molecules as well as the extension of the formalism to mixtures and its combination with scaled-particle theories are presently under investigation.

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NONLINEAR INTERACTIONS OF CYCLOTRON HARMONIC PLASMA WAVES*

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Experimental and theoretical evidence of resonant and nonresonant mode coupling of cyclotron harmonic plasma waves is presented.

Quasilinear theory and its extension to include wave-wave scattering (mode coupling) shows that plasma waves may interact and scatter in the following ways: (a) resonantly, namely, $\omega_{\vec{k}_1} \pm \omega_{\vec{k}_2} = \omega_{\vec{k}_1 \pm \vec{k}_2}$, (b) nonresonantly, namely, $\omega_{\vec{k}_1} \pm \omega_{\vec{k}_2} \neq \omega_{\vec{k}_1 \pm \vec{k}_2}$. The latter process produces "virtual" waves which can play an important role when interaction with the background particles is possible. Here $\omega_{\vec{k}}$ describes a normal mode of plasma oscillation with frequency ω and wave vector $\vec{k}$.[1,2]

The purposes of this Letter are (1) to report the observation of enhanced production of second-order fields with harmonic and sum frequencies in the vicinity of electron cyclotron harmonic frequencies in experiments where plasma waves are excited by external signals and (2) to present results of mode-coupling calculations which show that the experimentally observed resonances can be interpreted as manifestations of both resonant wave-wave scattering and nonresonant wave-wave-particle scattering.

The experiments have been carried out in a helium discharge in a magnetic field. Typical plasma parameters are as follows: background pressure $\sim 3\times10^{-3}$ Torr, electron density 10^8-10^{10} cm^{-3}, and electron temperature $T_e \sim 5$-6 eV. We note that the density is a function of discharge current and magnetic field.

The experimental setup is shown in Fig. 1 (inset). Radio-frequency signals f_1, f_2, in the range 200-700 MHz, are applied via capacitors, attenuators, and filters to one of two antennas which are aligned parallel to the magnetic field (1% uniform in the vicinity of the probes). The antennas are immersed in the uniform plasma region. The output of a receiver, f_3, which is tuned to the sum (f_1+f_2), difference (f_1-f_2), or harmonic frequencies (nf_1 or nf_2) of the injected signals, alternatively, is monitored by the vertical deflection of an XY recorder. The horizontal deflection of the recorder is directly proportional to the magnetic field which can be varied continuously in the range 0-500 G. It has been shown previously that probes such as those utilized here can excite electrostatic cyclotron harmonic waves with wave vectors $\vec{k}$ such that $\vec{k} = (\vec{k}_\perp, k_\parallel = 0)$, where $k_\parallel = (\vec{k}\cdot\vec{B})/B$.[3-5]

By proper filtering, we have been able to ensure that neither mixing of the applied signals in the receiver, nor noise emitted by the plasma in the absence of the applied signals produced more than negligibly small deflections on the XY recorder. By contrast, when mixing of the external signals occurred in the presence of the plasma, a large increase in the emitted signal occurred at critical magnetic fields, as shown in Fig. 1. Such results could be obtained with the received connected to either of the two probes, and the probes could be moved approximately 4 cm radially without changing the structure of

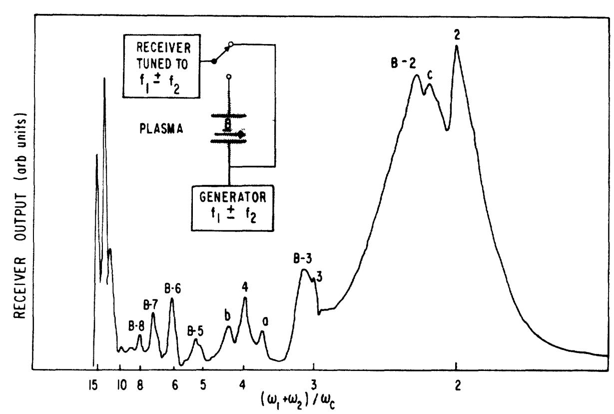

FIG. 1. A typical output of the receiver as a function of magnetic field. Injected signals: $f_1 = 520$ MHz, $f_2 = 450$ MHz. Receiver is tuned to $f_1+f_2 = 970$ MHz. Peaks a and b correspond to $2\omega_1 \simeq 4\omega_c$ and $2\omega_2 \simeq 4\omega_c$, respectively. Note peaks at $\omega_1+\omega_2 \simeq 3\omega_c, 4\omega_c$. Peaks B-n correspond to Bernstein modes associated with $\omega_1+\omega_2 \simeq n\omega_c$. Peak c is at $2\omega_2 = 2\omega_c$.